2.1 Introduction

The present chapter describes the synthesis of fly ash alumino-silicate refractories bricks specimens and their characterization using various techniques.

2.2 Raw materials

The raw materials used for the preparation of alumino-silicate refractories were lignite fly ash, ball clay, and sawdust. In the present investigation, lignite fly ash, a waste product of a coal-fired power plant collected from NLC India Limited, Bikaner, Rajasthan, India, was used as raw material. The fly ash was then sieved through a mesh size of 250 µm. The ball clay was collected from a local mine from Bikaner. The digital images of the powdered raw materials i.e. lignite fly ash, ball clay, and sawdust has been shown in **Fig. 2.1**, **Fig. 2.2**, and **Fig. 2.3**.

Fig. 2.1: Lignite fly ash

Fig. 2.2: Ball clay

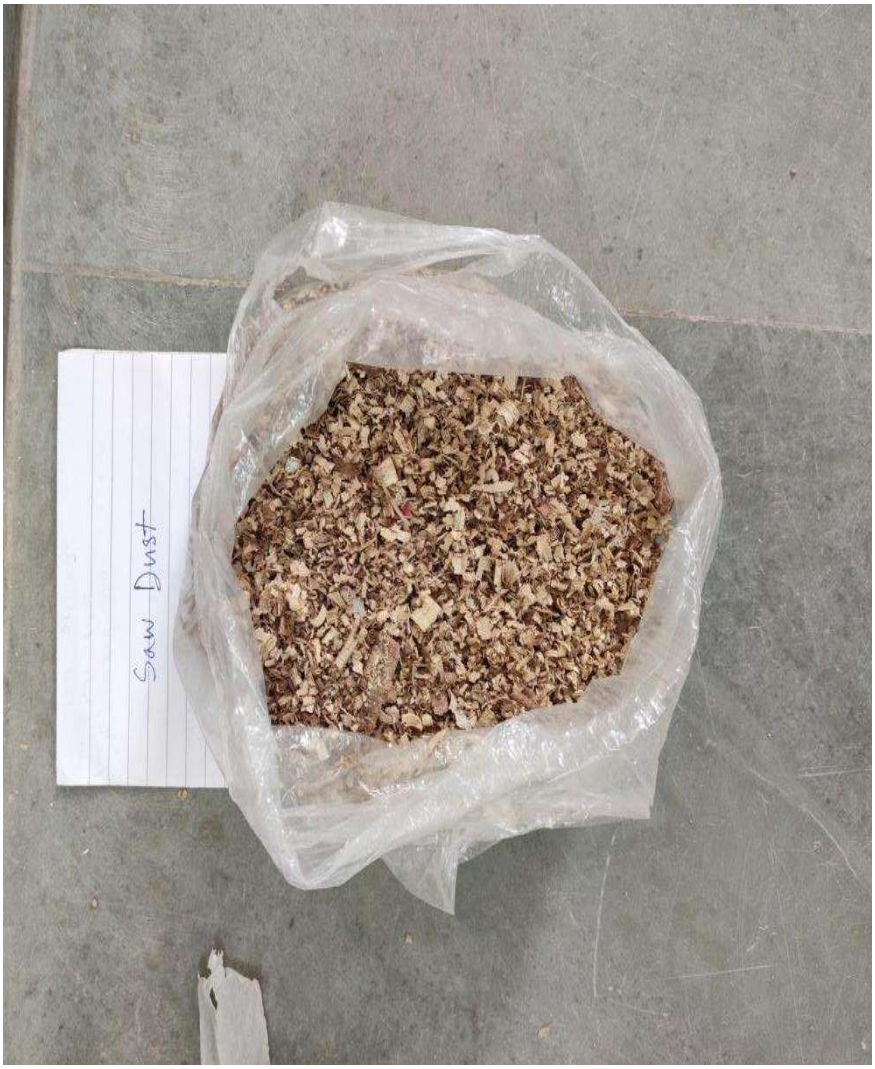

Fig. 2.3: Sawdust

2.3 Sample preparation

The formulations of five different batches by incorporating lignite fly ash (≤ 250 μm), ball clay (≤ 75 μm) and sawdust were mixed in different proportion as per the batch composition. In this research, the ball clay and fly ash content varied in different weight percentages. The raw materials were weighed as per the batch

compositions. The weighing materials were mixed in a porcelain pot mill for 10 minutes (300 rpm) with 4-5% water and a few drops of PVA solution (10 wt.%). Then the raw mixture was pressed hydraulically at 130-150 MPa pressure into a rectangular and circular shape. Then the bricks were kept in the air for 24 hours and dried in an oven at 120 °C for another 24 hours. After drying, the firing of the dried sample was performed in an electrically heated furnace with a heating rate of 10°C/min until 500°C, then holding for 1 hour. The temperature was further raised to 1000, 1100, and 1200 °C with the same heating rate and then holding it for 2hrs. A flow chart showing synthesis and characterization is shown in **Fig. 2.4**. A schematic diagram in **Fig. 2.5**. shows the whole firing schedule.

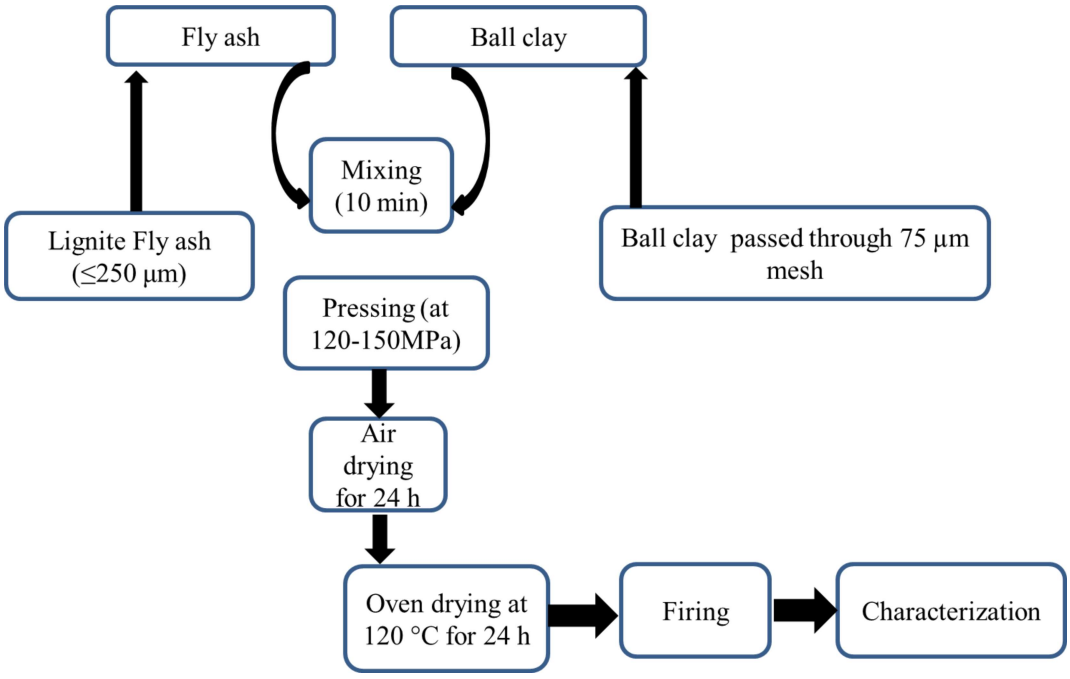

Fig. 2.4: Flow chart showing synthesis and characterization alumino-silicate refractories.

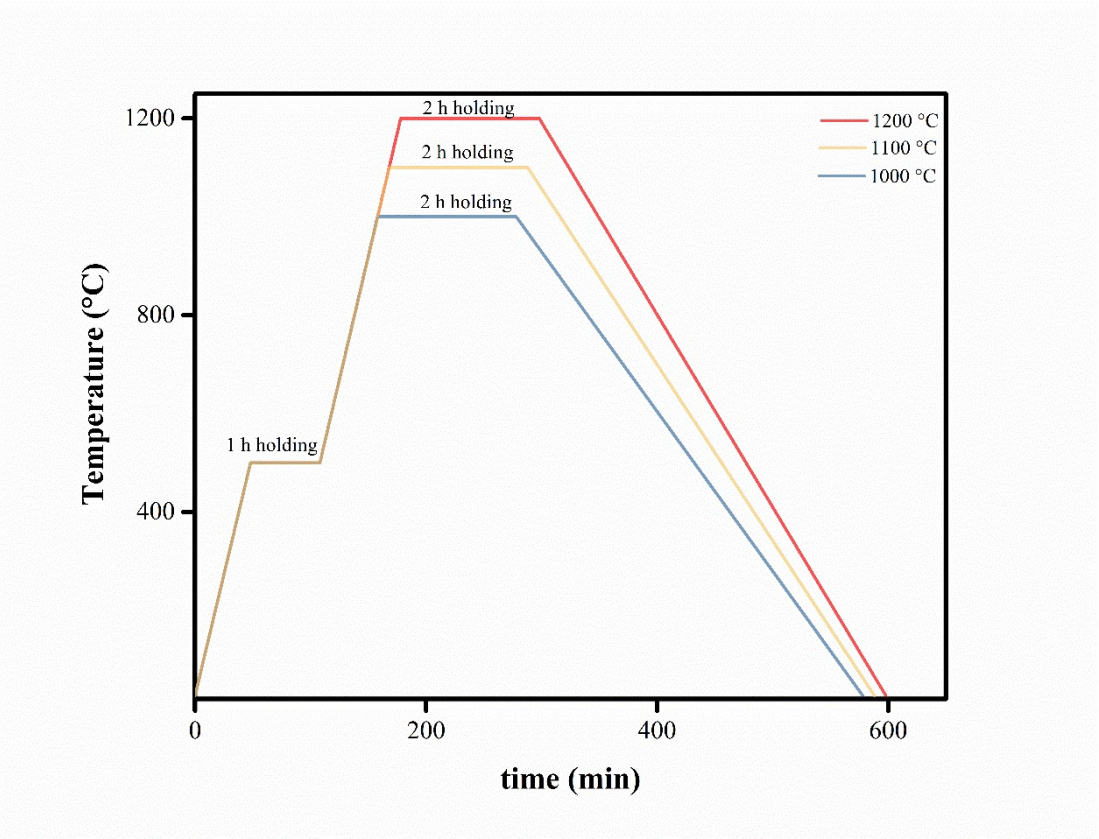

Fig. 2.5: Schematic diagram of firing schedule of different temperature.

2.4 Characterization Techniques

Different characterization techniques used for the analysis of various physical, mechanical and chemical properties of the raw materials, green sample and sintered specimens. These are discussed in subsequent section.

2.4.1 Thermogravimetric-Differential Thermal Analysis (TG-DTA)

TGA is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled rising temperature program. On the other hand, the DTA method consists of measuring the heat changes associated with physical or chemical transformations occurring during the gradual heating of substance. Thermal changes, such as dehydration, crystalline transition, lattice destruction, oxidation, and decomposition, are accompanied by an appreciable

rise or fall in temperature and are amenable to DTA investigation. Mutually the TGA and DTA facilitate as TG-DTA equipment and consist of a furnace, a temperature regulator, a specimen block, sensitive weighing machine, thermocouples, and a temperature-recording system.

The thermal properties of the samples were measured using an DTA8003 (OKAY, Libratherm Instrument) TGA/DT instrument. The melting temperature, crystallization temperature, and heat of fusion of all samples were undertaken at a scan rate of 10 °C min-1. A few milligrams of the test sample and an inert reference sample (Al_2O_3 powder) were placed in two alumina crucibles and put side by side in a heating block. Identical thermocouples were placed in each crucible and connected back to back. The net e.m.f. represents the temperature difference between the test sample and reference sample. The two crucibles were heated at a constant rate, and the temperature difference is plotted either against time or temperature. Any thermal changes occurring in the test sample will cause its temperature to either lag behind or lead the temperature of reference sample corresponding to an endothermic and exothermic peak respectively.

2.4.2 X-ray fluorescence (XRF)

Energy Dispersive X-ray fluorescence (EDXRF) Spectrometer of Model "S8 Tiger" was used for the analysis. The prepared pellets were carefully placed in the respective measuring positions on a sample charger of the machine. The following condition sets were made as the machine was switched on: elemental composition determination, nature of the samples to be analyzed as pressed powder (pellet), the current used as 20kv for the trace elements/rare earth metals, selected filters Ag/Al thin for the trace elements. The selection of filters was guided by a given periodic table

used for elemental analysis. Time of measurement for each sample was 100 seconds and the medium used was air throughout. The machine was then calibrated by the machines gain control, after which the respective samples were measured by clicking the respective positions of the sample charger.

The origin of X-rays is from the loss associated with the interaction of high energy electron with atoms. Electrons from x-ray tubes move towards the electronic field of the electrons in the various shells of the atoms of the targeted material. The incident electrons are decelerated and loses energy. Incident high energy electrons penetrate the outer orbital of the atoms and collide with an electron in the inner orbital. These inner electrons may be completely removed, leaving the atom in an unstable state. Electron rearrangement to restore stability takes place, leading to the release of energy in form of x-rays. X-rays generated in this way have discrete wavelength which is related to the atomic number of the atoms producing them. They are called characteristic x-rays. The detection and measurement of the characteristic x-rays are the basis of x-ray spectrometry.

2.4.3 X-ray Diffraction (XRD)

X-ray diffraction is a primary non-destructive analytical technique for the determination of the chemical composition and crystallographic structure of the materials. It is also helpful to determine the lattice parameters, lattice defects, lattice strain, crystallite size, and phage of known and unknown materials. X-ray diffraction utilizes the electromagnetic waves with a wavelength of the order of one angstrom. Because, the lattice constant of the different crystals is the same order of magnitude as the wavelength of the X-rays, which is the first requirement of diffraction. When the X-rays were incident upon a sample, diffraction from different atoms takes place.

Diffracted x-rays interfere with each other. In crystals, because the atoms are distributed in a periodic manner, the diffracted waves form sharp interference maxima (peaks) about the symmetry of atoms present in the crystal. The peaks maximum in an X-ray diffraction pattern is directly related to the atomic distances. Therefore, by measuring the distribution of diffraction pattern, one can deduce the crystal structure of material. According to Bragg's law, if diffraction occurs from a given set of lattice planes where 'd' is the inter-planer distance, the given condition should be followed:

$$2d \sin\theta = n\lambda \qquad (2.1)$$

Where 'θ' is the incident angle, 'λ' is the wavelength of the x-ray, and 'n' is an integer representing the order of the diffraction. This process is shown schematically in **Fig. 2.6**, and the experimental setup shown in **Fig. 2.7**.

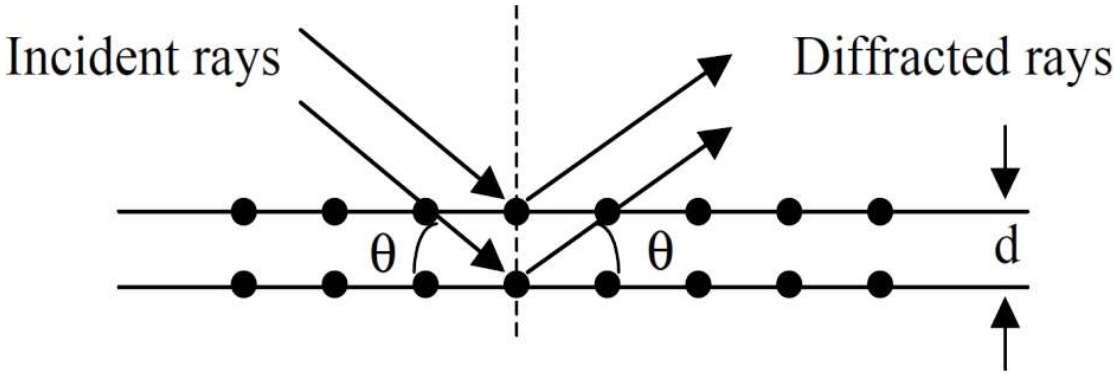

Fig. 2.6: Schematic of diffraction of X-rays by a crystal.

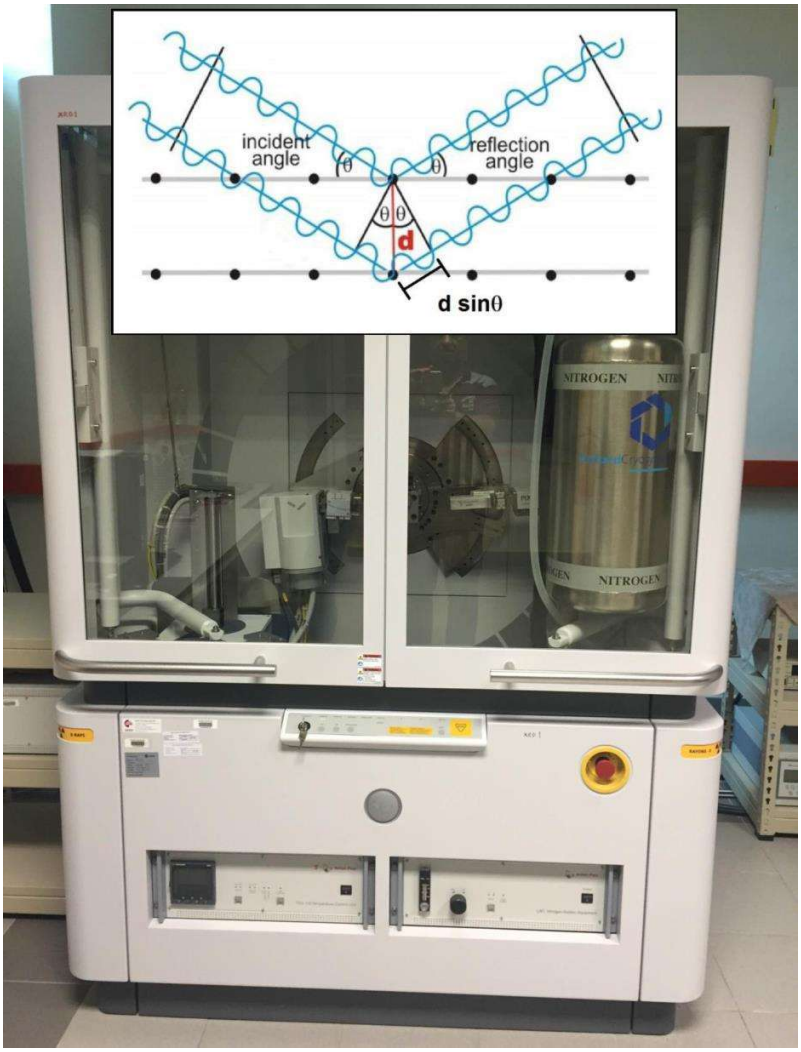

Fig. 2.7: X-ray Diffraction measurement setup.

In our study, the phase evolution and structure of the raw materials and sintered alumino-silicate refractories sample were studied by Bruker D8, U.K. X-ray diffraction experiments were performed using an 18 kW rotating anode (Cuk_{α}) based Rigaku high-resolution X-ray powder diffractometer operating in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffraction beam. The generator was operated at 40KV and 150mA. The powder samples were placed on a grooved quartz sample holder with the help of glass slide. The diffraction experiments

were applied at a fixed wavelength (λ, $CuK_{\alpha} = 1.54056A^{0}$) and diffraction angles (2θ) selected were in the range of 10-90^{0} with 5^{0}/min scanning speed.

2.4.4 Scanning Electron Microscopy (SEM)

Scanning electron microscope (SEM), were used for examination of morphology, size, and shape, the elemental composition of the materials. In SEM the electron was emitted from a tungsten cathode. The emitted electron was focused into a very narrow intense beam through two successive condenser lenses. Finally, the narrow beam of the electron was further focused on the sample surface with the help of two pairs of coils. In these primary electrons were emitted and transmit their energy inelasticity to the atomic electrons of the crystal lattice. On the sample, the several scattering processes were taking place. Among them, some electrons managed to leaves the surface and collected by the detector and known as secondary electrons. Finally, the signal was amplified by the photomultiplier tube (PMT) and modulating this signal with the intensity of a cathode ray tube (CRT), and the image of the sample was produced. The good quality image of the sample was produced with a resolution of ~50A^{0}. In our research work, all the samples were used in powder form for the SEM characterization.

The microstructure of the fractured surface was studied by using scanning electron microscopy (Nova Nano SEM 450 SEM) (FEI Company of USA (S.E.A.) PTE, LTD). Prior to the study the samples were gold coated to avoid the unwanted charge accumulation.

2.4.5 Energy Dispersive Spectroscopy (EDS/EDX)

In EDS, high energy electron beam is used as a source to excite core level

electron from the inner orbital (e.g. the 1s shell) of atom present in the sample. Due to the release of inner core electron, the formation of the hole takes place in a lower shell of an atom. Therefore, to fill the hole in a lower shell an electron from an outer shell of the atom (e.g. the 2s shell) releases its energy, which consequences in the form of X-ray emission. This X-ray emission is the characteristic of the particular atom present in the sample. Therefore, one could recognize the exact atom present in the sample by analyzing the X-ray spectral lines of the atom. To analyze the X-ray cooled Si (Li) detector with an ultrathin (diamond) X-ray window (lithium drifted silicon detector) is used in EDS. In most of the cases, EDS systems are attached with SEM and utilize the same electron beam source to excite X-rays from the sample subjected to analysis.

The compositional of samples were investigated by using EDS of (Team Pegasus Integrated EDS-EBSD with Octane Plus and Hikari Pro) X-ray system integrated with Scanning Electron Microscope (SEM).

2.4.6 Linear Shrinkage

The dried samples were fired in a electrical heating furnace at about 1200 °C and hold at that temperature for 2 hrs. After firing, the bars were observed for colour change, cracks and shrinkage. Shrinkage values were evaluated using the formula (ASTM C356-10) [111]:

$$\text{Linear Shrinkage (LS)} = \frac{(DL-FL)}{DL} \times 100 \qquad (2.2)$$

Where: DL = Dry length, FL = Firing length, LS = Linear Shrinkage

2.4.7 Apparent porosity (AP) and Bulk density (BD)

The bulk density and apparent porosity of the heat-treated specimens were determined according to standard ASTM C20-00 test method [112]. The AP and BD

were calculated using the following formulas:

$$BD = \frac{D}{W-S} \quad (2.3)$$

where, BD is the bulk density (gm/cm2), D is the dry weight of the specimen, W is the soaked weight after boiling the samples for 2hrs in de-ionized water, and S is the suspended weight.

$$AP = \frac{W-D}{W-S} \times 100 \quad (2.4)$$

Where, AP is the Apparent Porosity (%), D is the dry weight of the specimen, W is the soaked weight after boiling the samples for 2 hrs in de-ionized water, and S is the suspended weight.

2.4.8 Flexural strength

Flexural strength is the ability of a material to withstand bending forces perpendicular to its longitudinal axis. The resulting stresses are a combination of compressive and tensile stresses. If a refractory component is a beam subject to bending, a flexural test is more appropriate. In present work, in order to calculate the flexural strength of the synthesized alumino-silicate refractories, the flexural strength (bending tests) was performed by three-point bending tests for the samples using the universal testing machine (UTM), HEICO.

While performing the tests, the crosshead speed was maintained at 0.5 mm/min, the load applied was 10 kN. The Flexural strength was then calculated according to ASTM C133−97 equation [113]:

$$\text{Flexural strength } (\sigma) = \frac{3PL}{2bd^2} \quad (2.5)$$

Where, P=applied load (N); l= span length of the sample (mm); b= sample width (mm); d=thickness of the sample (mm).

2.4.9 Cold crushing strength (CCS)

The CCS of a material is the capacity of a material or structure to withstand loads tending to reduce size under compressive force. It measures the ability of a material to withstand a compressive load without failure. In present work, cylindrical samples were used as a specimen for compressive strength measurement was used for the uniaxial compression test. The compression test of the cylindrical samples was done on Universal Testing Machine (HEICO). The cylindrical shaped samples were tested by applying a load, and the values were obtained from the UTM. The values were obtained for three samples at each temperature and their average values were noted.

2.4.10 Thermal Conductivity (TC)

Thermal conductivity was measured by the calorimetry method according to ASTM C201-93 (2013) [114]. For that one side of the sample to be tested was in contact with a copper plate having water flow through it, and the opposite side was exposed to heat. Using the following equation, the thermal conductivity of samples was then determined [70].

$$\text{Thermal Conductivity } (k) = \frac{ql}{[a(t_h - t_c)]} \qquad (2.6)$$

where,

k = thermal conductivity

q = water flowing inside the calorimeter

l = thickness of the samples

a = surface area of the sample exposed to t_h

t_h = hot surface temperature

t_c = cold surface temperature