CHAPTER 2
MATERIALS AND METHODS

Chapter 2 describes the preparation of nano metal oxides and its characterisation studies. Three different metal oxide nanoparticles namely ZrO$_2$, TiO$_2$ and Al$_2$O$_3$ were prepared from natural minerals and then, they were incorporated into refractories. The physical, thermal and thermomechanical properties of the nano metal oxide incorporated refractories were investigated. The comprehensive characterisation tools used to interpret the properties of nanoparticles and refractories have been discussed in brief.

2.1 RAW MATERIALS AND CHEMICALS

Zircon from beach sand (62-65 wt. % ZrO$_2$) deposits were collected from Kerala state in India and used as the starting material for the production of nano zirconia particles. The raw ilmenite, which contains 45.8 wt. % of TiO$_2$ obtained from Kanyakumari region, coastal part of Tamil Nadu, India was used as the starting material for synthesis of TiO$_2$ nanoparticles. The commercial raw bauxite obtained from Lohardaga, Jharkhand was used as the starting material for preparation Al$_2$O$_3$ nanoparticle. The chemical reagents such as hydrochloric acid (37%), sulfuric acid (98%), aqueous ammonia (25%) and sodium hydroxide pellets (99%) were purchased from Merck. N-cetyl-N,N,N,N-trimethyl ammonium bromide (99%) was purchased from Loba. The above chemicals were used for preparation of ZrO$_2$, TiO$_2$ and Al$_2$O$_3$ nanoparticles without any further purification. The Double Distilled (DD) water was used in the preparation process.
2.2 SYNTHESIS OF ZrO\textsubscript{2} NANOPARTICLES

The zirconium oxychloride and zirconyl nitrate solution were extracted from zircon sand using alkali fusion followed by the acid extraction which has been used as the precursor for the production of ZrO\textsubscript{2} nanoparticles. Zircon (ZrSiO\textsubscript{4}) from beach sand deposits was collected from Kerala, India and used as the starting material for synthesis of ZrO\textsubscript{2} nanoparticles without any further purification. Table 2.1 presents the X-ray fluorescence (XRF) chemical composition of the zircon sand.

Table 2.1 Chemical compositions of zircon sand

<table>
<thead>
<tr>
<th>Elements</th>
<th>wt. % ± 0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO\textsubscript{2}</td>
<td>62.90</td>
</tr>
<tr>
<td>SiO\textsubscript{2}</td>
<td>31.23</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>03.77</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>00.30</td>
</tr>
<tr>
<td>CaO</td>
<td>00.08</td>
</tr>
<tr>
<td>Hf</td>
<td>01.50</td>
</tr>
</tbody>
</table>

2.2.1 Sol-gel Process

A dry mixture containing 20 wt. % of raw zircon sand and 80 wt. % of sodium hydroxide was fused at 873 K for 2 h using a muffle furnace. After the decomposition of the critical silicate phase of zirconium (zirconium silicate), the frit was leached with double distilled water to wash out the soluble sodium silicate from the fused mass. The remaining residue after the filtration of the frit (sodium zirconate and the undigested zircon sand) was
again digested in concentrated hydrochloric acid to form zirconium oxychloride and sodium chloride in excess of hydrochloric acid.

The resultant liquor was cooled to room temperature and then added to $N$-cetyl-$N$, -$N$, -$N$, -trimethyl ammonium bromide (Loba, 99%), which was maintained at 1 mM concentration. Dilute ammonia solution was added to the liquor to initiate flocculation. Effective flocculation was achieved in the pH range between 6 and 7 by stirring the solution continuously overnight at room temperature. Then, the obtained gel was washed with double distilled water to remove the alkali from the gel matrix. The washed hydroxide was dried at 283 K. The dried hydroxide powder was then freed from the agglomeration in a low energy vibro mill by milling for 5-6 h. The ultrafine powder was then fired at 873 K for 2 h. The process reactions of the production of nano zirconia from zirconyl nitrate employing sol-gel route are given in the following equations:

\[
\text{Alkali Fusion} \\
\text{ZrSiO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \quad (2.1)
\]

\[
\text{Extraction} \\
\text{Na}_2\text{ZrO}_3 + 4\text{HCl} \rightarrow \text{ZrOCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{NaCl} \quad (2.2)
\]

\[
\text{Floculation} \\
\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O} + 2\text{NH}_4\text{OH} \rightarrow \text{ZrO(OH)}_2 \cdot x\text{H}_2\text{O} + 2\text{NH}_4\text{Cl} \quad (2.3)
\]

\[
\text{Dried at 393 K} \\
\text{ZrO(OH)}_2 \cdot x\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + x\text{H}_2\text{O} \quad (2.4)
\]

The synthesised zirconia was tested for its thermo-mechanical properties suitable for refractory applications. For mechanical stability testing, 5 g of zirconia was taken in a planetary micro mill (pulveriser) and ground for 10-15 min. During the second part of the experiment, the zirconia sample as synthesised was tested for thermo-chemical stability. During the testing, 5 g
of the powders was taken in two separate porcelain crucibles and calcined at 1073 and 1273 K, respectively for 2 h.

2.2.2 Spray Pyrolysis

2.2.2.1 Preparation of Zirconyl Nitrate Precursor

Zircon sand was further fused with about four times its weight (100 g) of sodium hydroxide at 873 K for 3 h. The alkali fusion and acid extraction reactions were shown in the following chemical reactions:

\[
\text{Alkali Fusion} \\
\text{ZrSiO}_4 + 4\text{NaOH} \rightarrow \text{Na}_2\text{ZrO}_3 + \text{Na}_2\text{SiO}_3 + 2\text{H}_2\text{O} \quad (2.5)
\]

\[
\text{Hydrolysis} \\
2\text{Na}_2\text{ZrO}_3 + 4\text{H}_2\text{O} \rightarrow 4\text{NaOH} + 2\text{ZrO(OH)}_2 \quad (2.6)
\]

\[
\text{Extraction} \\
\text{ZrO(OH)}_2 + 2\text{HNO}_3 \rightarrow \text{ZrO(NO}_3)_2 + 2\text{H}_2\text{O} \quad (2.7)
\]

The fused mass was cooled to room temperature and then, the formed hot cake was leached with water and filtered using ordinary filter cloth. The insoluble residues consist of zirconium hydroxide, which was dissolved in 250 ml of 6 M nitric acid and then filtered using ordinary filter cloth. The obtained clear filtrate was repeatedly evaporated to dryness and the residue was extracted from filter paper using 250 ml of double distilled water. The extracted zirconyl nitrate was used as the precursor for the synthesis of nano ZrO\(_2\) particles.
2.2.2.2 Preparation of ZrO$_2$ Nanoparticles

The zirconyl nitrate was used as the starting precursor in spray pyrolysis to get nano ZrO$_2$ particles. The schematic diagram of automated spray pyrolysis experimental set-up used for mass production of nano ZrO$_2$ particles is shown in Figure 2.1. The working feature of automated system is described in the following headings:

a) Atomiser

It consists of two fluid nozzle with different size such as 0.7 mm, 1.0 mm and 1.5 mm diameter made of titanium metal. The atomiser was used to convert the precursor solution into fine droplets called atomisation. The atomised droplet size depends on the nozzle size and pressure of compressed air. The atomised spherical droplets get decomposed to form spherical particles.

Figure 2.1 Schematic diagram of automated spray pyrolyser experimental set-up
b) **Automated anti-block unit**

The blocking of nozzle has been anti-blocked by a sharp stainless steel rod (*AISI 316L*) which was automatically operated in a fixed interval of time. It is an essential process for continues operation of the system.

c) **Tubular electric furnace with Hot air blower**

It consists of one main heater and one auxiliary heater (supporting heater) with temperature controller. The auxiliary heater was used to produce hot air up to the required temperature to air blower. The temperature of air flow is monitored by an inlet temperature controller, which was present in hot air blower. An effective temperature sensor (*MC-2438*) has been used to monitor the fixed temperature with an accuracy of ±278 K. The blower speed was controlled employing *Select, PIC 101* RPM controller.

d) **Two way fluid nozzle with compressed air inlet and sample feeding port**

In spray pyrolyser, two way fluid nozzle was located at the top of reaction chamber which consists of one compressed air inlet port and one sample feeding port. The atomiser was formed by mixing the precursors with pressurised air at the edge of two fluid nozzle. The pressure of compressed air was regulated in PSI employing waaree pressure gauge regulator.

e) **Feed pump**

Peristaltic feed pump with precise RPM controller (*Select, PIC 101*) was used in the system to control the flow rate and uniform feeding of precursors in sample port. The adjustable speed pump was operated at a constant speed which was selected by the user. The pump was made up of stain steel (*AISI 316L*) corrosion resistant material. The pump was capable to run continuously and it can maintain the performance of atomiser. The
compressed fluid goes from initial stage to reaction chamber by constant and continuous manner and it has the ability to pump in the respective direction with equal efficiency. The operation of the pump was controlled using the control panel.

f) Reaction chamber

A cylindrical stainless steel (AISI 316L) tubular reaction chamber is connected with hot air blower and two fluid nozzles which are located at the top of the chamber. At the other end of the reactor, three different cyclones in zigzag arrangements are connected. It consists of four different parallel temperature zones which have been used to identify chamber temperature at different places. The atomised droplets get decomposed at the reaction chamber to form ultra fine spherical particles which are forced out to cyclones by internal air pressure.

g) Cyclonic sample collectors

The decomposed nano powders have been collected on three different cyclonic collection ports. The tangential location of orifice develops a downward, spiraling flow of solid particles. The centrifugal force developed at the collection chamber walls is a downward direction which was greater than that of gravity. This centrifugal force spins out the solid particles from the orifice. The solid particles strike and deposited on the collector wall. The coarse, fine and ultra-fine particles have been collected respectively at the initial, middle and end of collection port.

h) Purification system

It consists of two main parts such as reverse air jet filter and wet scrubber to avoid the fine particles enter into environments. The few
uncollected ultra fine particles have been deposited by reverse air jet filter and the decomposed gas molecules like NO$_2$ have been dissolved in flow water at wet scrubber which prevents the air pollution. In addition, wet scrubber contains an outlet port to release the drain.

In spray pyrolysis, reaction often takes place in solution in droplets, followed by solvent evaporation. The method was based on atomising the precursor and injecting the spray into a tubular reaction chamber. The atomised droplets of the precursor were converted into nano sized oxide crystallites or nano sized entities during their flow through the tubular reaction chamber. The hot air was introduced into the reaction chamber followed by the precursors were sprayed into the chamber with the use of two fluid nozzle along with compressor air inlet. The feed pump was used to control the flow rate of processors and formation of atomiser. The formation of atomiser was controlled by controlling the pressure of compressed air.

The sprayed and atomised nano entities were decomposed to obtain nano metal oxide powders which have been collected at different cyclones. The decomposed mass like H$_2$O, NO$_2$ etc., can be eliminated by ceramic water filter which was in the purification system. After the completion of one full cycle, the produced nanoparticles were collected from the cyclones. There are two main parts of cyclones which were used for the powder collection, such as second and third cyclones. These two cyclones consist of fine powders which were in nano range. The above process was known as spray pyrolysis or droplet-to-particle conversion. The total process was automated using a single power control panel which controls the process automatically.

An aqueous zirconyl nitrate precursor was flow into the inner nozzle through the peristaltic feed pump. The feed pump was used to control the flow rate of precursor. The feed rate was optimised and maintained as 0.2
L h\(^{-1}\). Passage of the compressed air (30-40 PSI) through the outer nozzle was forced out the contents of the precursor in an inner nozzle. Thus, the precursor was atomised to generate spray. The formation of atomiser was controlled by controlling the pressure of compressed air. Then, the atomised nano sized entities of zirconyl nitrate droplets were injected into the hot air zone, generated through hot air blower in the tubular reaction chamber. The temperature of reaction chamber was maintained in the temperature range of 773 to 873 K by adjusting the furnace temperature of hot air blower. In the hot air zone, the atomised droplets were dried and the constituent aluminium nitrates were decomposed at 773 K to form nano sized ZrO\(_2\) particles. The typical decomposition reaction of aluminium nitrate precursor in spray pyrolysis is given in Equation 2.8. The overall output by this method is 80±5 %.

\[
\text{Decomposition:} \quad \text{ZrO(NO}_3\text{)}_3 \rightarrow \text{ZrO}_2 + 3\text{NO}_2 + \text{O}_3
\]  
(2.8)

2.3 SYNTHESIS OF TiO\(_2\) NANOPARTICLES

The titanium sulfate solution was prepared from ilmenite using acid extraction which was used as the precursor for the synthesis of TiO\(_2\) nanoparticles.

2.3.1 Synthesis of titanium sulfate precursor

The ilmenite, which contains 45.8 wt. % of TiO\(_2\) obtained from Kanyakumari region, coastal part of Tamil Nadu, India was used as the starting material for TiO\(_2\) nanoparticle synthesis. Chemical analysis of ilmenite is given in Table 2.2. Raw ilmenite was digested with concentrated H\(_2\)SO\(_4\) in the temperature range from 473 to 573 K for 3 h. The resulted dry cake, the mixture of titanium and iron sulfate was leached with double-distilled water. Iron powder was added to the leached solution in order to
reduce the ferric sulfate into ferrous sulfate, and the precipitated ferrous sulfate was removed by filtration. The titanium sulfate obtained after filtration was used as precursor for the production of TiO$_2$ nanoparticles. The acid extraction process reactions are given in the following equations:

\[
\text{Conc. H}_2\text{SO}_4 \\
\text{FeTiO}_3 \rightarrow \text{Fe}_2\text{(SO}_4\text{)}_3 + \text{Ti(SO}_4\text{)}_2 \quad (2.9)
\]

\[
\text{Iron} \\
\text{Fe}_2\text{(SO}_4\text{)}_3 + \text{Ti(SO}_4\text{)}_2 \rightarrow 3\text{FeSO}_4 + \text{Ti(SO}_4\text{)}_2 \quad (2.10)
\]

Table 2.2 Chemical compositions of ilmenite through XRF analysis

<table>
<thead>
<tr>
<th>Elements</th>
<th>wt. % ± 0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>45.8</td>
</tr>
<tr>
<td>FeO</td>
<td>47.7</td>
</tr>
<tr>
<td>MgO</td>
<td>03.6</td>
</tr>
<tr>
<td>MnO</td>
<td>01.2</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>01.2</td>
</tr>
</tbody>
</table>

2.3.2 Sol-gel Process

The extracted titanium sulfate (Ti(SO$_4$_2) precursor (250 ml) was cooled to room temperature. Organic surfactant, N-cetyl-N,N,N,trimethyl ammonium bromide (Loba, 99%) was added into the precursor and it was maintained at 1 mM concentration. After that, the aqueous ammonia solution (5 N) was added into the precursor to begin the hydrolysis of titanium sulfate. The addition of aqueous ammonia continued until pH 10 to obtain well dispersed hydrous titania sol. The obtained titanium hydroxide gel was digested at 353 K for 28 h followed by drying at 373 K for 1 h in a hot air oven. Digestion led to control the nucleation of the gel. The organic surfactant
and ammonium sulfate were present in the gel matrix was removed by washing the dried gel with water. The synthesised sample was calcined at 573 K for 6 h to get TiO$_2$ nanoparticles. At last, the soft agglomerates of the fired samples were disaggregated by planetary ball milling in a dry medium at 500 rpm for 3 h. The present sol-gel process yields an output of 75±5% of nano TiO$_2$ particles.

2.4 SYNTHESIS OF Al$_2$O$_3$ NANOPARTICLES

Synthetic bayer liquor was prepared from bauxite by bayers process which is used as the precursor for the synthesis of Al$_2$O$_3$ nanoparticles.

2.4.1 Extraction of Bayer Liquor from Bauxite

The commercial bauxite was obtained from Lohardaga, Jharkhand, India and used as the starting raw material for the preparation of Bayer liquor. The chemical analysis of the bauxite is given in Table 2.3.

<table>
<thead>
<tr>
<th>Elements</th>
<th>wt. % ± 0.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>LOI</td>
<td>23.86</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>47.42</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>04.00</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>08.00</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>11.41</td>
</tr>
</tbody>
</table>

The fine grained bauxite was fused with sodium hydroxide in the ratio of 2:1 at 873 K for 3 h in a muffle furnace. The fusion product was leached using double distilled water. The obtained solution mixture was
adjusted to a pH value of 13 using 5N sodium hydroxide solution followed by vigorous magnetic stirring at 353 K for 1 h. Thus, the impurity in the bauxite which is in solid form was filtered. Then, the filtrate (Bayer liquor) was used as a precursor for the synthesis of Al$_2$O$_3$ nanoparticles. The extraction reaction is given as follows:

$$\text{Al}_2\text{O}_3 + 2\text{NaOH} \rightarrow 2\text{NaAl(OH)}_4$$  \hspace{1cm} (2.11)

2.4.2 Sol-gel Process

The extracted Bayer liquor was cooled to room temperature. Organic surfactant namely N-cetyl-N,N,N,trimethyl ammonium bromide was added into the Bayer liquor, which was maintained at 1 mM concentration. Six molar solution of nitric acid is added to the Bayer liquor to initiate the flocculation and the effective flocculation was achieved in the pH range of 7 to 8. The obtained aluminium hydroxide gel was digested at 353 K for 28 h followed by drying at 373 K for 1 h in a hot air oven. Digestion led to control the nucleation of the gel. Then, the dried gel was washed with water to remove the organic surfactant and other nitrates from the gel matrix. In order to reduce the agglomeration of the powder, water was replaced with ethanol, and then the gel was dried at 373 K for 1 h. The dried gel was fired at 773 K for 6 h to get nanosized Al$_2$O$_3$ particles. Ultimately, the fired samples of soft agglomerates were non-agglomerated using a planetary ball milling (PM 100, Retsch, Germany) in a dry medium at 500 rpm for 3 h. The total yield of the present sol-gel process was 80±5% in lab scale.

2.4.3 Spray Pyrolysis

2.4.3.1 Preparation of Aluminium Nitrate Precursor

The extracted Bayer liquor was hydrolysed through the drop by drop addition of 6 M HNO$_3$ solution under constant stirring. An amorphous
hydrated aluminium oxide was precipitated at pH 7. A characteristic white precipitate of Al(OH)$_3$.H$_2$O was appeared at this stage of the reaction. The obtained precipitate was filtered and washed several times in double distilled water until it was free from sodium nitrate and unreacted components. Further, the precipitate (Al(OH)$_3$.H$_2$O) was dissolved in 1 M HNO$_3$ solution to obtain the aluminium nitrate solution. The preparation reactions of aluminium nitrate precursor are as follows:

\[
\text{Precipitation} \\
\text{NaAl(OH)}_4 + \text{HNO}_3 \rightarrow \text{Al(OH)}_3\cdot\text{H}_2\text{O} + \text{NaNO}_3 \quad (2.12)
\]

\[
\text{Dissolution} \\
\text{Al(OH)}_3\cdot\text{H}_2\text{O} + 3\text{HNO}_3 \rightarrow \text{Al(NO}_3)_3\cdot4\text{H}_2\text{O} \quad (2.13)
\]

### 2.4.3.2 Preparation of Al$_2$O$_3$ Nanoparticles

The prepared aluminium nitrate was the starting material to get Al$_2$O$_3$ nanoparticles. The aluminium nitrate precursor was flow into the inner nozzle through the peristaltic feed pump. The feed rate was optimised and maintained as 0.2 L h$^{-1}$. Passage of the compressed air (30-40 PSI) through the outer nozzle was forced out the contents of the precursor in an inner nozzle. Thus, the precursor was atomised to generate spray. Then, the atomised nano sized entities of aluminium nitrate droplets were injected into hot air zone, generated through hot air blower in the tubular reaction chamber. The temperature of reaction chamber was maintained in the temperature range from 773 to 873 K by adjusting the furnace temperature of the hot air blower. In the hot air zone, the atomised droplets were dried and the constituent aluminium nitrates were decomposed at 773 K to form Al$_2$O$_3$ nanoparticles. The overall output by this method is 85±5 %. 
2.5 PREPARATION OF SUB ENTRY NOZZLE REFRACTORY

A formulation was designed as per the standard method recommended for the manufacturing of the sub entry nozzle (SEN). High purity zirconia, lime, and graphite have been taken as the starting material. The formulation has been made taking the optimum quantity of these materials with optimum grading. Three compositions have been designed by keeping 3.2% antioxidant as the base component and incorporating ZrO$_2$ nanoparticles by replacing the micron ZrO$_2$ in base compositions. The different portions from 0.8 to 1.6% of ZrO$_2$ nanoparticles were incorporated into the base compositions. The test samples (40 mm $\times$ 40 mm $\times$ 150 mm) were isostatically pressed using the formulated compositions. The physical, chemical, mineralogical, and thermo-mechanical properties of the SEN were characterized using international standards.

2.6 PREPARATION OF MAGNESIA CHROME REFRACTORY BRICK

Batch composition was formulated as per the standard method recommended for the manufacturing of the magnesia chrome bricks. Table 2.4 shows the typical chemical composition of raw materials (fused magnesia chrome grains, high-purity magnesia, and chrome ore) used for preparing magnesia–chrome bricks. The required chemical formulation was considered and the required optimum quantity of these materials with optimum grading was taken to achieve the highest packing density. Two weight percentages (0.25 and 0.75 wt. %) of TiO$_2$ nanoparticles were incorporated into the composition of magnesia–chrome bricks and the batches were formulated accordingly.

To compare the size dependent properties of TiO$_2$ particles, 0.25 wt. % micron rutile TiO$_2$ particles were incorporated into the brick
composition. The coarse and middling fractions of the raw materials were mixed properly for 20 min. The fine fractions along with the additives such as micron and nano titania particles were added and mixed for another 10 min. A constant quantity of molasses and water was added for the workability of green mix. All the formulations were compacted in a standard size (230 mm × 115 mm × 75 mm) at a specific pressure of 2000 kg cm⁻² in a friction screw press. In all the trials, the bulk density was maintained as 3.35 g cc⁻¹. The brick was dried in a tunnel dryer at 283 K for 48 h and then, the dried bricks were fired in a tunnel kiln at a peak temperature of 1973 K for 8 h. Identical granulometric compositions and manufacturing parameters (mixing, pressing, drying, and firing) were followed for all the experimental batches.

Table 2.4  Chemical composition of raw materials used for making magnesia-chrome bricks

<table>
<thead>
<tr>
<th>Elements (%)</th>
<th>Fused magnesia-chromegrains</th>
<th>High purity magnesia</th>
<th>Chrome ore</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>65.0</td>
<td>98.0</td>
<td>14.0</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>17.0</td>
<td>--</td>
<td>55.0</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>7.0</td>
<td>0.3</td>
<td>12.0</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>7.0</td>
<td>0.45</td>
<td>--</td>
</tr>
<tr>
<td>CaO</td>
<td>1.5</td>
<td>0.9</td>
<td>--</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.0</td>
<td>0.45</td>
<td>1.5</td>
</tr>
</tbody>
</table>

2.7  PREPARATION OF HIGH ALUMINA CASTABLES

Graded tabular alumina, reactive alumina and high alumina cement were taken as the starting materials to prepare precast seating blocks. Formulation was made by taking optimum quantities of these materials with optimum grading. Table 2.5 shows the typical chemical composition of raw
materials. 0.5 parts of Al$_2$O$_3$ nanoparticles were added to the composition. Two formulations were made and the mixtures were prepared by adding 5% water to reach a good flowability. It was cast under vibration into bars of 40 ×40 ×160 mm$^3$. After demoulding, the specimens were dried at 383 K for 24 h, and then fired at 1273 K for 3 h and 1773 K for 3 h respectively. The physical, thermo-mechanical and mineralogical properties were studied. Slag corrosion test was carried out by taking the above precast seating blocks for purging plugs (prefired at 1273 K for 3 h and 1773 K for 3 h) in a rotary drum with metal and slag at 1823 K. The precast seating block was prepared by using Al$_2$O$_3$ nanoparticles and used in a 150 T steel ladle.

Table 2.5  Chemical composition of raw materials used for making castable

<table>
<thead>
<tr>
<th>Elements</th>
<th>Tabular alumina (%)</th>
<th>Reactive alumina (%)</th>
<th>Cement (%)</th>
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</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$</td>
<td>99.4</td>
<td>99.8</td>
<td>72.7</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.33</td>
<td>0.06</td>
<td>0.19</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td>0.02</td>
<td>26.5</td>
</tr>
<tr>
<td>MgO</td>
<td>0.10</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>0.02</td>
<td>0.03</td>
<td>0.20</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.10</td>
<td>0.03</td>
<td>0.11</td>
</tr>
</tbody>
</table>

2.8  CHARACTERISATION

In this section, the different characterization techniques used in the present investigation are discussed briefly.
2.8.1 X-ray Diffraction Study

The phase and crystalline natures of all the prepared samples were identified through X-ray diffraction (XRD) analysis (XRD, X’ Pert Pro, PANalytical, Almelo, the Netherlands) using Cu-Kα as a radiation source (λ = 1.54060 Å. The diffractometer was operated at 20 mA and 30 kV at 2θ range 10–60°). The peak positions and the relative intensities of the powder pattern were identified in comparison with the reference powder diffraction data (JCPDS). The percentage of phase transformation obtained by XRD graph is based on Rietveld refinement (Garnweitner et al. 2007) of the XRD peaks. The positions of the peaks are corrected by successive refinements of systematic errors, taking into account the zero-shift and the sample displacement errors. Considering all the refined structural parameters of individual phases of a multiphase sample and the phase concentration (volume/weight fraction) in the mixture, a simple relationship between the individual scale factors has been determined. The weight fraction (Wi) for each phase was obtained from the refinement relation as,

\[ W_i = \frac{S_i(ZMV)I}{\sum S_j(ZMV)j} \]

(2.12)

where \( S_i \) is the value of \( j \) for a particular phase among the \( N \) phases present, \( S_j \) the refined scale factor, \( Z \) the number of formula units per cell, \( M \) the atomic weight of the formula unit and \( V \) the volume of the unit cell. The crystallite size distributions were obtained through XRD peak analysis based on Scherer’s equation (Cullity 1978).

2.8.2 Particle Size Analysis

The PSD was determined with a sub micrometer particle size analyzer (Nanophox, Sympatec, Clausthal-Zellerfeld, Germany) according to the dynamic light scattering technique. Three dimensional photon cross-
correlation technique was used to measure the particle size. It is used to measure the average particle size and distribution in the order of 1-1000 nm with a scattering angle of 90°. As-synthesised (ZrO₂, TiO₂ and Al₂O₃) nanoparticles dispersed in an aqueous solution, which contains 5 mM 4, 5-dihydroxy-m-benzenedisulphonic acid disodium salt (99%, Loba GR) under sonication. The sonochemically dispersed stable colloidal solution was used to obtain particle size distribution.

2.8.3 Surface Area Measurement

Brunauer-Emmett-Teller developed BET theory to describe specific surface area of materials on the basis of physical adsorption/desorption of gas molecules on the solid surface. Initially, the powder sample was heat treated and then degassed (inert gas) to remove the unwanted adsorbed gas molecules. During the process, a certain level of inert gas was adsorbed and desorbed within the sample. The desorbed gas molecules were used to determine the surface area of the sample. The analysis was carried out using a BET surface area analyser (Smart Sorb 92/93, Smart instruments, Mumbai, India).

2.8.4 Fourier Transform Infrared Study

The functional groups and their chemical bonds of the compound/molecules were identified by infrared absorption spectrum named Fourier Transform Infrared (FTIR) spectroscopy. Infrared absorption spectrum of an unknown sample was identified by standard KBr sample. The ratio of unknown and known sample was kept at 1:10. The mixture was thoroughly ground and prepared a pellet and used for FTIR measurement. The FTIR spectrum of all the prepared samples was recorded using the FTIR spectrophotometer (Spectrum 100, Perkin Elmer, USA) in the frequency range 4000-400 cm⁻¹.
2.8.5 **Electron Microscopic Analysis**

The surface morphology of the samples was inspected using a scanning electron microscope (SEM, JSM-6390LV, JEOL, Japan) with a secondary high energy electron beam as source. SEM electron beam was operated in the range of few hundred eV to 100 eV at high magnification. A high resolution images was generated through precise measurement of objects. The powder sample was prepared on a carbon-coated copper grid by putting a very small amount of the sample on the grid. Then, the sample grid was allowed to dry under a mercury lamp for 5 min. The SEM image of the microstructure was used to interpret the surface morphology of powder.

The primary particle size and its morphology were obtained through transmission electron microscopic images using a transmission electron microscope (TEM, CM200, Philips, USA) operated at 120 kV. TEM images are formed using transmitted electrons which produce magnification details up to 1,000,000X with resolution better than 10 Å. The process involves a high energy electron beam passing through sample, which reflects a dense area of objects. These differences give information about nanoparticles.

2.8.6 **X-ray Fluorescence Spectrometry**

X-ray fluorescence (XRF) is an analytical technique used to determine the concentration and purity of elemental compositions of all materials. The spectrum is observed from the interaction of X-rays with a material. The qualitative and quantitative elemental analysis of samples was performed using an X-ray fluorescence spectrometer (EDX-720, Shimadzu, Japan). The powder samples were analyzed directly without any preparation.
2.8.7 Chemical Analysis

The chemical purity of the alumina samples were determined through wet chemical analysis by the Ethylene Diamine Tetra Acetic Acid (EDTA) titration method according to the Indian Standard procedure (IS 1760, Part 3, 1992). The chemical purity of the zirconia samples were determined through wet chemical analysis using EDTA titration method (Sinha et al. 1967). The weight percentage and purity of titania samples were determined spectrophotometrically by the hydrogen peroxide method at $\lambda_{\text{max}} = 410$ nm (Vogel 1978) (Mahmoud et al. 2004).

2.8.8 Characterisation of Refractory Bricks

The physical, chemical, mineralogical, and thermo-mechanical properties of the refractory bricks were characterized using international standards that are conventionally used for refractory characterization. Apparent porosity and bulk density were determined by the boiling water method, as described in ISO 5017:1998. Cold Crushing Strength (CCS), Modulus of Rupture (MOR), and refractoriness under load were determined as described in ISO 8895, ISO 5014, and ISO 1893, respectively.

The pore size distributions of the samples were analyzed by Pore Master (PM-33; Quantachrome, Florida, USA). Phase analysis was carried out by an X-ray diffractometer (PANalytical, X’Pert PRO, Almelo, the Netherlands) using copper target and nickel filter. Microstructural analysis was carried out under reflected light in a universal optical microscope (12 MEST; Leitz Laborlux, Wetzlar, Germany). The surface morphology of the brick samples was studied using a scanning electron microscope (S-3400W; Hitachi, Tokyo, Japan). CCS was measured using a CCS testing machine (Model 1515; Toni Technik, Berlin, Germany). Refractoriness under load was determined using a refractory testing machine (RUL 421; Netzsch, Berlin, Germany).
Selb/Bayern, Germany) in hot and cold condition were tested using an MOR machine (Model-MRSG 3000107; Pereny Equipment, Columbus, OH).

2.8.8.1 Apparent Porosity and Bulk Density

Apparent porosity (AP) is the percentage relationship between the volume of open pore space and the total volume of the sample. Closed porosity is the pores that are not penetrated by the immersion liquid, whereas open porosity are those pores which are penetrated by the immersion liquid.

Bulk density (BD) is the weight per unit volume of the refractory including the volume of open pore space. The boiling water method generally measures both bulk density and apparent porosity. The test specimen should be of size 65 mm × 65 mm × 40 mm. The sample is boiled for 2 h. Then, the soaking and suspended weights are taken.

Apparent porosity (%) = \((W - D) \times 100 / (W - S)\) \hspace{1cm} (2.13)

where D, S & W are dry, suspended and soaked weight respectively.

Bulk Density (gmcc\(^{-1}\)) = \(D / (W - S)\) \hspace{1cm} (2.14)

where D, S & W are dry, suspended and soaked weight respectively.

2.8.8.2 Cold Crushing Strength

It is properties of refractory to fail due to dead loading in cold condition. Cold Crushing Strength (CCS) of refractories is carried out by placing a suitable refractory specimen on a flat surface followed by application of a uniform load to it through a bearing block in standard mechanical or hydraulic testing machine. The load at which cracks appears in
the refractory specimen represent the CCS of the specimen. The test specimen should be of size minimum 40 mm and maximum 100 mm cube.

Cold crushing strength (kg cm\(^{-1}\)) = \(\frac{W}{A}\) (2.15)

where \(W\) is the total maximum load in kg and \(A\) the area of top in cm\(^2\).

2.8.8.3 Modulus of Elasticity

Modulus of elasticity (MOE) basically relates to the elasticity or flexibility of a material. The value of modulus of elasticity is very much significant relating to deflection of certain materials used in the construction industry. Young's modulus (E) describes tensile elasticity, or the tendency of an object to deform along an axis when opposing forces are applied along that axis; it is defined as the ratio of tensile stress to tensile strain. It is often referred to simply as the elastic modulus. The MOE of the brick indicates the spalling resistance of the bricks.

\[
E = \frac{F/A_0}{\Delta L/L_0} \quad (2.16)
\]

where, \(F\) the force exerted on an object under tension, \(A_0\) the original cross-sectional area through which the force is applied, \(\Delta L\) the amount by which the length of the object changes and, \(L_0\) the original length of the object.

2.8.8.4 Modulus of rupture

Modulus of Rupture (MOR) i.e., flexural strength is more important than cold crushing strength. When a transverse load is applied to refractory bricks, it may break into two pieces if MOR is low, in spite of high CCS. The modulus of rupture indicates the product's bending or tensile strength. MOR is the maximum stress that a rectangular test piece of specified dimensions can
withstand when it is bent in a three point bending device. This test method applies to all types of refractories that can be formed to the required specimen dimension.

A test specimen is to be placed on rail of 100 to 180 mm span and the load applied at mid span. The load shall be applied uniformly during testing. The load at which the brick or specimen fails shall be noted. MOR of the brick indicates the load bearing capacity of a brick at room temperature and the handling strength of a refractory brick.

For a rectangular sample under a load in a three-point bending set-up,

$$\sigma = \frac{3FL}{2bd^2}(2.17)$$

where $F$ is the load at the fracture point, $L$ the length of the support span, $b$ the width of the specimen and $d$ the thickness of the specimen.

### 2.8.8.5 Corrosion test

Rotary drum test has been conducted to study the corrosion behaviour of the zirconia carbon sub entry nozzle (SEN). It has been carried out in an oxidizing atmosphere at 1823 K for 1 h to measure the corrosion level. A blend of 50% metal and 50% Linz-Donawitz (LD) slag has been used as the medium for corrosion. After 30 minutes of testing, the molten metal and slag were tapped out from the machine and fresh slag and metal again added to it for further testing. Similarly, another tapping was done after 30 min. After 2 nos. of tapping, the test was stopped and after cooling the eroded samples was taken out of the rotary drum and the eroded depth was measured by means of slide callipers.
2.8.8.6 Spalling test

Spalling is the cracking or fracture of refractory product caused by differential expansion due to thermal shock. The specimen of size 50±2 mm in the form of a square with 75 mm height were first coated with the high temperature anti-oxidant material to protect them from oxidation and then the specimen were kept for drying for 10 h followed by air cooling. Then, the samples were initially kept in the furnace maintained at 1773 K for 30 min followed by sudden air quenching for 10 min after that samples were again kept in furnace for 10 min then again suddenly brought down to ambient condition by cooling it in air for 10 minutes. The number of cycles before any crack in the specimen was noted down as the spalling resistance.

2.9 SUMMARY

In this chapter, the complete experimental procedures used for the synthesis of ZrO₂, TiO₂ and Al₂O₃ nanoparticles from natural minerals employing different methods have been discussed. The incorporation of ZrO₂, TiO₂ and Al₂O₃ nanoparticles in refractories like SEN, Magnesia chrome and precast seating block respectively were explained briefly. The characterisation details such as XRD, XRF, FTIR, PSD, BET, SEM, and TEM used for the characterisation of the samples are discussed in detail. The necessary experimental detail used for characterisation of the refractory bricks in the present investigation is also explained. Thus, the optimisation of the processing methods for the production of different metal oxide nanoparticles such as ZrO₂, TiO₂ and Al₂O₃ for refractory applications can be achieved easily using the above procedures.