Chapter Three

LITERATURE SURVEY
3. Literature Survey

Monolithic refractories differs from refractory bricks in that they are unshaped and non-fired before use. They are easier to install in the place of applications and in situ fired during use, although the chemical and physical properties are similar and sometimes better. The raw materials play a prominent role in the formulation of the monoliths and its performance behavior.

3.1 What is refractory castables?

Refractory castables referred to as refractory concretes consisting of 80-98 % (w/w) carefully graded refractory as aggregate, 0-20 % (w/w) refractory cement, phosphates as binding system; certain micro constituents and dispersing agents to enhance flowability and workability. Nowadays castables are very much used in iron & steel, ceramic, cement, petrooum and paper industries.

3.2 Different aggregates for refractory castables:

The rapid advancement of unshaped monoliths with gradual entry into cement free new generation castables from conventional refractory castables during last few decades has opened up a new era to the refractory manufactures, consumers and ceramic technologist.

Various sintered/fused material are generally used as aggregates like calcined grog, sintered bauxite, calcined kyanite, tabular Al₂O₃, partial stabilized zirconia (PSZ), sintered synthetic mullite, brown fused Al₂O₃, white tabular Al₂O₃, fused mullite in formulation of high Al₂O₃ castables from 45-95%(w/w) Al₂O₃ content, while dead burnt magnesite, fused magnesia, dead burnt sea water magnesia,chrome-magnesite, magn-chrome, sintered dolomite and forsterite, MgO-Al₂O₃ spinel are recommended as aggregate for making basic refractory castables.

3.3 Advantages of refractory castables over brick lining:

Refractory castables have distinct advantages over burnt refractories as listed below
(i) Elimination of brick joints.
(ii) Possibility of simple, complex and fully anchored construction.
(iii) Easy maintenance and repairs.
(iv) Quicker and cheaper installation by ramming, pneumatic gunning, Vibro-casting, and trowelling etc.
(v) Ready availability of varieties of castables.
(vi) Good thermal shock resistance, little shrinkage.
(vii) Significant energy savings due to in situ firing.
(viii) Thermal conductivity is $\frac{1}{2}$ and $\frac{1}{3}$ to that of the burnt bricks.

3.4 Disadvantages of refractory castables:

Though the castables have many advantages over brick lining, still they have some limitations like

(i) Castables are porous in nature which are highly susceptible towards gas permeability and metal-slag attack.
(ii) The chemical composition of the cement in the castables is normally different from that of the aggregate which in most cases leads to decrease in refractoriness.
(iii) Due to presence of more water, cracks are developed during rapid removal of water at 100-110°C if proper firing schedule is not maintained.
(iv) Significant strength retrogression in the intermediate temperature ranges in between 500-1000°C

3.5 Function of ingredients in refractory castables:

Aggregates: Aggregate functions as the major matrix in refractory castable composition. It improves impact strength, mechanical strength, wear resistance, corrosion resistance, thermal stability and spalling resistance of the castable refractory and reduces co-efficient of thermal expansion and glass content at higher temperature.
**Binders** : The conventional bonding agent for refractory castables is high purity calcium aluminate cement with Al$_2$O$_3$ content ranging from 65-80%(w/w) particularly for composing high Al$_2$O$_3$ castables. Depending on property requirements and the usage of castable, the cement quantity may vary from 1-20%. The binding properties of high alumina cement results from the hydration of different phases (CA,CA$_2$,C$_{12}$A$_7$) of calcium aluminates. The rate of hydration will differ with different phases present. The rate of hydration diminishes as C/a ratio decreases i.e. C$_{12}$A$_7$ is most reactive and CA$_3$ is least reactive. Higher the cement content in castable composition, more water is required for casting, more porous is the structure on firing. Other cementitious binders in very high temperature castables is barium aluminate cement (BaAl$_2$O$_4$). Other binders like Al(H$_2$PO$_4$)$_3$, mono aluminum phosphate, sodium tripolyphosphate, hexametaphosphate, H$_3$PO$_4$ and long chain polyphosphates are also used. Ethyl silicates and polymeric resins can act as excellent binders nowadays.

**Additives** : Along with finer aggregates, certain microfine constituents like fumed microsilica, reactive alumina are added to extend workability and flowability with minimum quantity of water (~4%). Certain other additives like graphite flakes, carbon fines, SiC, carbon black, pitch are added to make castables non-wetting to metal and slag and also making it spalling resistant. To prevent oxidation of C and SiC, metallic Al and Si powder are also added in minute quantities. Special micro-constituent’s like fumed SiO$_2$, reactive Al$_2$O$_3$, Cr$_2$O$_3$ sols, MgO-Al$_2$O$_3$, MgO-Cr$_2$O$_3$ and ZnO-Al$_2$O$_3$ binary hydrosols are used as plasticizers. Lithium carbonates are particularly used for increasing the flowability of the castables.

**Dispersants** : To reduce water requirement and for good flowability, some defloculants like Na-hexametaphosphate (SHMP), citric acid, citrates, carboxy methyl cellulose (CMC), polycarboxylate ether (PCE) are extensively used.

**Fibres** : Fibres are also incorporated to prevent dryout cracks e.g. steel fibre, synthetic polymer fibres, glass fibres, alumino-silicate ceramic fibres, carbon fibres, asbestos fibres to improve strength, ductility and heat resisting.
**Evolution and growth of castable:**

The huge applications of advanced refractory castable products using less cement in formulation have been the key to explosive growth of castable technology.

- Conventional castable (10-20% High alumina cement)
- Low cement castable (≤4% High alumina cement)
- Ultralow cement castable (≤1% High alumina cement), microfine silica, alumina
- No cement castable with phosphate, silica sol, microfine silica, reactive alumina
- New generation castables (self-flow with micro constituents)
- Gel bonded self-flow castable

**Fig.1 Schematic of new generation refractory castables evolution.**
Based on the various positive aspects of quality monoliths over burnt bricks, the share of refractory castables gains substantial market especially in steel and petrochemical sectors.

### 3.6 Classification of refractory castables:

Refractory castables are broadly classified into the following categories:

![Diagram of classification of refractory castables](image)

**Fig 2. Schematic for classification of new generation refractory castables**
3.7. Major applications of refractory castables:

Refractory castables are used in various fields like:

(i) Castables are very much in use in iron and steel, cement, petroleum, paper industries and power plant etc.

(ii) It is also used for construction of different types of furnaces like soaking pit furnace, end pusher furnaces, walking beam furnaces, aluminium double-inductor furnaces and for making coke oven doors, for runners and troughs etc.

(iii) The burner nozzles of the hydrocracker unit in petroleum industry are made of the castables.

(iv) The different zones in the cement/shaft kilns are lined with different types of castables.

Refractory consumers are benefited significantly by use of newer castable technology for the increase in productivity and reduction in labour cost and energy savings.

3.8. Background towards development of basic refractory castables:

The fast changing technology for making of inclusion-free steel by using LD, OH, KAL-DO converters, electric arc furnace followed by continuous casting technique has exclusively demanded a new generation superior refractory materials which would have to withstand not only hostile operating conditions such as higher temperature of melting, stronger agitation, longer holding time for secondary metallurgy but also to ensure longer service life of the furnaces. In coming days cement free basic monolithic castable refractories appear most promising refractory materials for such applications.

3.9. Evolution of new generation basic refractory castables:

Cement-free MgO-dolime castables have been developed using microsilica as the bonding phase\textsuperscript{16}. These castables have good casting characteristics and high strength at low temperatures. At higher temperatures, however, the strength are considerably reduced. To
increase the hot strength, the reaction between MgO and SiO$_2$ for producing forsterite are being allowed. Earlier attempts by use of AlF$_3$ and Al$_2$O$_3$ were not successful because refractoriness was drastically lowered due to the formation of cordierite. Silicon nitride and Si metal have been found suitable bond-phase modifiers and improved the hot strengths considerably.

### 3.9.1. Ingredients for basic refractory castables:

Basic refractory castables are composed of properly graded dead burnt magnesia, fused magnesia, dead burnt sea water sea magnesia, sintered dolime, mag-chrome, chrom.magnesia, spinel clinkers as aggregate and Sorel cement, oxysulphate or phosphate as bonding agents, minor quantity of defloculant and ultrafine reactive sols like bohemite, alumina silica sols, titania sols, spinel gels as coagulation bonding agents. Dead burnt periclase, dolime, forsterite and spinels has possessed high melting point, high corrosion resistance to high basicity slag and iron oxide.

### 3.9.2. Function of aggregates in basic refractory castables:

1. Improves impact strength, mechanical strength and wear resistance.
2. Improves corrosion resistance.
3. Enhances thermal stability and spalling resistance.
4. Reduces co-efficient of thermal expansion and glass content at higher temperature.

### 3.9.3. Specific applications of basic refractory castables:

(i) Alumina-magnesia castable are useful for steel making vessels and ladle lining with better slag corrosion and spalling resistance behaviour.

(ii) Magnesia based castables are suitable for hot repairing of bottom linings of molten metal furnace.

(iii) Dolomite and periclase containing castables are useful for repairing of steel-making furnaces.
(iv) Hydraulically and chemically bonded basic castable are useful for manufacturing of slide-gate refractories.

(v) Spinel containing basic castable with certain percentage of high-alumina are mainly applied in lining of steel ladles and vacuum degassing furnaces.

(vi) Corrosion resistant mag-chrome based castables are used in steel-making troughs.

(vii) Dolime based basic castables are mainly used in lining of teeming ladles.

(viii) Large shaped magnesia castables have been made for applications in electric furnace runners and basic oxygen furnace tap-hole blocks.

3.9.4. Structure and physical properties of magnesium oxide:

Magnesium oxide (MgO), also known as magnesia, is an alkaline earth metal oxide. It is a white powdery solid material with a formula mass of 40.31 g mol$^{-1}$, and a density of 3.58 g ml$^{-1}$. Magnesium oxide has a face centred cubic system crystal structure and melts at a high temperature of 2827 ± 30$^\circ$C. It has a solubility value of 0.00062 g in 100 g of water at room temperature$^{17}$. The crystal structure$^{18}$ of MgO is shown in Fig. 3.

![Fig.3 Crystal structure of MgO](image)
3.9.5. Production of magnesium oxide/periclase

Magnesium oxide was detected as a mineral contaminated with ferrous oxide, and was called periclase, which is the high temperature form of magnesium oxide.

The majority of MgO is produced by thermal treatment of naturally occurring magnesia-rich minerals, of which Brunnerite (MgCO$_3$ + FeCO$_3$) is the most common. Other sources of MgO production include minerals such as dolomite [CaMg(CO$_3$)$_2$], hydromagnesite [Mg(CO$_3$)$_2$·4H$_2$O], brucite [Mg(OH)$_2$], and serpentine [MgSiO$_{10}$(OH)$_8$]. Sea water, underground salt deposits of brines and salt beds$^{17,19-20}$. 

Magnesium carbonate (MgCO$_3$) decomposes into MgO and CO$_2$ when calcined at 650 -700°C. In this process, an active phase of magnesia sensitive to moisture hydration is produced and it is reported highly suitable for removal of silica from industrial water.

$$\text{MgCO}_3\text{(s) } \xrightarrow{\text{heat}} \text{MgO (s) + CO}_2\text{(g)}$$

On further heating of the carbonate, the MgO formed may be transformed into different forms. The extent of calcination temperature or time leads to the formation of different types or grades of MgO. Various types of MgO includes light burnt caustic magnesia, hard burnt magnesia, dead burnt magnesia and fused magnesia.

3.9.6. Different grades of magnesium oxide

The thermal decomposition of natural magnesite into magnesia and carbon dioxide gas in the temperature range from 600°C up to 3000°C produced different forms or types of magnesium oxide and the resultant MgO had different physico-chemical properties. These properties are dependent on the mode of origin of the magnesite, the mineralogical composition of the natural magnesite and the calcination temperature chosen. Table 1 gives the physico-chemical properties of different grades of magnesium oxide.
Table 1: Physico-chemical properties of different grades of magnesium oxide\textsuperscript{19-20}

<table>
<thead>
<tr>
<th>Property</th>
<th>Caustic Calcined MgO</th>
<th>Hard burnt MgO</th>
<th>Dead burnt MgO</th>
<th>Fused MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface area (m\textsuperscript{2}/g)</td>
<td>1-200</td>
<td>0.1 to 1.0</td>
<td>&lt; 0.1</td>
<td>Extremely small surface area</td>
</tr>
<tr>
<td>Crystal size (μm)</td>
<td>1-20</td>
<td>Characterized by moderate crystallite size</td>
<td>Characterized by large crystal size (30 -120)</td>
<td>Extremely large crystal size (500-1000)</td>
</tr>
<tr>
<td>Acid solubility</td>
<td>Readily soluble in dilute acids</td>
<td>Readily soluble only in concentrated acids</td>
<td>Reacts very slowly with strong acids</td>
<td>Reacts very slowly with strong acids</td>
</tr>
<tr>
<td>Hydration behaviour</td>
<td>Readily absorbs water vapor and carbon dioxide from the atmosphere to form a basic magnesium carbonate</td>
<td>Hydrates very slowly to form magnesium hydroxide</td>
<td>Does not readily hydrate or react with CO\textsubscript{2}</td>
<td>Does not readily hydrate or react with CO\textsubscript{2}</td>
</tr>
<tr>
<td>Chemical reactivity</td>
<td>Moderate to high chemical reactivity</td>
<td>Low chemical reactivity</td>
<td>Very low chemical reactivity</td>
<td>Very low chemical reactivity</td>
</tr>
</tbody>
</table>
(i) Caustic magnesia

Low calcined magnesite, also known as caustic magnesia or medium reactive magnesia, is obtained by calcining magnesium carbonate in a shaft or rotary kiln in between 600 and 1000°C. Because of incomplete dissociation, it still retains 8 to 10% carbon dioxide as carbonate. Low calcined magnesia when mixed with water forms a feebly plastic paste. Industries like paper, rubber, ceramic, asbestos products, glass, etc mostly use caustic magnesia. Hard burnt magnesia is produced in the temperature range in between 1100 to 1650°C.

(ii) Dead-burnt Magnesite (DBM)

When the raw magnesite is calcined in between 1700-2000°C, carbon dioxide is expelled completely and a dense product 'dead-burnt magnesite' is obtained. Dead-burnt magnesite refers to the formation of periclase, a crystalline variety of MgO that is chemically inert i.e., 'dead' because it has been calcined at a temperature high enough to enable it in suitable burnt magnesite brick making or monolithic hearths without difficulty arising out of hydration or shrinkage.

(iii) Fused magnesia

Fused magnesia is produced by the fusion of the high-grade magnesite in Higgin's or electric arc tilt furnaces between 2500-3000°C. It is resistant to the action of molten metals, basic slags and fluxes at high temperatures. It is used in the form of moulded vessels and as compressed material for covering resistant elements of the furnaces used in the melting of lead, tin, etc.

(iv) Dead burnt sea water magnesia (SWM)

Sea water or lake bitterns is an alternative source for obtaining magnesia by chemical reaction. The main raw materials required other than sea water are dolomite or limestone, fresh water and sulphuric acid. The magnesia content in sea water is about 0.2% and even by enrichment with dolomite, around 300 kilograms sea water needs processing to obtain a kilogram magnesia. The sea water magnesia must be calcined in rotary kilns at very high temperature of 1700-1800°C for the manufacture of dead burnt sea water magnesia.
3.9.7. The reactivity of magnesium oxide:

The most important physical properties of calcined magnesia are the crystal size and the surface area, which determine the reactivity of magnesium oxide\(^2^6\). For the purpose of this study, the reactivity of magnesium oxide refers to the extent and the rate of hydration of MgO to give Mg(OH)\(_2\) when exposed to water or magnesium acetate solutions.

Girgis and Girgis\(^2^7\) investigated the surface and pore structure of talcmagnesite, and mentioned that the calcination temperature and the duration of thermal treatment are among the important factors determining the surface properties of calcined MgO and hence the reactivity of MgO since less surface area and pores are available for reaction with other compounds. During the hydration of magnesium oxide, the reactivity of magnesium oxide gives an indication of the extent or the degree of hydration to Mg(OH)\(_2\) when magnesium oxide is exposed to water, moisture or any other hydrating agent. The thermal treatment of the calcination process has an effect on the surface area and the pore size and hence the reactivity of magnesia. The source of magnesia also determines the nature of impurities present in the calcined material. The most common impurities in magnesium oxide are CaO, Al\(_2\)O\(_3\), Fe\(_2\)O\(_3\), SiO\(_2\) and B\(_2\)O\(_3\). The typical chemical composition and properties of dead burnt magnesite of different origin are given in Table 2.
Table 2: Typical composition (wt%) of natural dead burnt magnesite, fused magnesia and dead burnt sea water magnesia \(^{28-31}\).

<table>
<thead>
<tr>
<th>Types/Origin</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Fe(_2)O(_3)</th>
<th>CaO</th>
<th>B(_2)O(_3)</th>
<th>Cr(_2)O(_3)</th>
<th>MgO</th>
<th>B.D(g/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural magnesite, Grecian</td>
<td>1.60</td>
<td>0.07</td>
<td>0.54</td>
<td>2.94</td>
<td>0.01</td>
<td>0.01</td>
<td>94.87</td>
<td>3.3-3.4</td>
</tr>
<tr>
<td>Natural magnesite, Turky</td>
<td>1.16</td>
<td>0.04</td>
<td>0.61</td>
<td>2.28</td>
<td>0.01</td>
<td>0.02</td>
<td>95.88</td>
<td>3.3-3.4</td>
</tr>
<tr>
<td>Natural magnesite, Austria</td>
<td>1.0</td>
<td>1.0</td>
<td>5.0</td>
<td>3.0</td>
<td>&lt;0.01</td>
<td>-</td>
<td>90</td>
<td>3.35</td>
</tr>
<tr>
<td>Natural magnesite, Australia</td>
<td>0.5</td>
<td>0.15</td>
<td>0.1</td>
<td>2.0</td>
<td>&lt;0.01</td>
<td>-</td>
<td>96.5</td>
<td>3.35</td>
</tr>
<tr>
<td>Sea water magnesite, British</td>
<td>0.80</td>
<td>0.40</td>
<td>1.30</td>
<td>0.80</td>
<td>0.15</td>
<td>0.02</td>
<td>96-97</td>
<td>3.3-3.4</td>
</tr>
<tr>
<td>Sea water magnesite, Sardinian</td>
<td>0.50</td>
<td>0.20</td>
<td>0.20</td>
<td>0.60</td>
<td>0.15</td>
<td>0.02</td>
<td>98-99</td>
<td>3.3-3.4</td>
</tr>
<tr>
<td>Sea water magnesite, Ireland</td>
<td>0.20</td>
<td>0.109</td>
<td>0.15</td>
<td>1.9</td>
<td>0.04</td>
<td>-</td>
<td>97.4</td>
<td>3.44</td>
</tr>
<tr>
<td>Sea water magnesite, Israel</td>
<td>0.05</td>
<td>0.03</td>
<td>0.04</td>
<td>0.5</td>
<td>0.005</td>
<td>-</td>
<td>99.4</td>
<td>3.43</td>
</tr>
<tr>
<td>Sea water magnesite, Japan</td>
<td>0.15</td>
<td>0.07</td>
<td>0.06</td>
<td>0.68</td>
<td>0.01</td>
<td>-</td>
<td>99.03</td>
<td>3.43</td>
</tr>
<tr>
<td>Sea water magnesite, Netherlands</td>
<td>0.20</td>
<td>0.15</td>
<td>0.40</td>
<td>0.65</td>
<td>0.02</td>
<td>-</td>
<td>98.5</td>
<td>3.44</td>
</tr>
<tr>
<td>Sea water magnesite, US</td>
<td>0.7</td>
<td>0.02</td>
<td>0.20</td>
<td>2.20</td>
<td>0.02</td>
<td>-</td>
<td>97.5</td>
<td>3.40</td>
</tr>
<tr>
<td>Fused magnesia, Japan</td>
<td>0.2</td>
<td>0.1</td>
<td>0.20</td>
<td>0.5</td>
<td>0.005</td>
<td>-</td>
<td>98.5</td>
<td>3.50</td>
</tr>
<tr>
<td>Fused magnesia, China</td>
<td>1.0</td>
<td>0.5</td>
<td>0.60</td>
<td>1.0</td>
<td>0.001</td>
<td>-</td>
<td>98.0</td>
<td>3.45</td>
</tr>
</tbody>
</table>

The total world production of magnesia from all sources is estimated as eleven million tonnes. Of this, roughly 8.5 million tonnes are derived from natural magnesite and the rest 2.5 million tonnes from sea water.
3.10. Various aspects of literature survey relating to the development of new generation basic refractory castable may be classified into the following categories on the basis of

1. Effect of different aggregates on castable system
2. Effect of different binder on castable system
3. Effect of particle size and dispersant on castable composition
4. Choice and generation of double hydroxide hydrogel spinel precursors
5. Effect of double hydroxides hydrogel precursors on sintering of refractory castables
6. Important properties of basic castables

3.10.1. Effect of different aggregates on castable system:

Aggregate plays an important role for the consolidation of refractory castable because it is the matrix component in the castable system.

Tabular alumina\(^{32}\) based castable with 80% alumina content provides exceptionally high hot strength (16MPa at 1510°C) and excellent corrosion resistance to slag. R.Stieling et al\(^{33}\) highlighted the vibratable castable with thixotropic behavior by using different bonding agents. They reported that the casting water reduced from 7% to 5.3% with only 8% high alumina cement in combination with 4% silicate compound using fused alumina aggregate.

High alumina castable\(^{34}\) containing alumina-magnesia spinel are composed with both sintered and fused forms. Nowadays, it is exclusively used in refractory applications because MgO-Al\(_2\)O\(_3\) spinel remains stable phase at high temperature, low thermal expansion co-efficient and excellent corrosion resistance to basic slag. The stoichoimetric composition of 1:1 MgO-Al\(_2\)O\(_3\) spinel is MgO-28.3% and Al\(_2\)O\(_3\)-71.7% by weight. The composition of the spinel may change either in MgO rich zone (up to 32%) or Al\(_2\)O\(_3\) rich (up to 95%). The performance of MgO-Al\(_3\)O\(_3\) spinel castable is improved by addition of fine
grains of MgO and Al$_2$O$_3$ which leads to the formation of in situ spinel instead of the addition of preformed fine spinel grains$^{35}$.

Watanabe et al$^{36}$ showed that magnesia containing castable prevents the slaking of MgO in water by adding Al$_2$O$_3$, SiO$_2$, TiO$_2$ and ZrO$_2$ to 98% MgO based material. They showed that 2.4% of Al$_2$O$_3$ addition provides the best resistance to slaking and beyond which leads to cracks and disintegration.

Henry and Stendera$^{37}$ prepared large shaped phosphate bonded MgO based castable for electric furnace runners and basic oxygen furnace tap-hole blocks using white fused alumina and magnesia. They reported that addition of 0-50% alumina to the castable with 5.3% water gives the better corrosion resistance and addition of Al$_2$O$_3$ also improved the structural spalling and thermal shock resistance. The hot MOR has also improved with increasing alumina addition but starts to fall with alumina content beyond 25%

Colle et al$^{38}$ developed no cement refractory castable and a low-cements refractory castable using 73% coarse-grain fraction (tabular alumina, high-alumina spinel), 21% fine-grain fraction (fired alumina, reactive alumina, high-alumina spinel), 5% bond (hydrated alumina for NCC and fired alumina for LCC) and <1% dispersant.

Prestes et al$^{39}$ fabricated and analysed hot erosion properties of nano-bonded refractory castables containing tabular alumina, mullite grog or fused silica following Alfred’s packing model (q=0.24–0.26). Tabular alumina ($D_{\text{max}} \leq 6$ mm) and mullite grog ($D_{\text{max}} \leq 6.73$ mm,) compositions is comprised of 85.5wt% of the aggregates for each composition. In the systems, 2.5wt% of sintering additives, consisting of a mixture of Al powder and a light element. The silica castable composition contained 70wt% of fused silica ($D_{\text{max}} \leq 4.75$ mm), 16 wt% of tabular alumina (-0.2 mm) and 1 wt% of sintering additives. The matrix of the three refractory systems comprised of 10wt% reactive alumina (CL370C) and 2wt% of fumed silica (MS971).

Braulio et al$^{40}$ showed magnesium borate as an outstanding additive for cement-bonded alumina-magnesia castables due to: (i) its ability to speed up both spinel (MgAl$_2$O$_4$) and calcium hexaluminate (CA$_6$) formations, ensuring that the castable’s ad-
vance microstructure would be attained at lower temperatures; and (ii) its high creep resistance, high hot modulus of rupture and suitable corrosion resistance at usual working temperature. The increase in the hot modulus of rupture as a function of firing time at 1550°C reinforced that either the formation of a crystalline phase or boron volatilization took place. The overall results indicated that by adding magnesium borate, the final and expected castable’s phases can be attained at lower temperatures than for those containing silica fume and also results in much better thermo-mechanical performance.

3.10.2. Effect of different binders on castable system:

Binding system plays a vital role in different processing steps, including flowability, workability, drying-out, microstructural development and service performance. Therefore, all efforts are to be concentrated for improving the bonding agents\textsuperscript{41-42} in the castable system. The evolution of bonding system in refractory castable has been presented in Table 3
Table 3: Successive progress in binding system for refractory castables\textsuperscript{41-42}.

<table>
<thead>
<tr>
<th>Binding Mode</th>
<th>1920s</th>
<th>1930s</th>
<th>1940s</th>
<th>1950s</th>
<th>1960s</th>
<th>1970s</th>
<th>1980s</th>
<th>1990s</th>
<th>2000s</th>
<th>2010s</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydraulic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional cement bonded castable (Silicate cement, low purity CA cement)</td>
<td>Pure CA cement bonded castable (CA cement with improved purity)</td>
<td>High purity CA cement bonded castables (High purity CA cement + ufAl\textsubscript{2}O\textsubscript{3})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pure CA cement bonded castable (CA cement with improved purity)</td>
<td>Hydratable Al\textsubscript{2}O\textsubscript{3} bonded castables</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chemical</td>
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<tr>
<td>Phosphate bonded castables [H\textsubscript{3}PO\textsubscript{4} or Al(H\textsubscript{2}PO\textsubscript{4})\textsubscript{3}+MgO or CA ]</td>
<td>Water glass bonded castables [Na\textsubscript{2}O nSiO\textsubscript{2}+Na\textsubscript{2}SiF\textsubscript{6}]</td>
<td>Sulphate, chloride bonded castable. [Al\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} + CA, MgCl\textsubscript{2} or MgSO\textsubscript{4}]</td>
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<tr>
<td>Polymerisation</td>
<td>Polyphosphate bonded castables [Na\textsubscript{3}P\textsubscript{2}O\textsubscript{10} or (NaPO\textsubscript{3})\textsubscript{6} + MgO,CaO or CA]</td>
<td>Resin bonded castables (Phenol resin, Novalac resin+cross linker)</td>
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<tr>
<td>Hydraulic + Coagulating</td>
<td>Low cement castables (CA cement + Clay, CA cement + uf-SiO\textsubscript{2} Clay bonded castables (Ca-clay or Na-clay +CA)</td>
<td>Ultra low cement Castables [uf-SiO\textsubscript{2}+ uf. Al\textsubscript{2}O\textsubscript{3}+CA] Cement–free castables(non-cement castables) (uf-SiO\textsubscript{2}, uf-Al\textsubscript{2}O\textsubscript{3} +electrolyte, uf-SiO\textsubscript{2}+ MgO) Sol bonded castables (Silicasol,alumina sol+electrolyte)</td>
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<td>Coagulating</td>
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<td>Carbon bonded</td>
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<tr>
<td>Nano engineered</td>
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uf = ultra fine
Traditionally, calcium aluminate cement is used as a conventional binder for making spinel based refractory castables. It is suitable for the refractory castable because of its unique characteristics like setting time, demoulding time and corrosion resistance. Addition of CAC in the castable system may also lead to expansion from CA$_2$ and that ultimately transforms into CA$_6$ phase.

However, crystallization of acicular calcium hexa-aluminate can enhance thermomechanical properties like thermal shock and creep resistance. Because of needle like shape it acts as in situ whiskers resulting in increased toughness of the materials. In spite of many advantages, the formation of excessive CA$_6$ with whisker like morphology may again lead to structural damage because of cracking.

The expansion behavior of CA$_6$ can be mitigated by replacing CAC with hydratable alumina. In general, it is proved that commercial hydratable alumina products are mainly based on the metastable phase, $\rho$-Al$_2$O$_3$ possessing rehydration ability that helps in hydraulic setting at room temperature.

Nowadays, magnesia based basic refractory castable finds wide spread industrial applications because of its some unique inherent properties like, high refactoriness and excellent corrosion resistance towards highly basic slag. That is why, these materials are more favored over neutral, basic or alumino-silicate refractories. Moreover, system containing Al$_2$O$_3$ and MgO augments the formation of in situ spinel which can improve thermal shock resistance.

Conventionally, basic refractory castable are fabricated using hydraulic binder like high alumina cement and chemical binder like alkali phosphate. In both the cases, the high hot strength property decreases rapidly when the conventional high-alumina cement is used, it tends to form low melting phases like monticelite or merwinite. When chemical bonding agent is used, the formed low melting phases released P$_2$O$_5$ at high temperature. It is shown that MgO.Al$_2$O$_3$ hydroxide hydrogel improves the green strength of the castable system by coagulation and in situ spinel acting as sintering aid.
Intensive research works are in progress for the development of new generation basic refractory castable with better properties for the applications in modern steel making furnace, EAF, ladle lining, tundishes\textsuperscript{55-57}.

Though these basic refractory castable materials have many inherent qualities to be a prospective member for above mentioned areas of application, the main draw backs for MgO based castable lies in its inherent tendency to form Mg(OH)\textsubscript{2} crystal due to hydration which invariably expands and cracks\textsuperscript{58}.

Generally the use of finer size fraction of the periclase aggregate is more prone to hydration. In presence of water, MgO undergoes hydration reaction resulting in different densities between periclase (MgO) (3.5g/cc) and brucite (2.4g/cc)\textsuperscript{59}. The control of this type of expansion is the main challenge in the magnesia based basic refractory castable body because it tend to lead to excessive swelling, cracking and finally damaging integrity of the refractory castable system\textsuperscript{60}.

Efforts to curb the tendency of cracking of basic refractory castables prescribe the formation of chelating complex of Mg ions and phosphatic component. The another way in controlling the cracking tendency of the castable involves the reduction of the water content. Cement free castable using micro silica leads to the formation of magnesium hydrate gel that gives high green strength at relatively low temperature but fails to give high hot strength properties\textsuperscript{61-63}.

Moreover, in presence of silica, a metastable Al\textsubscript{2}O\textsubscript{3}-SiO\textsubscript{2} liquid is formed at temperature near about 1250\textdegree{}C providing densification of alumina castable systems bonded with hydratable alumina\textsuperscript{64}. This effect counterbalances the \textit{in situ} spinel expansion, imparting the volumetric stability of Al\textsubscript{2}O\textsubscript{3}-MgO refractory castable.

Zhang and Li\textsuperscript{65} examined the effect of alumina polymorphism on the synthesis of magnesium aluminate spinel from 1000-1600\textdegree{}C and noticed that the use of γ-Al\textsubscript{2}O\textsubscript{3} or ρ-Al\textsubscript{2}O\textsubscript{3} leads to shrinkage during spinel formation where as α-Al\textsubscript{2}O\textsubscript{3} resulted in initial expansion followed by a small contraction which is attributed to the higher density of α-Al\textsubscript{2}O\textsubscript{3} in comparison with that of γ-Al\textsubscript{2}O\textsubscript{3} or ρ-Al\textsubscript{2}O\textsubscript{3}.
Table 4: Physico-chemical properties of high alumina cement based castables.

<table>
<thead>
<tr>
<th>Class</th>
<th>45% Al₂O₃</th>
<th>50% Al₂O₃</th>
<th>55% Al₂O₃</th>
<th>65% Al₂O₃</th>
<th>95% Al₂O₃</th>
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<td>95.8</td>
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<td>3.6</td>
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<td>38.6</td>
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<tr>
<td>TiO₂</td>
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<td>1.6</td>
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<tr>
<td>Fe₂O₃</td>
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<td>1.0</td>
<td>1.1</td>
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<table>
<thead>
<tr>
<th>CMOR (MPa) at</th>
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<td>110°C</td>
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<tr>
<td>815°C</td>
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<td>1370°C</td>
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<table>
<thead>
<tr>
<th>CCS (MPa) at</th>
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<td>815°C</td>
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<tr>
<td>1370°C</td>
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<table>
<thead>
<tr>
<th>HMOR (MPa) at</th>
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<tr>
<th>PLC (%)</th>
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<tbody>
<tr>
<td>815°C</td>
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<tr>
<td>1370°C</td>
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</table>
Table 5 Physico-chemical properties of low cement high alumina castables$^{66}$.

<table>
<thead>
<tr>
<th>Class</th>
<th>60% Al$_2$O$_3$</th>
<th>65% Al$_2$O$_3$</th>
<th>70% Al$_2$O$_3$</th>
<th>85% Al$_2$O$_3$</th>
<th>90% Al$_2$O$_3$</th>
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<tr>
<td>Al$_2$O$_3$</td>
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<td>91.5</td>
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<td>CaO</td>
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<td>1.4</td>
<td>1.8</td>
<td>1.4</td>
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<tr>
<td>SiO$_2$</td>
<td>35.5</td>
<td>31.6</td>
<td>28.5</td>
<td>7.9</td>
<td>7.3</td>
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<td>1.0</td>
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<td>Fe$_2$O$_3$</td>
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<td>815°C</td>
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<td>1370°C</td>
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<td>1.550</td>
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<tr>
<td>815°C</td>
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<td>26.0</td>
<td>30.3</td>
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<tr>
<td>1370°C</td>
<td>31.0</td>
<td>31.0</td>
<td>28.6</td>
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<td>31.4</td>
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<td>CCS(MPa) at</td>
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<td>HMOR(MPa) at</td>
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<td>27.0</td>
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<td>9.3</td>
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<tr>
<td>1430°C</td>
<td>1.8</td>
<td>3.2</td>
<td>4.5</td>
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</tbody>
</table>
Studart et al. developed different colloidal processes as alternative approaches to consolidate high-alumina refractory castables free from hydraulic binders (zero-cement) through coagulation methods. They narrated three in situ reactions based on the direct coagulation casting (DCC) technique to promote castable coagulation using: (1) the autocatalytic hydrolysis of gluconic acid lactone, (2) the gradual dissolution of hydroxyaluminum diacetate particles in water, and (3) the enzyme-catalyzed hydrolysis of urea. The enzyme-catalyzed hydrolysis of urea seemed to be the most appropriate mechanism to promote the coagulation of initially self-flow zero-cement refractory castable compositions.

Ustyansev et al. showed that reaction between phosphate bonds and magnesium oxide results in formation of magnesium phosphates which are responsible for improving hardness in the magnesia systems.

Salomao and Pandolfelli examined the effects of calcium aluminate cement (CAC) and hydratable alumina (HA) on magnesia hydration behavior in aqueous suspensions. They examined the affect of binders on magnesia hydration in refractory castables using pH, apparent volumetric expansion, mechanical strength and porosity measurements and hydration–dehydration tests.

Mukherjee and Samaddar demonstrated the bond forming properties of magnesium aluminate hydrate with magnesia grains. They showed that a very small amount (0.25%) of the new binder MgAl2O4 was effective in forming strong bonds.

Gower and Gower developed a magnesium-phosphate bonded castable utilizing a closely graded sintered mullite aggregate with magnesium phosphate/magnesium oxide/aluminium oxide binder.

Platonov and Maryasev employed a new generation binder for cement-free periclase concretes based on MgO-SiO2 binder with a service temperature from 1500-1700°C. They also showed that when microdispersed SiO2 is added to periclase filler, it enters into reaction with water, as a result of which there is formation of magnesia-silica hydrate phases which promote concrete setting and also strong bonds with high strength properties.
Banawalikar et al.\textsuperscript{73} developed two new type hydraulic binders namely calcium dialuminate (CA\textsubscript{2}) cement mainly for aluminous castable and barium aluminate (BA) cement specially for basic castables and chemically bonded magnesium aluminate hydrate MAH for monolithic/preshapes. They replaced CA\textsubscript{2} based cement by CA based binder and conventional calcium aluminate cement with barium aluminate cement imparting high cold crushing strength & hot MORs to alumina castable which can enhance the life of refractories at temperatures above 1700°C. The better hot properties and better compatibility with basic slags, magnesium aluminate hydrate binder showed a great promise in arresting the drop in mechanical properties at intermediate temperatures for the basic castables/preshapes.

Antonov\textsuperscript{74} prepared periclase-carbon refractories using phenol-formaldehyde binder which showed higher service life as that of fired periclase articles in the lining of electric arc steel-melting furnaces.

Khoroshavin et al.\textsuperscript{75} demonstrated the forming processes of magnesia concrete with sodium phosphate bond. They found that bryanite Na\textsubscript{2}CaMg(PO\textsubscript{4})\textsubscript{2} formed with MgO. They obtained the better results from sodium hexametaphosphate (NaPO\textsubscript{3})\textsubscript{6} bonded magnesia concrete.

Ustyantsev et al.\textsuperscript{76} explained that during the reaction of phosphate bonds with magnesium oxide, magnesium phosphates are formed conferring hardness to the magnesia concretes. Aluminophosphate bond and magnesia reacts with monosubstituted aluminium phosphate and under these conditions di-and trisubstituted magnesium phosphates and aluminum orthophosphate are formed, which in turn react with magnesia at temperatures above 1000°C with the formation of magnesium orthophosphate and magnesia-alumina spinel. The aluminophosphate bond has a greater contribution to recrystallization of the periclase compared with H\textsubscript{3}PO\textsubscript{4}, magnesium-and chromium-phosphate bonds.

Ding et al.\textsuperscript{77} discussed the mechanism of magnesium phosphate cement (MPCs) bonded dead burned magnesia and mono-potassium phosphate (MPP) by taking fine powder and grains of dead burned magnesia. The microstructure of specimens was analyzed by SEM, TEM, XRD and optical microscopy. According to the analysis, struvite exists in both crystalline and amorphous form.
Semler\textsuperscript{78} highlighted the recent development of raw material and unshaped refractories. These are including attrition milling of kyanite, nano-bonded MgO-C, TiB\(_2\) cement, ceramic foam filter material, particle size and aggregate to matrix interface.

Kingery\textsuperscript{79} studied on the cold-setting bonds formed from oxide-phosphoric acid reactions, phosphate-phosphoric acid reactions or by direct addition of liquid phosphate bond. No weak temperature zone appears on heating with these bonds because of the gradual loss of “combined” water and gradual crystallization of the dehydration products.

Kingery\textsuperscript{80} showed the adsorption of monoaluminum phosphate on Florida plastic kaolin was 13.3 m.eqv. per 100 gm., whereas North Carolina kaolin adsorbed 9.6 m.eqv. per 100 gm. Ground monoaluminum phosphate having a high adsorption capacity showed almost no salt migration, a rate of drying like that of water, and no surface deposition of monoaluminum phosphate.

Ismael \textit{et al}\textsuperscript{81} demonstrated the use of colloidal silica as calcium-free binding agent for refractory castables to minimize the drawbacks exhibited by the calcium aluminate cement (CAC), and found to be good new refractory binder for monolithic refractories. They attained low porosity colloidal silica bonded castables by proper particle-size distribution (PSD) optimization and adjustment of colloidal silica.

Suvorov \textit{et al}\textsuperscript{82} developed phenol-furfural binder for production of periclase-graphite, lime-periclase, and corundum-graphite parts and ramming compounds for lining steel teeming ladles, converters, electric furnacees and steel teeming parts.

Magliano \textit{et al}\textsuperscript{83} explained the effect of silica sols with different solid content/particle size ratios in the properties of refractory castables based on tabular alumina, calcined alumina and fume silica. They reported that reactive silica sols reduces the workability, decrease the fluidity and deteriorate the cold and hot mechanical properties of refractory castables due to the significant microstructure cracking during the drying stage.

Freidenberg\textsuperscript{84} developed the mixtures based on chamotte and magnesite with varying contents (8-42\%w/w) of liquid phenol-formaldehyde resin (PFR) as the binder. The addition of asbestos increases the mechanical strength of the samples, but causes practically no change in their gas permeability and density. The addition of iron scale causes a
decrease in the compressive strength and refractoriness. With the addition of technical-grade carbon and the presence of the refractory filler and asbestos, the service characteristics of the material become poorer.

Sokhatskaya et al\textsuperscript{85} studied the performance of spinel bonded magnesite refractory in rotary kilns. During reaction stable compounds of helenite $2\text{CaO}.\text{Al}_2\text{O}_3.9\text{SiO}_2$, and merwinite $3\text{CaO}.\text{MgO}.2\text{SiO}_2$ were formed. The magnesite refractory with the spinel bond is very resistant to the action of Portland cement clinker for lining in the sintering zones of rotary kilns, especially when firing clinker for producing white cement.

Antonov et al\textsuperscript{86} showed that it was possible to obtain magnesium sulphate bonded periclase, periclase-chromite and chromite-periclase refractories. Periclase-chromite articles have an irregular structure and consist of sections of periclase, grains of chrome-spinel and fine-grained bonding mass. They estimated the phase composition as follows: (i) periclase with secondary spinel 65-70%, chrome spinel 15-20%, silicates 14-15%. (ii) periclase with secondary spinel 25-30%, chrome-spinel 55-60%, and silicates 15-16% of chromite-periclase refractory.

Ustyantsev et al\textsuperscript{87} studied the reaction of spinels with phosphate bonded magnesia-spinel refractory concretes used for lining steel melting units. They reported that the reaction between $\text{MgAl}_2\text{O}_4$ and $\text{MgCr}_2\text{O}_4$ with orthophosphoric acid and sodium chromophosphate bond at $1300^\circ\text{C}$. The composition by weight of sodium chromophosphate bond: 60\% $\text{Na}_2\text{Cr}_2\text{O}_7.2\text{H}_2\text{O}$, 10\% $\text{H}_3\text{PO}_4$, and 30\% $\text{H}_2\text{O}$. The orthophosphoric acid reacts with part of the $\text{MgAl}_2\text{O}_4$ according to the equation

$$\text{MgAl}_2\text{O}_4 + 3\text{H}_2\text{PO}_4 \rightarrow (\text{MgHPO}_4.3\text{H}_2\text{O}) + 2(\text{AlPO}_4.\text{H}_2\text{O}).$$

Golshan et al\textsuperscript{88} tried to develop a forsterite bond with micro silica rather than other types of binders in the basic refractory castables. Effects of replacement of microsilica by colloidal silica in forsterite bond intended for magnesia based refractory castables were evaluated. They measured the physical properties of prepared samples with different amount of colloidal silica versus temperature and phase variation and microstructural evolution of sintered specimens at 1000, 1200 and $1400^\circ\text{C}$ by X-ray diffraction (XRD) and scanning electron microscope (SEM). They reported that due to reaction of magnesia
with microsilica and colloidal silica, magnesium hydrate and magnesium silicate hydrate formed in the dried samples strengthening the texture of the samples while forsterite formed from about 1000°C and gradually increased with temperature and better forsterite formation occurred by increasing the colloidal silica content.

Sarkar et al\textsuperscript{89} developed the oxysulfate bond with interaction of hydrated microfine alumina and sulfate compound which is considered as a prospective bond of aluminosilicate refractories. The minor addition of bond to calcined clay and calcined bauxite based refractories results in good mechanical and thermal properties which may be efficiently used in different parts of ladle furnace.

Zhou et al\textsuperscript{90} developed MgO-SiO\textsubscript{2}-H\textsubscript{2}O bonded MgO-based castables for both self-flowing and vibration type such as pumpable and sprayable which exhibited significant improvement of cold and hot properties as well as slag resistance. Different samples were subjected to slag attack by rotary slag test to compare their slag resistance using two kinds of steel-making slag with high and low CaO/SiO\textsubscript{2} ratios.

Milanez et al\textsuperscript{91} developed calcium aluminate cement (CAC) bonded alumina-magnesia refractory castables for steel ladle applications. As a result of \textit{in situ} formation of spinel and CA\textsubscript{6} leads to high basic slag resistance and thermal shock resistance but causes cracks. The results showed that calcium aluminate cement affects the volumetric stability of MgO-spinel system as follows: the lower the CAC content, the lower is the shrinkage.

Badiee and S.Otroj\textsuperscript{92} studied the effect of nano-silica sol on the self-flow characteristics of high-alumina self-flowing non-cement castable in terms of bulk density, apparent porosity, mechanical and microstructural development of fired castables at different temperatures. By increasing of firing temperature up to 1000°C, porosity and pore sizes of castable tend to decrease, because of complete dehydration of reminder hydroxyl groups leading to increasing of strength. The use of nanometer-sized colloidal silica particles with high surface area, the solid phase sintering of the nano-sized particles and mullite formation can occur in the low temperatures.
Daspoddar et al.\textsuperscript{93} employed silica sols derived through different routes viz. inorganic, organic and ion-exchange routes in the low cement alumina castable composition in various proportions. The effect of different sources of such sols on the physico-mechanical properties of the castables such as bulk density, apparent porosity, compressive strength, volume shrinkage and residual strength after spalling have been reported. The silica sol synthesized through cation exchange routes showed significant beneficial role on the properties of castable with 3.0\% addition.

Adhikari et al.\textsuperscript{94} synthesized magnesium hydroxy phosphate compounds through coprecipitation technique using different basic medium. They detected only crystalline phase Mg(OH)\textsubscript{2} in the coprecipitated precursor. Triethanolamine favours the formation of more amorphous phases that ultimately gives rise to highest amount of crystallized Mg\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} at 1000\degreeC by thermal decomposition. Further rapid solid state reaction with the matrix it became an effective binder for MgO based refractories.

Gschiel et al.\textsuperscript{95} produced MgAlON bonded alumina refractories through in situ reaction of AlN, MgAl\textsubscript{2}O\textsubscript{4} and fine Al\textsubscript{2}O\textsubscript{3} powders.

3.10.3. Effect of particle size and dispersant on castable composition:
The physical properties of castables depended on the packing of ingredients in the castable. Density, porosity, strength characteristics and thermal stability are controlled by the compaction of the castable. Regardless of the choice of aggregates for a particular use, the grain size distribution must be taken to account to obtain the maximum compaction. The water requirement of the castable also has a direct correlation with the selection of the grain sizing in the aggregates and matrix. The different method of securing compactness in concrete mixes were demonstrated by furnas\textsuperscript{96} and Anderegg\textsuperscript{97} The main object is to obtain the maximum packing and minimum casting water requirement for the castable composition.

The effect of calcined alumina and deflocculants\textsuperscript{98} was investigated in a high alumina low cement castable. They used calgon (sodium hexa metaphosphate) empiphos (sodium tripolyphosphate, darvan 7S (sodium poly methacrylate) and darvan 811D (sodium polyacrylate) as deflocculants. Out of the different deflocculants, calgon gives the best results with 4.5\% cast water with only 0.05\% (total weight basis) addition. Both cal-
gon and empiphos exhibited similar hot strengths at 1200°C but calgon showed the highest at 1400°C.

The deflocculating mechanism\textsuperscript{99} may vary between an inorganic and organic dispersant. The most widely used dispersants are sodium hexametaphosphate and sodium polyacrylate. They observed that phosphate might adhere to the microsilica surface, more or less cleaning impurities from the surface, where as high molecular weight organic molecules might actually curl up between the particles, keeping them apart. The dissolution of dispersants in water produces ions that find oppositely charged particles in the cement where as the micro silica, keeping them apart, produce movement of the particles which, under the vibrational energy, causes the mix to flow.

Li et al\textsuperscript{100} showed the effects of typical organic and inorganic deflocculants on zeta potential of calcium aluminate cement, ultra-fine Al\textsubscript{2}O\textsubscript{3} and Cr\textsubscript{2}O\textsubscript{3} slurries, and on rheological behavior and flowability as well as microstructure of the castables. The inorganic deflocculant increases zeta-potential of the colloidal particles and adds to repulsive force of static electricity between the particles, thus dispersing the particles while the organic deflocculant has a minor effect on zeta-potential and its dispersing effect is believed to be mainly attributed to the steric stabilization caused by the organic deflocculant.

N.Li et al\textsuperscript{101} examined interstitial free (IF) samples heated at 1600°C for 90 min in graphite crucibles lined with MgO based castables bonded with microsilica. As the microsilica content in the MgO castable increased from 3 to 7 Wt\%, the TOC of the IF steel decreased due to the formation of a various liquid layer between the molten steel and the refractory which prevents dissolution of oxides from the refractory into the molten steel and so decreases the TOC of IF steel and act as an absorber for oxide inclusion in the molten steel.

S.Mukhopadhyay and S.K.Das\textsuperscript{102} showed that alumina bearing sol prepared through sol-gel route can be used as a bonding agent in low cement refractory castable composition. They reported that the simple tapping technique is cost effective to achieve desired high temperature properties. XRD and SEM studies confirmed the presence of corundum as a major phase and mullite as a minor.
Nandi et al.\textsuperscript{103} compiled the matrix composition of spinel forming high alumina castable to determine the effects of silica, magnesia and temperature on spinel formation. They suggested that medium and fine magnesia particles and optimum amount of silica in the matrix composition of spinel forming castable were necessary to obtain a matrix increased alumina rich spinel content with controlled permanent linear shrinkage and apparent porosity when exposed to high temperature service.

Sako et al.\textsuperscript{104} studied the anti hydration properties of high performance magnesia based castable with addition of microsilica. According to them, microsilica hindered the magnesia hydration and provided an additional bonding mechanism due to the reaction with MgO and water thereby controls the material’s volumetric change by reducing the expansion associated with the spinel formation.

Hommer and Wutz\textsuperscript{105} investigated the function of different types of dispersants for refractory castable regarding to their chemical structure, the mode of action and the influence of these additives on cement hydration. The effects and benefits achieved with these new classes of dispersants particularly polycarboxylate ether (PCE) in low cement self flow castables regarding flow properties and strength development focused that they improve the fresh as well as the hardened properties of the concrete, which is essential in the production of enhanced refractory materials.

Salomao and Pandolfelli\textsuperscript{106} showed that the polymeric fibers (Polypropylene) are efficient drying additives for refractory castables due to reduced risks of explosion during the first heat-up. They reported that when fibers are melted, they increase permeability, enhancing the drying rate and reducing vapor pressure behind this fibers can induce mixing and pumping difficulties due to particle entanglement.

Salomao and Pandolfelli\textsuperscript{107} pointed out that the formulation of castable composition, the main requirement was the particle size distribution (PSD) which is responsible for the large differences in their rheology, creep and corrosion resistance. They correlated the permeability and drying behaviors of fiber containing refractory castables to their PSD by using polypropylene fibers. They also mentioned that permeability measurements and explosion tests were associated to the maximum paste thickness (MPT) and interparticle separation (IPS) parameters and to the fine/coarse particles ratio.
Amaral et al.\textsuperscript{108} employed different chelate additives to dead burnt magnesia suspensions in order to check their effectiveness as inhibitors of the magnesium oxide hydration. Zeta potential, ionic conductivity, pH and temperature measurements were used to provide information related to the magnesia surface and the chelant adsorption. They reported that citric acid can inhibit hydration to some extent, whereas ethylenediamine tetraacetic acid (EDTA) was more effective in preventing volume expansion. An addition of 0.3 wt\% of these chelants was sufficient to prevent hydration and avoid expansion.

Salomao and Pandolfelli\textsuperscript{109} showed that the volumetric expansion of MgO castable results in cracks or even explosion during the first heating-up. They reported the citric acid (CA) and other chelants can significantly reduce MgO hydration rate in aqueous suspensions by forming an insoluble magnesium citrate protective coating on the magnesia particles surface.

Oliveira and Pandolfelli\textsuperscript{110} illustrated the influences of dispersants on the refractory castable properties with the firing temperature. The hydrates formed during the curing process of castable depends on the dispersing additive used. The FS60, polycarboxylate ether, induced the AH\textsubscript{3} formation and its decomposition resulted in a more stable hydrate (AH), which increased the splitting strength with the thermal treatment temperature. At a high temperature, the CA\textsubscript{2} and CA\textsubscript{6} formation is also favored in the presence of this additive.

Otroj et al.\textsuperscript{111} investigated the effect of four commercial dispersants on the properties of alumina-spinel self-flowing refractory castables. The evaluated the self-flow value, water demand, physical and mechanical properties as well as microstructure of these castables. The results showed that the polycarboxylate ether (0.1\%) is the most effective dispersant in increasing self-flowability because of its electrosteric dispersion mechanism. The results also indicate that the sodium hexametaphosphate has a great effect on the green strength of the castable. The microstructural evaluations indicated that the platy crystal of CA\textsubscript{6} was formed inside the grain boundaries of refractory castable after firing at 1500°C.

Braulio et al.\textsuperscript{112} evaluated the effect of different microsilica content for different magnesia grain sizes (<45 or <100 mm). Due to a faster spinel formation with the fine
MgO source, microsilica counterbalanced the MgAl$_2$O$_4$ expansion. Conversely, for the coarser MgO, silica increased the Mg$^{2+}$ dissolution, speeding up the spinel formation and expansion. Therefore, microsilica presented opposite roles, pointing out that it does not always counterbalance the spinel expansion.

Odegard et al.\textsuperscript{113} formulated cement free MgO castables with MgO-SiO$_2$-H$_2$O bond with respect to flowability, flow decay and hot properties by using mixture of superfine fraction microsilica and/or reactive alumina. Two particle size distributions were tested, one with a q-value of 0.25 (self flowing) and one with a q-value of 0.28 (vibratable). R.U.L value at T$_a$ above 1650\textdegree C for the MgO-SiO$_2$ and MgO-Al$_2$O$_3$ systems. All compositions were subjected to rotary slag testing to compare their slag resistance, with an alumina-spinel using BOF and EAF slag. MgO based castables showed better slag resistance to both slags than the reference castable.

3.10.4. Choice and generation of double hydroxide hydrogel spinel precursors

Various parameters controlling the synthesis and characterization of micro fine single and multi component oxide precursors have been summarized by several workers involving sol-gel route, gel-co-precipitation, organic gel-assisted citrate complexion (modified Pechini process), hydrothermal route, flame spray pyrolysis and combustion routes etc. Some workers deal with the preparatory technique using different metals salts, solvents, concentration of the metal salts solution and basic medium for precipitation while others emphasize on the structural changes occurred during thermal changes. Another approach concerned the application of these precursors in diverse fields.

The two principal types of precursor used in the sol-gel synthesis of ceramics are metal alkoxides and metal salts. Alkoxides offer the potential of freedom from anionic contamination and the promise of obtaining pure materials. They are however, rather expensive and can introduce complications associated with residual organic groups and their conversion to carbonaceous species. Moreover, every possibility of retention of residual porosity after sintering may be encountered.
Metal salts, on the other hand, offer economic advantages but introduce anions into structure. These, in turn, lead to complications of purifications and can be a source of diversity in structure\textsuperscript{114}.

Spinels with general formula $\text{AB}_2\text{O}_4$ where $\text{A}=\text{divalent cation (Mg}^{2+},\text{Zn}^{2+} \text{etc.)}$ and $\text{B}=\text{trivalent cation(Al}^{3+},\text{Cr}^{3+},\text{Fe}^{3+} \text{etc})$ are cubic in structure having 8 molecules per unit cell. The oxygen ions form almost a perfect cubic closed packed arrangement with metal ions distributed in position of 4 fold and 6 fold co-ordination. The maximum number of possible tetrahedral and octahedral holes are 64 and 32 respectively. Two trivalent cations present in the octahedral sites while divalent cations in the tetrahedral sites in normal spinel structure. Normal spinel material belongs to superior class of refractory materials. Nowadays, magnesium aluminate, zinc Aluminate and magnesium-chromite spinels have attracted special attention as an important class of ceramic materials at high temperature because of its high mechanical strength, excellent chemical durability and superior thermal shock resistance at higher temperatures.

**MgAl$_2$O$_4$ System**

Various attempts have been made for synthesis and fabrication of spinels adopting solid state reactions techniques from their respective pure oxides, hydroxides or carbonates components. But it has several disadvantages like higher temperature of sintering, longer processing time for repetition of calcination steps accompanied by non-uniform and abnormal grain growth and remanant porosity. Moreover, spinel synthesis utilizing solid state reaction is accompanied by 5 to 7 % volume expansion which makes the production impossible by single step sintering process. Several synthetic methods such as co-precipitation, sol-gel, citrate-nitrate route, hydrothermal and micro wave assisted combustion routes are followed to synthesize ultrafine, homogenized poly metallic spinel precursors which are characterized by high purity, high surface area, huge chemically active sites and narrow particle size distributions.

Reaction sintering of magnesia rich magnesium aluminate spinel (34 w/w\% MgO) was done in the temperature range of 1600-1700$^\circ$C by R.Sarkar et al\textsuperscript{115}. Reactivity of constituent alumina was varied by changing the calcination temperature up to 1600$^\circ$C. Thermal expansion curves (through dilatometric study) were used to study the effect of
alumina reactivity on spinel formation. Final sintered powder was characterized by densification, phase analysis, hot strength measurement and micro structural analysis to evaluate the influences of alumina on sintered behavior.

Rufner *et al*\(^{116}\) synthesized MgAl\(_2\)O\(_4\) nanoparticles via polymeric precursor (Pechini) and coprecipitation methods. The Pechini method allowed the formation of ultrafine spinel nanoparticles with a bimodal size distribution centered around 12 and 27 nm, respectively. Pechini method was limited to a relative density of 54\% after 20 min at 1300\(^{\circ}\)C due to the combination of the gas formation during sintering (carbonate decomposition) and significant agglomeration where as the coprecipitation method was used successfully to synthesize ultrafine spinel nanoparticles of 5–6 nm under simple synthesis conditions and significantly lower temperatures were required.

Zawrah\(^{117}\) synthesized Mg-Al spinel powders with a molar ratios (Al\(_2\)O\(_3\)/MgO) of 1.0, 1.1, 1.2, 1.3 and 1.4 by co-melting method from the corresponding magnesium and aluminum nitrate to investigate the lattice parameter, and properties of the obtained powders. XRD, TGA, TEM, and IR were used to investigate the prepared powders. Another series of stoichiometric Mg-Al spinel (molar ratio1.0) with addition 0.5, 1.0 and 2.0 wt% of Fe\(_2\)O\(_3\) as a sintering aid were prepared by the same method. Effect of sintering temperature up to 1650\(^{\circ}\)C on the densification and properties of the sintered bodies were studied.

The results revealed that well crystalline Mg-Al spinel were obtained after calcination at 1000\(^{\circ}\)C. Their crystallinity decreased with the higher alumina content than the amount required to form stoichiometric spinel due to the decrease of lattice parameter and grain sizes. The obtained crystal size was between 12 to 59 nm and particle size around 10-60 nm. Infrared spectroscopy showed bands corresponding to the existence of Al\(_6\)O\(_6\) groups building up the magnesium aluminate spinel, which was the only crystallite present at 1000\(^{\circ}\)C. The presence of 0.5, 1.0 and 2 wt% of Fe\(_2\)O\(_3\) as sintering aid for stoichiometric spinel lead to the increase of sinterability on firing up to 1650\(^{\circ}\)C. The higher density was for the samples containing 2 wt\% Fe\(_2\)O\(_3\) which reached about >98 TD and the prepared ceramics had improved mechanical properties.
Li et al. used ammonium carbonate as the precipitant to synthesize Mg-Al spinel precursors from a mixed solution of magnesium and aluminium nitrates. The precursor, composed of crystalline ammonium dawsonite hydrate \([\text{NH}_4\text{Al(OH)}_2\text{CO}_3\cdot\text{H}_2\text{O}]\) and hydrotalcite \([\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_16\cdot4\text{H}_2\text{O}]\) phases, transformed to pure spinel at ~900°C via the decomposition of hydrotalcite at 400-800°C and a solid state reaction between MgO (decomposition from hydrotalcite) and \(\gamma\)-\(\text{Al}_2\text{O}_3\) (derived from \(\text{NH}_4\text{Al(OH)}_2\text{CO}_3\cdot\text{H}_2\text{O}\)) at 800-900°C. Sinterability of the resultant spinel powders was evaluated by the constant rate of heating sintering method. The effect of calcinations temperature on particle morphology and sinterability of the resultant spinel powders was investigated. Spinel ceramics of 99% dense were produced by vacuum sintering at 1550°C for 2 hrs from the powder calcined at 110°C for 2 hrs.

Adhikari et al. synthesized and characterized co-precipitated hydrogel of magnesium and aluminum in relation to different basic media namely 1:1 ammonium hydroxide, ammonium hydroxide-triethanol amine and ammonium hydroxide-ammonium carbonates mixture. The same co-precipitation technique was also carried out in CO₂ atmosphere. The nature of compound formed was observed to depend on the type of precipitating agent as well as pH and reaction environment. The co-precipitated hydrogel dried at 110°C and heat treated at different temperatures was characterized by X-ray diffraction, DTA, TGA, particle size analysis and IR spectroscopy. The thermal treatment of the co-precipitates revealed the formation of \(\text{MgAl}_2\text{O}_4\) spinel phase at temperature as low as 600°C.

Lopez et al. synthesized hydrated magnesium aluminium hydroxide carbonates by the sol-gel process using aluminium and magnesium alkoxides as precursors. These materials resemble hydrotalcite in which magnesium cations are octahedrally coordinated to the surrounding hydroxide ions to form layer and \(\text{Mg}^{2+}\) ions are replaced by \(\text{Al}^{3+}\) resulting in an excess of positive charge which is compensated by the carbonate anions in the interlayer space. According to authors if the calcinations temperature is higher than 500°C, \(\text{Mg}_6\text{Al}_2\text{O}_8(\text{OH})_2\) is formed but in the presence of water and \(\text{CO}_3^{2-}\) ions, hydrotalcite is reformed and if the temperature is higher than 600°C, the decomposition of hydrotalcite is irreversible and at 1000°C spinel (\(\text{MgAl}_2\text{O}_4\)) is formed.
Gusmano et al\textsuperscript{121} hypothesized a mechanism of MgAl\textsubscript{2}O\textsubscript{4} spinel formation from the thermal decomposition of Mg-Al hydroxy compounds derived from NH\textsubscript{4}OH as co-precipitating agent. They showed that the decomposition started with the loss of interlayer water and completed at about 220°C. At the same time the conversion of Al-hydroxide to \(\eta\)-alumina occurs and becomes complete at about 280°C. \(\eta\)-alumina thus produced reacted with mixed hydroxides to give a transition phase similar to hydrated spinel which finally decomposed to MgAl\textsubscript{2}O\textsubscript{4} at 400°C.

Mukherjee and Samaddar\textsuperscript{122} postulated a different mechanism for the spinel formation. The authors reported that when Mg-Al double hydroxides MgO.Al\textsubscript{2}O\textsubscript{3}.16H\textsubscript{2}O was heated, it gradually eliminated 9 moles of water of crystallisation at 500°C due to the formation of magnesium aluminate hydrate (MgO. Al\textsubscript{2}O\textsubscript{3}.7.9 H\textsubscript{2}O) a new compound claimed by them. At 572°C a spinel like phase was obtained with some gamma-alumina which on further heating at 960°C under reduced pressure generates anion vacancy due to sublimation of aluminium. Formation of spinel started from 800°C and non-stoichiometric spinel (MgO\textsubscript{0.865}Al\textsubscript{1.83}O\textsubscript{3.64}) was formed at 1100°C. Spinel formation was completed at 1250°C where some \(\gamma\)-alumina goes in the solution with spinel. Finally at 1350°C exsolution of \(\alpha\)-alumina occurred during the cooling of MgAl\textsubscript{2}O\textsubscript{4}.

Recently, colloidal solutions obtained from the hydrolysis of alkoxide precursors have been used to prepare high surface area materials.

Wang et al\textsuperscript{123} prepared MgAl\textsubscript{2}O\textsubscript{4} spinel powders utilizing aluminium isopropanoxide and magnesium methoxide as starting materials. The authors reported that the degree of crystallinity increases with the calcination temperature and all the peaks of the spinel structure are clearly observed in powder calcined at 1200°C. The particle size of the spinel powder calcined at 1100°C is about 50 nm and highly dense, transparent, polycrystalline MgAl\textsubscript{2}O\textsubscript{4} has been obtained by sintering, utilizing hot isostatic pressing technique.

Adhikari et al\textsuperscript{124} investigated thermal behavior of co-precipitated Mg-Al hydroxides gel towards the formation of composite powders of periclase and MgAl\textsubscript{2}O\textsubscript{4} spinel at low temperature. The co-precipitated Mg-Al hydroxyl compounds were synthesized at two different temperatures and at pH ranges in between 8.56 and 9.20 from chloride salts.
of respective ions with molar ratio for MgO:Al$_2$O$_3$ as 2:1 using various combinations of ammonium hydroxides, triethanol amine(TEA) and ammonium carbonates mixture as basic media for co-precipitation. The co-precipitated hydroxide gel dried at 110°C and heat treated at different temperatures up to 1000°C were characterized by DTA, TGA and XRD studies. In all cases the co-precipitated Mg-Al hydroxyl phases collapsed at 400°C with the conversion to transient amorphous phases. Further heat treatment at higher temperatures led to the formation of MgAl$_2$O$_4$ spinel and minor periclase phases at temperature as low as 600°C. The co-precipitated Mg-Al hydroxides gel derived from TEA-NH$_4$OH basic media exhibited promising results so far as transformation to composite powders of MgAl$_2$O$_4$ spinel and periclase at relatively low temperature is concerned.

Prabhakaran et al$^{125}$ showed that magnesium nitrate, aluminum nitrate and urea formaldehyde polymer formed a transparent gel after drying under self sustained combustion when initiated by burning splinter. Combustion product on calcination at 850°C resulted in formation of MgAl$_2$O$_4$ spinel which after ball milling resulted in particles of median particle size of 1.58 μm. The Spinel particles are agglomerates of nanocrystals of size in the range of 10-30nm. The compact prepared by uniaxial pressing of spinel powder was sintered to >99% TD at 1600°C.

Andrievskikh et al$^{126}$ prepared spinel by sintering caustic magnesite and technical alumina containing materials composed of slag of aluminothermic production of nonferrous metals. As the results the periclase powder on spinel binder obtained has become the base fabricating periclase spinel refractories.

Wang et al$^{127}$ developed magnesia-alumina spinel using mainly weakly fired magnesia powders, bauxite with minor addition of Fe$_2$O$_3$, CaO and TiO$_2$ at the temperature range of 1650°C to 1750°C. Prepared spinel mainly composed of magnesia aluminate along with some silicate and titaniferous minerals. According to authors the Al$_2$O$_3$/MgO ratio has great effect on all the mineral compositions but the ratio in spinel is directly proportional to that in the specimen.

Gonsalves et al$^{128}$ demonstrated the processes of preparing raw materials and properties of magnesia-spinel brick for cement rotary kilns. Synthetic-fused spinel was produced by electrofussion of calcined alumina and dead burned or caustic magnesia.

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The melt was slowly cooled to accelerate crystal growth. Finally the authors concluded that magnesia-spinel brick manufactured from natural magnesite and fused-spinel grain, showed higher resistance to hydration, carbonation and alkali sulphate attack than a similar product obtained from sea water magnesia and sintered spinel.

Magnesia spinel refractories have been widely used in the transition zone of cement rotary kilns but the refractories showed structural degradation due to incorporation of alkali salts coming mainly from fuel. Imai\textsuperscript{129} studied the influence of alkali salt on magnesia-spinel bricks. The authors used $\text{K}_2\text{SO}_4$, $\text{KCl}$ and $\text{K}_2\text{CO}_3$ salts for their experiments followed by heat treatment at different temperature cycle. Finally the authors concluded that the effect of alkali salt resistance could be overcome by improving the hot properties and densification character of the bricks.

Evans\textsuperscript{130} described the manufacturing process of magnesia-alumina spinel brick using magnesium hydroxide obtained from sea water magnesia especially quality alumina. The authors reported that the main advantages of these bricks in rotary kilns could be summarised as follows: (a) high resistance to thermo-mechanical stress (b) chemical resistance to sulphur and alkali deposits (c) low thermal expansion, (d) high resistance to kiln atmosphere, (e) low content of secondary oxides and (f) elimination of chromite.

Alper et al\textsuperscript{131} measured the limits of the solid solution of Al ions in periclase and Mg ions in spinel for the determination of liquidus, solidus and subsolidus of the MgO - MgAl$_2$O$_4$ system using high purity MgO and Al$_2$O$_3$. Induction heating technique was utilised to determine the limits of solid solution by heating the pressed sample at 1975°C for 2 hours. Authors concluded maximum periclase solid solution was found at 82% MgO, 18%Al$_2$O$_3$(9.5% Al$^{3+}$) and maximum spinel solid solution at 39%MgO, 61%Al$_2$O$_3$(6%Mg$^{2+}$).

Serry et al\textsuperscript{132} studied the effect of composition and microstructure of MgO-Al$_2$O$_3$ refractories on their densification and refractory properties. The authors used chinese dead burnt magnesite and calcined bauxite as the initial raw materials. Different batches were prepared and heat treated at 1700°C to produce periclase, magnesia-spinel, spinel, spinel alumina and corundum refractory grains. Finally the authors recommended these
refractories for application cement, steel and glass furnaces to replace chrome bearing refractories in order to eliminate its dangerous environmental pollution.

Bakker and J.G.Lindsay\textsuperscript{133} reported complete formation of magnesia spinel body at a temperature as low as 1000°C using AlF as a mineraliser. Al(OH)\textsubscript{3} and Mg(OH)\textsubscript{2} prepared from aluminium trihydrate and brucite respectively, were mixed together and heat treated. Addition of 1.5wt\% percent AlF\textsubscript{3} as mineraliser helped to initiate the process of spinel formation at 900°C and complete it at 1000°C. On addition of excess amount of MgO to the mineralised system the spinel formation was completed at 1050°C. The excess MgO did not affect the reactivity and remained as periclase in the sintered body. On the other hand addition of excess amount of Al\textsubscript{2}O\textsubscript{3} was found to form solid solution in the spinel phase which ultimately slowed down the reactivity by inhibiting the grain boundary diffusion of oxygen ions during sintering.

\textbf{MgCr\textsubscript{2}O\textsubscript{4} System}

MgCr\textsubscript{2}O\textsubscript{4} is an important refractory material having high melting point (2350°C) and excellent resistance to slag attack. It is used in basic open hearth furnace and various metallurgical applications. In recent years it has been found that there is ample possibility of using high purity in electronic industries or as bonding material, sintering aids, emissive coating and high temperature stain. This type of materials of high purity can be prepared by various methods like

(1) Solid state reaction using high purity oxides, hydroxides by heat treatment at high temperature

(2) Gel co-precipitation technique using pure metals salts

Many investigators synthesized the above materials and studied the different aspects of sintering, semi conduction, humidity sensitivity, electrical conduction and micro structure with an objective to find out its potential use in different fields.

Kaliev and Popil\textsuperscript{134} synthesized MgCr\textsubscript{2}O\textsubscript{4} by using chromium oxide and periclase. Authors found that formation of magnesium chromite along with chromium oxide was
identified at 1350°C, 1500°C and the reaction was completed at 1750°C with the formation of some solid solution of MgCr₂O₄.

Somiya et al.\textsuperscript{135} investigated the phase relations in the system Cr₂O₃-MgO-TiO₂ in air at 1400°C and observed Cr₂O₃ could be soluble up to 8 wt% in to MgO in the Cr₂O₃-MgO system and MgO also soluble up to a certain percentage in Cr₂O₃ but Cr₂O₃ and MgO could not enter into MgCr₂O₄ lattice to form solid solution.

Park and Kim\textsuperscript{136} reported that electrical conductivity of MgO doped Cr₂O₃ within the solubility limit was increased with MgO content due to creation of holes and annihilation of chromium vacancies and the same was decreased above solubility limit with increasing MgO content due to the formation of MgCr₂O₃.

Prasad et al.\textsuperscript{137} investigated the sintering behaviour of different combination of MgO, Al₂O₃ and Cr₂O₃ using alumina, magnesium hydroxide and anhydrous chromium oxide as starting materials. Compacts of different composition were heat treated at 1450°C to 1650°C and different properties were measured to evaluate the suitability of the materials for proper applications. The authors concluded that

(i) Densification increased with the increase in sintering time and temperature for all the compacts.

(ii) Maximum density of 3.219gm.cm⁻³ was obtained at 1650°C with soaking for 4h.

(iii)Phases were mainly Mg-Al and Mg-Cr spinel

(iv)Microstructure showed rounded and polygonal grains of closely spaced spinel

Large amount of chromite-periclase and periclase-chromite base refractories are produced in Russia for cement industry. Now a days, the experience of the world cement industry shows that perclase refractories may be a very good prospective material in place of periclase-chromite refractories. Spinel refractories should be especially stressed, because it makes cement production ecologically safe due to the substantial decrease in the concentration of harmful hexavalent chromium.
Shubin and Nikonorov\textsuperscript{138} prepared periclase-spinel refractories using brucite and commercial alumina as starting raw materials. Finally the authors compared the properties of the synthesised periclase spinel refractories with periclase-chromite and chromite-periclase refractories and found that the developed refractory had much better properties specially the heat resistance than other refractories used in the cement industries.

Anderson\textsuperscript{139} studied the influence of oxygen activity on the sintering of MgCr\textsubscript{2}O\textsubscript{4} and reported that densification of magnesium chromite needs high temperature above 1700\textdegree{}C at <10-6 atm. in oxygen partial pressure.

Yoshida et al\textsuperscript{140} studied the formation process of magnesium chromite spinel prepared by hydrazine method. The authors used magnesium chloride, chromium chloride and hydrazine monohydrate as starting materials. Ultimately the authors reported that dense magnesium chromite ceramics with 99.55\% theoretical density can be constructed possible by introducing plasma sintering procedure at 1400\textdegree{}C for 5 min and 30MPa

Packtet and Resnap\textsuperscript{141} studied the dehydration of hydroxichromite obtained from mixed slution of Cr\textsuperscript{+3} and Mg\textsuperscript{2+}. Sodium hydroxide was used as basic precipitation agent for coprecipitation. Three types of coprecipitates were prepared with increasing amount of MgO. Authors reported that strong lines of crystalline MgCr\textsubscript{2}O\textsubscript{4} was obtained at 800\textdegree{}C

Moriwake et al\textsuperscript{142-143} sintered magnesium chromite at various holding times. They observed that all the samples had a single phase spinel structure and were p-type semiconductors. The lattice constant was increased with increasing the holding time. The authors also reported that oxygen partial pressure dependence of electrical resistivity was divided into two gropus according to the difference of holdng tome.

Adhikari et al\textsuperscript{144} synthesized 1:1 molar ratio of mixed hydroxides gel of MgO-Cr\textsubscript{2}O\textsubscript{3} system by wet chemical interaction of Mg\textsuperscript{42} and Cr\textsuperscript{43} at 60\textdegree{}C and at pH 8.5 using 1:1 ammonium hydroxides as basic medium.teh synthesized gel exhibited high specific surface area with average spherical particle diameter of 0.3\textmu{}m. The mixed hydroxides gel when heat treated at 500\textdegree{}C transformed into poorly crystalline MgCr\textsubscript{2}O\textsubscript{4} spinel.
3.10.5. Effect of double hydroxides hydrogel precursors on sintering of refractory castables

MacZura et al\textsuperscript{145} highlighted the effect of different additives on the water requirement, flowability, working time, and strength characteristics of alumina castables. They studied the effect of liquid isopropyl alcohol, sodium gluconate, with filler (plastiment), sodium tetraborate, sodium chloride, calcium chloride, calcium hydroxide, calcium carbonate, magnesium carbonate and supplementary additives like methanol, and polyvinyl alcohol. The castable was based on tabular alumina with 15\% HAC (80\% alumina). Liquid isopropyl alcohol and 1-2\%, cement was found the most functional retarder with water reduction, good plasticity and flow property with minimum strength reduction. Sodium gluconate also reduces the water but is more critical in strength impairment. A combination of 0.25\% each of sodium bicarbonate and citric acid was proved to be effective as additive in retarding free lime in unstable calcium aluminate cements.

Khalil and Wahsh\textsuperscript{146} improved two commercial refractory castables based on mullite or magnesia aggregates through addition of 0–25 wt.\% nano-magnesium aluminate spinel (MA) powder and reported that 10 wt.\% nano-MA spinel powder was optimum in terms of its good sintering, mechanical as well as refractory properties.

Twigg et al\textsuperscript{147} studied the wet erosive wear of model polycrystalline alumina materials containing intergranular phases derived from a range of silicate based sintering additives. The effects of intergranular phase composition on wear rate were interpreted in terms of different strains, concentrated at grain edges and faces. These strains will affect the energy input, provided by particle impact, required to initiate and propagate grain boundary micro cracks.

Galusek et al\textsuperscript{148} studied the wet erosive wear of polycrystalline alumina of mean grain size -1 micron, containing up to 10 wt\% of magnesium silicate sintering aid. For pure crystalline alumina, the dominant wear mechanism was grain boundary micro fracture, leading to partial or complete grain removal. In the case of liquid phase sintered materials, wear rates could be as low as 25\% of those of pure alumina of the same main grain size, and the main material removal mechanism was transgranular fracture combined with tribochemical wear. The use of Cr\textsuperscript{3+} photoluminescence line broadening
showed much higher levels of total stress in the magnesium silicate sintered materials (about 450MPa) than that of the pure alumina materials (about 200 MPa). Grain boundary compressive hoop stresses, caused by the thermal expansion mismatch between a continuous magnesium silicate film and the alumina grains, provide an explanation for the improved wear resistance.

Lankard and Hackman\textsuperscript{149} reported that admixture is providing safe water reduction. Plaster of paris seemed to be a good accelerator in amounts of 1-3% of cement basis while small additions of lithium compounds (below about0.1% cement weight basis) found to be good accelerators for strength development.

Lee et al\textsuperscript{150} placed a small amount of anorthite (2CaO.Al\textsubscript{2}O\textsubscript{3}.3SiO\textsubscript{2}) powder on the top center of the pure alumina powder compacts and then sintered at 1600°C. During sintering some grain grew extensively along the radial direction from the liquid source. By considering an automatically smooth solid liquid interface structure of alumina, grain growth controlled by two dimensional (2-D) nucleation was suggested. The elongation has been explained in terms of nucleation advantage of grain boundary reentrant edges (GBRE) formed dominantly at non-basal planes.

Bataille \textit{et al}\textsuperscript{151} upgraded super plastic deformation of the fine grained bluming by graphite particles and considered alumina ceramics are not usually good candidate for super plasticity as the grain growth reduces quickly their deformation performance. In order to impede the grain boundary mobility and to limit the grain growth, zirconia has often been associated with the alumina since the early 80s. In this work, a dense MgO doped alpha alumina containing a small amount of carbon has been produced. The sintering and the deformation behavior of the material are compared to those of a MgO doped alumina. The presence of small carbon particles reduces greatly the grain growth during the sintering, during the compression experiments. The super plasticity of the carbon containing alumina is greatly improved.

Klyucharov and Meshalkina\textsuperscript{152} demonstrated the interaction between MgA\textsubscript{12}O\textsubscript{4} and MgCr\textsubscript{2}O\textsubscript{4} spinels and their solid solutions with calcium ferrites that are essential constituents of various slag reagents at 1600-1750°C i.e. under conditions approaching those existing during service of the perielase-spinel and thermally resistant magnesiochromite.
refractories used in lining steel-melting furnaces. With the action of highly ferruginous melts on magnesioehromite, the resulting solid solution increases in volume, and a distortion is observed at the boundary of the reaction.

The effect of chromium oxide on the sintering of aluminosilicate precursor leading to mullite formation was investigated by Mitra and co-workers\textsuperscript{153}. It revealed that the chromium oxide plays a positive role in the formation of mullite at temperatures of 1450°C from aluminosilicate precursors.

Parya \textit{et al}\textsuperscript{154} demonstrated that minor addition of co-precipitated Zinc aluminate spinel precursor acts as a potential sintering aids for pure alumina ceramic which results in high mechanical strength and uniform microstructure where \textit{in-situ} formed zinc aluminate spinel dopant functioning as an grain growth inhibitor in the alumina system.

Pal \textit{et al}\textsuperscript{155} studied the effect of CaO doping on the microstructure and properties of alpha alumina. The doping with small amount of CaO in alpha alumina resulted in heterogeneous microstructure at 1700°C for 2 h wherein calcium aluminate glassy phases were present in the grain boundary region.

The studies on sintering behavior of spinel-alumina composites revealed that solid solubility of alumina in MgAl\textsubscript{2}O\textsubscript{4} spinel decreases rapidly with decreasing temperature which causes exsolution of alumina from spinel phase\textsuperscript{156}. However exsolution of alumina makes some interlocking structure in between alumina and spinel phases. SEM study of the samples does not reveal the distinct precipitation of needle shaped $\alpha$-alumina from spinel but has some effect on the densification process of spinel-alumina composites.

The work of Wu \textit{et al}\textsuperscript{157} on preparation, sintering and fracture behavior of Al\textsubscript{2}O\textsubscript{3} - LaAl\textsubscript{11}O\textsubscript{18} ceramic composites in presence of AlF\textsubscript{3} additive at 1550°C revealed that enhanced low temperature sintering was achieved and rod like LaAl\textsubscript{11}O\textsubscript{18} grains were distributed homogeneously in Al\textsubscript{2}O\textsubscript{3} matrix. The results also showed that LaAl\textsubscript{11}O\textsubscript{18} grains reduced grain growth of alumina and increased the fracture toughness of Al\textsubscript{2}O\textsubscript{3}-LaAl\textsubscript{11}O\textsubscript{18} composites. The improvement of fracture toughness of the composites is attributed to the mechanism of crack deflection.
Mukhopadhyay and Daspoddar\textsuperscript{158} prepared modified \textit{in situ} spinel-alumina castables by using 8.0 wt.% of calcined hydrated magnesium aluminate additives synthesized via sol gel and coprecipitation routes. They compared the properties of prepared castables in terms of bulk density, apparent porosity, cold crushing strength and spalling resistance to see the excellent performance of the sol gel additive having nanocrystalline feature. The quality of castable was illustrated with the same prepared by commercially available spinel fines. They concluded that the spinel-alumina castable prepared by the sol gel additive could be a potential candidate for application in steel plants.

Titov \textit{et al}\textsuperscript{159} explained the properties of magnesium chromite and magnesium aluminate. The article presents the relationships between the average sizes of the crystallites, the specific surface and the porosity of powdered materials in the MgCr$_2$O$_4$-MgAl$_2$O$_4$ system, and their composition and synthesis temperature, and also the relationship between the shrinkage of the specimens during. The studied materials were synthesized by using oxides of chromium (VI) and magnesium, and hydroxides of magnesium and aluminum of chemical purity.

Kashcheev \textit{et al}\textsuperscript{160} mentioned the method for synthethic materials in the MgO-Cr$_2$O$_3$ system based on the interaction of caustic MgO with chromic anhydride. An increase in the proportion of MgO above the stoichiometric MgCr$_2$O$_4$ fails to obtain an ideal solution. The powders were dried and granulated at 130-160°C. The subsequent heat treatment of the magnesium chromate and dichromate at 850-1200°C, MgO + MgCr$_2$O$_4$ and MgCr$_2$O$_4$ is obtained. The phase composition of the composite material was periclase (10-15%) and magnesiochromite (85-90%). The sintering behavior of the MgO-MgCr$_2$O$_4$ composite was better than that of analogous mixture based on the pure oxide.

Khoroshavin\textsuperscript{161} showed that periclase-chromite, chromite-periclase and fused chrome-spinel articles contain ecologically dangerous hexavalent chromium Cr$^{6+}$. Therefore, to replace the production of these products highly resistant periclase-spinel, periclase-lime, lime-periclase and fused or sintered magnesia-alumina spinel MgO-AI$_2$O$_3$ are useful. Mullite-chromite contained one order less Cr$^{5+}$ than periclase owing to the formation of silicate films on the chromite grains; thus preventing oxygen diffusion and reduce the free oxygen content.
Azhari et al\textsuperscript{162} added nano iron oxide up to 8 wt.\%, to mag-chrome refractory matrix through stirring in ultrasonic bath in an alcohol media and evaluated the phase and microstructure of samples heated up to 1650\degree C by XRD and SEM/EDS respectively. The dissolution of iron oxide and ionic migration improved the sintering process in the matrix of the refractory at low temperature. The presence of nano iron oxide also influenced the bonding structure in a way that direct bonding was enhanced while silicate bonding was hindered.

Braulio et al\textsuperscript{163} investigated the effect of the spinel content, grain size, calcium aluminon cement and hydratable alumina on the general castables properties. They pointed out that the use of mineralising compounds, the addition of nano-scaled particles and the evaluation of the effect of expansion under constraint and also alternatives for the design of high-performance alumina-magnesia refractory castables.

Sako et al\textsuperscript{164} evaluated a cement-bonded alumina–magnesia castables using dead-burnt magnesia of different particle size ranges. Microstructural observations suggested that the faster Mg\textsuperscript{2+} migration during the spinel formation led to vacancy accumulation and consequently to pore generation as a direct result of the Kirkendall effect. Additionally, the overall expansion of alumina–magnesia castables seemed to be ruled by two main factors: its sintering efficiency and the different possibilities of the Al\textsubscript{2}O\textsubscript{3} and MgO interactions in the mixture.

Kashcheev\textsuperscript{165} estimated a thermodynamic calculation of the probable reactions of interaction in mixtures of the MgO- MgCr\textsubscript{2}O\textsubscript{4} - MeC (Me = Si, Ti) system. They investigated the sintering properties of MgO+ MgCr\textsubscript{2}O\textsubscript{4} mixture with additions of titanium and silicon carbides. It was established that the maximum density (96\% of the theoretical value) of sintered specimens of MgO + MgCr\textsubscript{2}O\textsubscript{4} mixture was attained at a 0.5\% mass fraction of titanium or silicon carbide at a firing temperature of 1850\degree C.

Oliveira and Pandolfelli\textsuperscript{166} employed chemical additives to the castable for different purposes such as, dispersing the matrix particles and controlling the cement hydration reaction. The results showed that some additives not only affect the particle dispersion (matrix and binder) but also the yielded hydrates. Particularly, the polyglycol (FS60) additive favored both the dispersion of castables and the casting water reduction, result-
ing in $\text{C}_3\text{AH}_6$ and $\text{AH}_3$ hydrates, which can be correlated to the tensile strength development. On the other hand, in presence of citric acid, this formation of hydrates is hindered due to its retarding effect via calcium ion complexation. The $\text{AH}_3$ formation was favored when Secar71 is used as a binder resulting in a greater splitting tensile strength.

Han et al\textsuperscript{167} studied the effects of $\text{WO}_3$ on properties of MgO-based refractories and microstructures by scanning electron microscopy (SEM) with EDS. $\text{WO}_3$ can improve the sintering of MgO-based refractories <$2\text{wt}\%$ $\text{WO}_3$ is favourable to improve the cold modulus of rupture of MgO-based refractories, but high levels of $\text{WO}_3$ have an negative effect on cold MOR and thermal shock. The low melting phases $\text{MgWO}_4$ and $\text{CaWO}_4$ formed in MgO boundries results in increased liquid volume. The foemation of $\text{CaWO}_4$ leads to C/S ratio change and decreased levels of $\text{C}_3\text{S}$ and $\text{C}_2\text{S}$ and the low melting phase CMSforms. Thus, the densification is improved by phase liquid sintering. SEM observation confirms the existence of $\text{CaWO}_4$ and $\text{MgWO}_4$ grain boundary phases.

Nelson and Cutler\textsuperscript{168} estimated the effect of transition metal, alkali, alkanine-earth and heavy metal oxide on the sintering of magnesia determined by means of bulk density and shrinkage. The unusual effect of titanium, zirconium, silicon, lithium, iron and zinc oxides in promoting high sintered densities was explained on the basis of the defective crystal structure produced by these additions.

Zhang et al\textsuperscript{169} investigated the hydration behaviour of commercially pure Al powder in distilled water at 25-100\textdegree C. Bayerite $\text{Al(OH)}_3$ product layers formed on Al at 25-45\textdegree C were porous so the hydration rate, although very slow at 25\textdegree C, increased rapidly with increasing temperature from 25-45\textdegree C. On further increasing temperature from 45 to 95\textdegree C, initial hydration rate increased, but changed little over long hydration periods due to the formation of denser and more continuous product layers. At 100\textdegree C, because of rapid water evaporation, hydration product layers [composed of $\text{Al(OH)}_3$ and a small amount of boehmite $\text{AlO(OH)}$] became detached from the Al surfaces, so offering less protection, so that the hydration rate of Al increased again.

Haldar et al\textsuperscript{170} fabricated magnesite-chrome composites utilizing sintered magnesite and friable chrome ore in presence of titania as additive which played a significant role in improving the bulk density and strength. They evaluated the physical as well as
thermo-mechanical properties and microstructural features of the sintered aggregates. The common feature observed in the microstructures was the exsolution of spinel phase in magnesia grains. The hot properties of the composites were superior when the Cr$_2$O$_3$ content is increased to 30%.

Othman and Khalil$^{171}$ investigated the effect of calcined kaolin additions on sinterability of dead-burned magnesia through additions of Egyptian kaolin. Five batches containing powders of 100/0, 90/10, 80/20, 70/30 and 60/40 magnesia/kaolin were mixed, dried and fired up to 1550 $^\circ$C for 4 h. The phase compositions of the fired batches were investigated using X-ray diffraction as well as scanning electron microscope to illustrate the effect of the different developed phases on the above properties compared with the main magnesia source itself. Generally, samples containing 10–20 wt.% kaolin were characterized by their high sintering, mechanical and refractory properties, so they are recommended for use as a lining for different parts of steel furnaces as well as heating zone of cement rotary kilns. Samples containing 30–40 wt.% kaolin with lower refractory properties can be used in the heat exchangers or as kiln furniture in ceramic industries.

Sahin and Aksel$^{172}$ showed the effects of ZrSiO$_4$–3 mol% Y$_2$O$_3$ into MgO–MgAl$_2$O$_4$ composite refractories by mechanical properties and thermal stress resistance parameters. The observations are (i) the increase in resistance to crack initiation and propagation due to formation of Mg$_2$SiO$_4$ phase after decomposition of zircon; (ii) propagation of the microcracks formed in the structure for a short distance by interlinking each other; (iii) arresting or deviation of microcracks when reaching pores or ZrO$_2$ grains released after dissociation of zircon, located together with Y$_2$O$_3$ particles, and furthermore; (iv) co-presence of both intergranular and transgranular types of cracks, and with incorporation of zircon–Y$_2$O$_3$; (v) increase in density; and (vi) a significant reduction in MgO grain size.

Shon et al$^{173}$ studied the rapid sintering action of nanostructured MgO–MgAl$_2$O$_4$ composites with a high-frequency induction heated sintering process. They investigated the sintering behaviors, grain sizes and mechanical properties of MgO-MgAl$_2$O$_4$ composites. The Vickers hardnesses of MgO and MgAl$_2$O$_4$ composites sintered from MgO–10 wt% Al$_2$O$_3$, MgO–20 wt% Al$_2$O$_3$, MgO–30 wt% Al$_2$O$_3$, MgO–40 wt% Al$_2$O$_3$, and MgO–
50 wt% Al₂O₃ powders milled for 4 h were 583, 638, 958, 1073, and 1277 kg/mm², respectively. The hardnesses of the MgO-MgAl₂O₄ composites increased with an increase in MgAl₂O₄ content without decrease in fracture toughness.

Sarkar et al\textsuperscript{174} investigated the behavior of reaction sintering of magnesia rich magnesium aluminate spinel (MgO-34 wt.%) in the temperature range of 1600-1700°C. Final sintered products were characterized by densification, phase analysis, hot strength measurement and microstructural analysis for evolution of the influence of reactivity of alumina on the sintered characteristics.

Ganesh et al\textsuperscript{175} prepared a stoichiometric dense MgAl₂O₄ spinel according to a conventional double stage firing process using AlCl₃ as a sintering aid. Among the spinels sintered at 1550°C for 1 h, spinel incorporated with 2.733 wt% AlCl₃ exhibited superior properties in terms of bulk density, apparent porosity and water absorption, SEM and EDAX and electron probe microanalysis (EPMA). Finally, 20 wt.% of the stoichiometric spinel incorporated with 2.733 wt.% AlCl₃ prior to sintering was added to high-Al₂O₃ and MgO-C refractories to evaluate its effect on slag erosion and penetration resistance as well as on repeated permanent linear change (PLC) of these bricks. By the addition of stoichiometric MgAl₂O₄ spinel, the slag erosion and penetration resistance of high Al₂O₃ and MgO-C refractories was improved remarkably, and their PLCs exhibited more steady and stable positive values after spinel addition.

Yu et al\textsuperscript{176} reported that the properties of the MgO-ZrO₂ refractory were improved makedly by adding Y₂O₃. The bulk density of the sample with 1.0% added Y₂O₃ reached maximum value, and when the amount of Y₂O₃ addition was more than 1.0%, the slag corrosion resistance increased. The microstructure of the MgO-ZrO₂ refractory was changed by adding Y₂O₃. The Y₂O₃ and ZrO₂ phase reside among the MgO particles and matrix, and this would be the main reason for the improved slag corrosion resistance of the MgO-ZrO₂ refractory.

Banerjee et al\textsuperscript{177} investigated the incipient formation of low crystalline nanosized domains in the still-hydrated spinel. Spinel nanoparticles are protected by a thin chemisorbed layer of (OH) groups held around the active surface of the aggregates. Selected properties of conventional Al₂O₃-spinel and Al₂O₃-MgO castables were. Cold and hot
strengths of the refractory castable containing commercial spinel with excess alumina powder were the best, while the same bonded by reactive magnesia and coprecipitated spinel fines were not satisfactory. Performance of sol-gel spinel is comparable to the preformed spinel with 78% alumina.

Ghosh et al\textsuperscript{178} studied the effect of ZrO\textsubscript{2} additive on magnesite-chrome aggregates from friable chrome ore and magnesia. The reactivity of magnesia played an important role in the final properties of samples. Introducing less reactive sintered magnesia improved all the properties of the aggregates. ZrO\textsubscript{2} functioned as a good sintering aid in the magnesite-chrome composites.

Lodha et al\textsuperscript{179} analysed magnesia and alumina powders along with tetravalent oxide additives for their role in densification of spinel in a single stage firing process in order to achieve a better binding system for magnesia-based refractories. These tetravalent oxides on reaction with magnesia form spinel solid solution with MgAl\textsubscript{2}O\textsubscript{4} as they have similar crystal structure. The spinel solid solution formed using oxide additives is expected to have higher solubility in magnesia than magnesium aluminate spinel, resulting in improvement of the bonding during sintering through increased in solid solubility at elevated temperatures followed by precipitation of secondary spinel phases, similar to the complex spinel in magnesia-chrome refractories. The formation of spinel during firing remains as a second phase that retards the grain growth of periclase.

Rangelov and Stefanov\textsuperscript{180} investigated the impact of additives consisting of finegrained waste chrome magnesia on high alumina castables containing brown and white fused alumina, calcined bauxite and calcium aluminate as binder.

3.10.6. Properties of basic refractory castables:

Sarpoolaky et al\textsuperscript{181} evaluated the microstructural features on firing and quenching avibratable ultralow cement and an in situ spinel low cement castable refractory. The refractory phases like calcium hexaaluminate, magnesium aluminate spinel and mullite have beneficial effects on hot bend strength and refactoriness under load due to the development of morphologies which interlocked other phases and pore filling from expansion reactions.
Y.C. Ko\textsuperscript{182} estimated the smaller grain size of the spinel in Al\textsubscript{2}O\textsubscript{3}–MgO castables compared to that in Al\textsubscript{2}O\textsubscript{3}–spinel castables by the recrystallization of the \textit{in situ} spinel only occurring in Al\textsubscript{2}O\textsubscript{3}–MgO castables as revealed by the XRD patterns at ambient temperature and at 1500°C. The larger amount and smaller grain size of the \textit{in situ} formed spinel in the matrix mostly account for the better slag resistance of Al\textsubscript{2}O\textsubscript{3}–MgO castables, compared to Al\textsubscript{2}O\textsubscript{3}–spinel castables.

Borisenko \textit{et al}\textsuperscript{183} studied the slag resistance behavior of periclase-carbon specimens based on modified phenol formaldehyde resin using different forms of fillers i.e. sintered and fused periclase. Penetration of molten slag and its reaction with refractory is independent of the form of periclase filler and reduction in slag penetration into refractory with introduction of modifying additions. Slag resistance of periclase-carbon objects with use of sintered periclase as a filler and modifying additions appears somewhat inferior to that for similar materials based on fused periclase.

Braulio \textit{et al}\textsuperscript{184} investigated the better performance of spinel-containing refractory castables when in contact with basic slag which was mainly associated with their higher corrosion resistance. Based on the physical properties (apparent porosity, linear thermal expansion and pore size diameter distribution) and also on the phases generated (detected by SEM, before and after corrosion), a basic slag corrosion mechanism for the set conditions was proposed. The results revealed that lower penetration is attained by reducing the pore size diameters, whereas chemical corrosion resistance is a consequence of higher content of fine alumina, lower amount of calcium aluminates and the lack of liquid phase in the castable matrix.

Braulio \textit{et al}\textsuperscript{185} demonstrated the effect of microsilica on alumina-magnesia castables. Fine MgO and cement, microsilica counterbalanced the spinel expansion and generating a high content of liquid phase to reduce the overall expansion. Decreasing the MgO grain size highlights the microsilica’s speeding up ability, leading to a huge expansion. However, an alternative for lowering the expansion of castable is the use of hydratable alumina, which strongly counterbalances the spinel expansion as a consequence of its shrinkage behavior.
Marsui et al.\textsuperscript{186} investigated the corrosion behavior of MgO grains during slag penetration by microstructural analysis of magnesia refractory brick after the corrosion test at 1550°C, using calcium aluminosilicate slag. They concluded that MgO grains dissolved into slag indirectly and the spinel phase formed at the interface between magnesia refractory brick and the slag dissolved directly into the newly penetrating slag.

Domiciano and Pandolfelli\textsuperscript{187} performed the corrosion test with Al or Si containing castables prepared with the different binders and pointed out that an unexpected passivation mechanism could be actuating on aluminium and silicon powders in some particular systems. The metal particles can be protected by a stable aluminosilicate coating which provides a superior corrosion resistance to either Al or Si, making feasible their application as antioxidant to high–carbon containing refractory castables. They came to the conclusion that the use of cement, hydratable alumina or colloidal alumina was suitable alternatives for Si powder application and for Al powder, only the colloidal silica was found to be suitable binder.

Ewais et al.\textsuperscript{188} analysed the interactions between hot slag mixer and magnesia containing refractory, magnesia aluminate spinel and magnesite chrome. Parameters of molten slag in terms of temperature (1450-1550°C), basicity “CaO/SiO\textsubscript{2} or C/S (C/S=0.5-2) time (60-80min) and slag quantity (0.5-1.5 kg) were considered. They reported that temperature, basicity and interaction time of the molten slag is found to be effective parameters on the dissolution process of the refractories. Their microstructure revealed that magnesite chrome refractory in the frame of the boundary condition is the best type of mixer lining in comparison to that of magnesia aluminate spinel.

Obana and Tsuchinari\textsuperscript{189} examined the penetration resistance, corrosion resistance and spalling resistance for bricks made from different co-existent MgO-CaO clinker and bricks made from separately added clinkers to determine the most desirable structure in the MgO-CaO system.

Zhang et al.\textsuperscript{190} investigated the penetration and corrosion resistance of high purity sintered and fused magnesia grain by model EAF (CaO/SiO\textsubscript{2}= 1.38) and BOF “late slag” (CaO/SiO\textsubscript{2}=3.29) at 1600°C by SEM with EDS, and XRD analysis. The large magnesio-wustite grains limit the potential for grain boundary penetration into the sintered magne-
sia. The magnesiowustite layer formed with the EAF slag took up more Fe₃O from the slag than that formed with the BOF slag, which was partially responsible for a lower slag penetration into sintered magnesia grain since the remaining silica rich local liquid was rendered more viscous. The EAF slag was not saturated with respect to MgO, so the magnesiowustite which did form later reacted with Ca and Si ions remaining at the MgO/EAF slag interface to form low melting phases such as merwinite, C₃MS₂, and then dissolved in to the slag, rendering the dissolution process essentially indirected. The BOF late slag was already oversaturated with respect to MgO, so slag penetration only occurred in the sintered magnesia grains.

Ismael et al\textsuperscript{191} demonstrated that colloidal silica important alternative for the traditional CAC binders because of its potential to speed up drying, reducing the amount of liquid phase at high temperatures and inducing mullite formation for Al₂O₃- SiO₂ and Al₂O₃-MgO castables. They optimized colloidal silica formulations based on permanent linear change (PLC), apparent porosity (AP) and cold (MOR) and hot (HMOR) modulus of rupture and compared the results with those of a CAC reference castable.

K.Goto et al\textsuperscript{192} analysed the microstructure of MgO-MgAl₂O₄ bricks corroded at 1400-1450\textdegree C by calcium aluminosilicate slag. It revealed that secondary spinel, monticellite, merwinite is formed. The secondary spinel forms an incomplete layer close to the MgO grain and corrosion mechanism was thermodynamically calculated.

Amin et al\textsuperscript{193} investigated slag penetration into a magnesia refractory monolithic by crucible test method using a synthetic calcium aluminate slag for 1,2,3,4,5 and 6 hours at 1450\textdegree C and 1600\textdegree C. They have shown that the penetration rate is controlled by a diffusion mechanism at 1450\textdegree C and dissolution of refractory components at 1600\textdegree C.

Hon et al\textsuperscript{194} investigated MgO-Cr₂O₃ bricks with molten MgO-Al₂O₃-SiO₂-Fe₂O₃ by using a dynamic rotary slag corrosion test for number of cycles at 1650\textdegree C. The open porosity decreases from 15.3 to 4.0% for three cycles, then it gradually increases from 4.0 to 4.8% when test is extended to nine cycles in which the penetrating depth of the slag maintains at about 20mm. The XRD pattern of the permeated layer shows the presence of the MgO, MgCr₂O₄ and CaMgSiO₄ phases. In the interior of the permeating layer, cracks are formed and corrosion starts at the pores and cracks of MgO and decreases gradually.
However, at 20-40 mm beneath the permeated layer edge, different shapes of MgO particles are found.

Yan et al.\textsuperscript{195} found that the corrosion and penetration resistance depend on the microsilica content. Microsilica content strongly affects liquid phase formation in the matrix, changes the porosity, pore size distribution of matrix, and viscosity of slag penetrated, and thus affects its corrosion and penetration resistance. With increasing microsilica content, decrease in the porosity, or increase in the viscosity of the penetrating slag improves. The penetration resistance increased abruptly with an increase of the microsilica content from 0.65 to 1.95 wt\%, but changed slightly with increase of the microsilica content from 1.95 to 3.90 wt\%. The corrosion resistance increased with an increase of the microsilica content from 0 to 2.60 wt\%, but slightly decreased with a further increase of the microsilica content to 3.90 wt\%. 1.95–2.60 wt\% microsilica addition appears conducive for low corrosion and low penetration.

Sako et al.\textsuperscript{196} highlighted corrosion performance of spinel-containing castables under the different conditions present in the ladle bottom. In this region due to strong variations in the atmospheric environment could drastically change the interactions between refractory and molten slag. The main corrosion mechanisms of an alumina-magnesia castable in two environmental conditions (oxidizing – $P_{O_2} = 0.21$ atm or reducing – $P_{O_2} = 1015$ atm atmosphere) showed that the slag penetration was suppressed in the presence of oxygen due to the precipitation of a great amount of calcium monoaluminate (CA) crystals as the refractory interacted with slag. Conversely, the CA phase was not stable under reducing conditions and, therefore, many more refractory components ($\text{Al}_2\text{O}_3$, MgO, and MgAl$_2$O$_4$) had to be dissolved to precipitate calcium dialuminate (CA$_2$) by reacting with infiltrating slag.

Martinovic et al.\textsuperscript{197} investigated the mechanical properties and level of cavitation damage to alumina-based low-cement castable. Cold crushing and flexural strength were determined using the standard laboratory procedures for destructive testing. The nondestructive methods such as ultrasonic measurements and image analysis were used for measuring the elasticity modulus and level of surface deterioration caused by cavitation testing. Cavitation damages in the alumina-based refractory specimens were induced by the modified vibratory cavitation setup. The rise of temperature treatment from room temperature to 1600\textdegree C resulted in strength increase by almost four times, with a slight
drop occurring at 800°C. The values of Young’s modulus were around 20 GPa at all stages of temperature treatment, with an obvious decrease at 800°C and 1200°C. Because the results show that the sintered low-cement castable exhibited very good resistance to the cavitation erosion, this material can be successfully used in the conditions where the cavitation resistance is needed.

H. Sarpooldaky\textsuperscript{198} investigated corrosion mechanism involves initial reaction of the most penetrating slag with the fine alumina and calcium aluminates of the matrix. In the WFA system, a complete CA\textsubscript{6} layer forms around the grain, whereas in the TA system, this layer is incomplete. In both systems, extensive penetration occurs, although corrosion is low. In the BFA system, titanates are released from the grain into the bond, leading to increased densification of the refractory, via liquid-phase sintering, and consequent low penetration. However, the resulting large volume of fluid liquid dissolves easily in the slag, so that corrosive wear is high, even though a CA\textsubscript{6} layer forms around the grain.

Simonin \textit{et al}\textsuperscript{199} investigated the thermomechanical behavior of a high-alumina refractory that contains 10 wt\% of synthetic spinel. Results correlated with the microstructural and mineralogical evolutions using X-ray diffraction and scanning electron microscopy as function of the firing temperature. The thermal expansion mismatch between coarse grains and the matrix was observed to be responsible for the degradation in mechanical strength at low firing temperatures. Material exhibited a quasi brittle with diffuse and localized damage behavior at 1000°C analyzed by comparison of the load–strain bend curves to a smeared crack model. At temperatures of >1000°C, viscoelasticity–plasticity dominated the mechanical behavior conducting load–relaxation tests.