PROGRESS ON LITHIUM CERAMIC BREEDER MATERIALS DEVELOPMENT, CHARACTERIZATION AND R&D ACTIVITIES IN IPR

PARITOSH CHAUDHURI[1,2]
[1]Institute for Plasma Research,
Bhat, Gandhinagar, Gujarat – 382428, India
paritosh@ipr.res.in
[2] HomiBhabha National Institute
Anushaktinagar, Mumbai - 400094, India

MAULICK PANCHAL[1], AROH SHRIVASTAVA[1]
[1]Institute for Plasma Research
Bhat, Gandhinagar, Gujarat – 382428, India

Abstract

Several materials have been developed and being investigated for reliable and sustainable breeder candidate material. Lithium meta-titanate (Li_2TiO_3) and Lithium ortho-silicate (Li_4SiO_4) are the prominent among the suitable candidate materials for tritium breeders. Indian Lead-Lithium cooled Ceramic Breeder (LLCB) is one of the tritium breeding blanket concept in which $Li_2TiO_3$is proposed as the tritium breeder materials in the form of pebble bed for LLCB TBM. Li_2TiO_3 power was prepared by solid state reaction using $LiCO_3$ and TiO_2 followed by ball-milling and calcination. Li_2TiO_3 pellets and pebbles are prepared from this powder followed by high temperature sintering. Effect of sintering time and temperature on the properties of pebbles has been studied. At every stage of preparation, extensive characterizations are being carried out to meet the desired properties of these materials. The geometry and loading conditions of the breeder blankets makes the analysis complex. For a robust design of blankets requires a thorough understanding of the thermo-mechanical response of the breeder materials at different loading conditions. In this context, the material characterization plays a vital role in determining the breeder response. It is essential to measure the mechanical and thermo-mechanical properties of pebble bed. Experimental set ups have been built indigenously at IPR for the measurement of effective thermal conductivity of pebble bed using steady state-axial heat flow and transient hot wire methods. The effective thermal conductivity (k_{eff}) of pebble beds is an important parameter for the design and analysis for a fusion tritium breeder blanket. The k_{eff} of Li_2TiO_3 pebble bed is measured as a function of average bed temperature from RT to 500 °C in different environment (vacuum, helium gas etc.). Initial results obtained from these experiments will be discussed in this paper. Details of lithium ceramic breeder material development, their characterizations and related R&D activities will be discussed in this paper.

1. INTRODUCTION

Tritium breeding blanket research and its development is recognized as one of the most important areas for realizing an energy-producing fusion reactor worldwide. The R&D activities on tritium breeding materials development have been initiated at Institute for Plasma Research (IPR), Gandhinagar in collaboration with many other institutes and universities within India. The candidate tritium breeder materials must a.) exhibit thermo-physical, chemical, and mechanical stability at high temperature, b.) be compatible with other blanket and structural materials, c.) efficient release of tritium, and d.) possess desirable irradiation behavior. Lithium, in some form, is the only material suited for this task. Several lithium ceramics (lithium oxide, aluminate, silicate, and zirconate etc.) have been developed and being investigated worldwide for reliable and sustainable tritium breeder candidate material. Among them, Lithium meta-titanate (Li_2TiO_3) and Lithium ortho-silicate (Li_4SiO_4) are accepted as the prominent and suitable candidate materials for breeders [1-3]. India has proposed Lithium meta-titanate (Li_2TiO_3) as the tritium breeder materials in the form of pebble bed for Lead Lithium Ceramic Breeder (LLCB) Test Blanket Module (TBM) [1]. Li_2TiO_3 powder was prepared by solid state reaction using $LiCO_3$ and TiO_2 followed by ball-milling and calcinations. After ball milling, the desired size of spherical shaped Li_2TiO_3pebbles are produced by Extrusion-Spherodization method.

For a robust design of blankets requires a thorough understanding of the physical and thermo-mechanical response of the breeder materials at different loading conditions. The ceramic breeder materials development program provides the material property database to the design team through various characterization processes. At every stages of preparation (powder, pellet and pebble), extensive characterizations are being carried out to meet the desired properties of these materials. A wide spectrum of property characteristics necessary for the blanket design analysis which includes density (lithium density, bulk density), open and close porosity, phase determination, microstructure, specific heat, thermal diffusivity, thermal conductivity, Coefficient of thermal expansion (CTE), elastic constants, thermal creep etc. The improvement of one property may reduce the performance of another. For example an increase in density will improve the mechanical behaviour, but may decrease the porosity which may reduce the tritium release. In this context the material characterisations plays a vital role in determining the breeder response. Stability of the lithium ceramics at high temperatures is also very important from a safety perspective. The preparation of powder and pebbles and their different characterizations are discussed in detail in this paper.

2. EXPEWRIMENTAL PROCEDURE

SYNTHESIS OF Li_2TiO_3 POWDER: Li_2TiO_3 powders can be prepared by various methods like solid-state reactions, combustion synthesis, sol-gel method etc. The most common method of preparation of Li2TiO3 powder is to mix the oxides of using $LiCO_3$ and TiO_2, but, this will lead to the formation of coarser particles which may adversely affect the higher sintered density. This problem can be get rid of by using high energy ball mill. Li_2TiO_3 powder were prepared by Solid state reaction method in which the raw materials of $LiCO_3$ and TiO_2 were used 50:50 mol% to obtain the stoichiometric composition. This corresponding to the Li/Ti atomic ratio of 2.They were mixed properly and blended by using a Planetary ball mill with the help of Iso-Propyl Alcohol (IPA) as the wetting agent for 4 hours. Finally Li2TiO3 powders were formed by calcining the dried precursors at 700 C for 4 h in air atmosphere based on the following chemical reaction.

$$Li_2CO_3 + TiO_2 \rightarrow Li_2TiO_3 + CO_2\uparrow$$

The prepared material was confirmed with the help of powder X-ray diffractometer for its phase analysis and weight reduction will be estimated with the help of TG-DTA. The elemental analysis has been carried out with the help of ICP-MS.

2.1 Preparation of Li_2TiO_3 pellets

The Li_2TiO_3 powder was compacted in a uniaxial hydraulic press at 100 MPa to make the pellets and subsequently sintered at 1000 C for 10 hrs to get the desired diameters..Finally, samples of Li_2TiO_3 pellets of different diameter 10 mm and different thicknesses (from 2 to 4 mm) were prepared for thermal diffusivity measurements by laser flash method, microstructural analysis by scanning electron microscopy Some sintered samples were also used for the measurement of density in Helium Pycnometer and open porosity using Mercury Porosimeter.

2.2 Fabrication of Li_2TiO_3 pebbles

The calcined powder were milled again to make its fine powder for pebble preparation. A dough was made with the powder using suitable binder. The prepared dough was put into the extruder. The extruded strips were fed into a spherodizer to prepare spherical pebbles. The spherical green pebbles were dried in a dryer at 100 °C. The dried pebbles were sintered at 900°C for different duration to achieve the density of 80-90%. The sintering time and temperature were optimized to get the desired density and porosity of Li_2TiO_3 pebbles. FIG. 1 shows the flow sheet of preparation of Li_2TiO_3 pebbles.

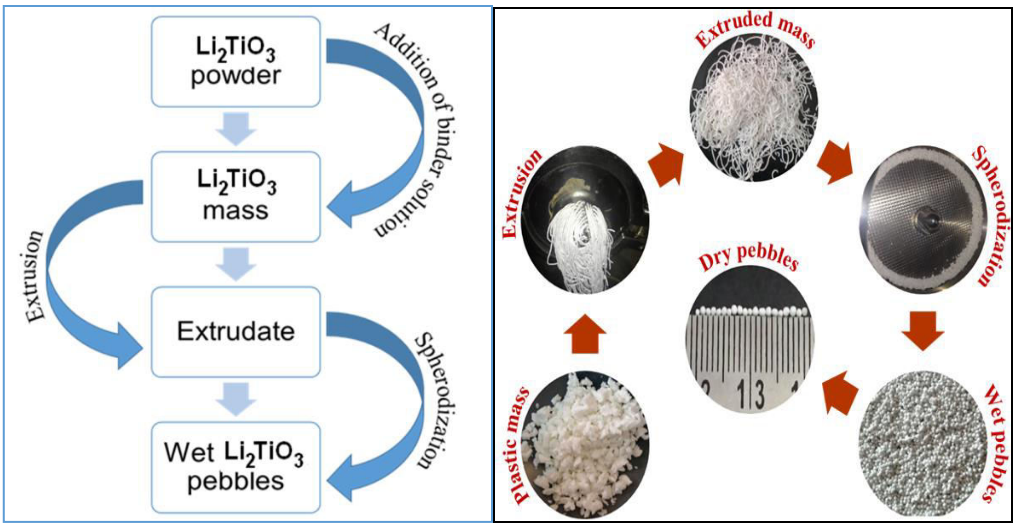

FIG. 1. Flow sheet of preparation of Li_2TiO_3 pebbles

3. CHARACTERIZATIONS OF LITHIUM CERAMICS

Various characterizations have been performed on Li_2TiO_3materials in order to study the physical and thermo-mechanical properties which will finally lead to the preparation of the material properties database. FIG. 2 shows road map of different characterizations performed at different stages of preparation of Li_2TiO_3 powder, pellets and pebbles.

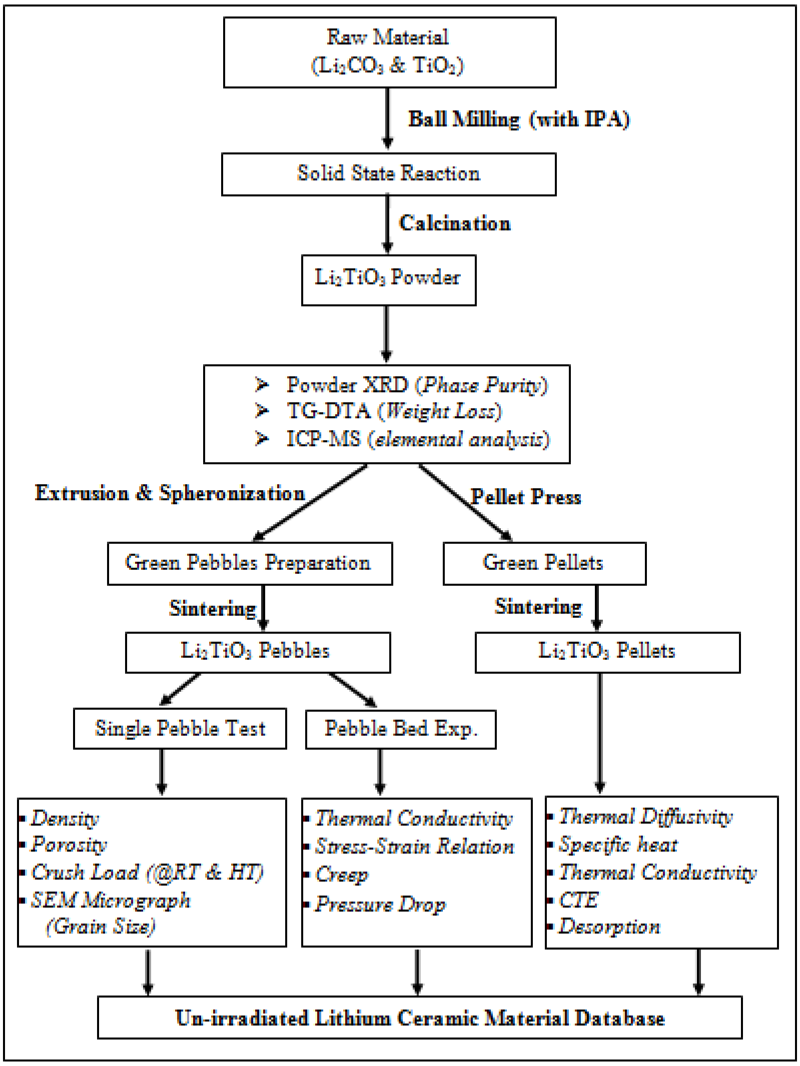

FIG. 2. Ceramic breeder Material Development and characterization road map

3.1 Physical Properties:

Size and spherocity: Size of the pebbles was measured by using an optical microscope having calibrated eye piece. The spherocity of the pebbles were determined from the ratio of diameters of the pebbles measured at right angles Microstructure of Li_2TiO_3 material was investigated out by Scanning Electron Microscopy (SEM).

Bulk Density and Porosity: The bulk density of the pebbles was measured by the Helium Pycnometer. it is observed that the bulk density of pebbles increases with sintering time. The measurement of pore diameter and pore volume of sintered Li_2TiO_3 pebbles were carried out using mercury porosimeter (Model: Quantachrome Poremaster). The experiments were carried out at pressures from 1 to 4000 bars. The open pores were quantified between 10-15 % whereas the closed pores were found less than 2%.

XRD Analysis: The powders obtained after solid state reaction were characterized by X-ray diffraction using Bruker powder X-ray diffractometer with Cu Kα radiation (35 kV, 30 mA) for phase analysis (scanning with a step size of 0.02°at ambient temperature for the angular range 10-70° of 2θ). The XRD pattern at different calcinations temperature is shown in Fig. 3. It shows that above 600C, the crystallinity increases and pure Li_2TiO_3 phase are observed on XRD pattern after calcination at 1000C. It is also observed that in all temperature

Li_2TiO_3 phase has been formed but with certain variation in the phase purity as per the Bruker-TOPAS software. The lattice parameters of Li_2TiO_3 were determined using Rietveld refinement on XRD data.

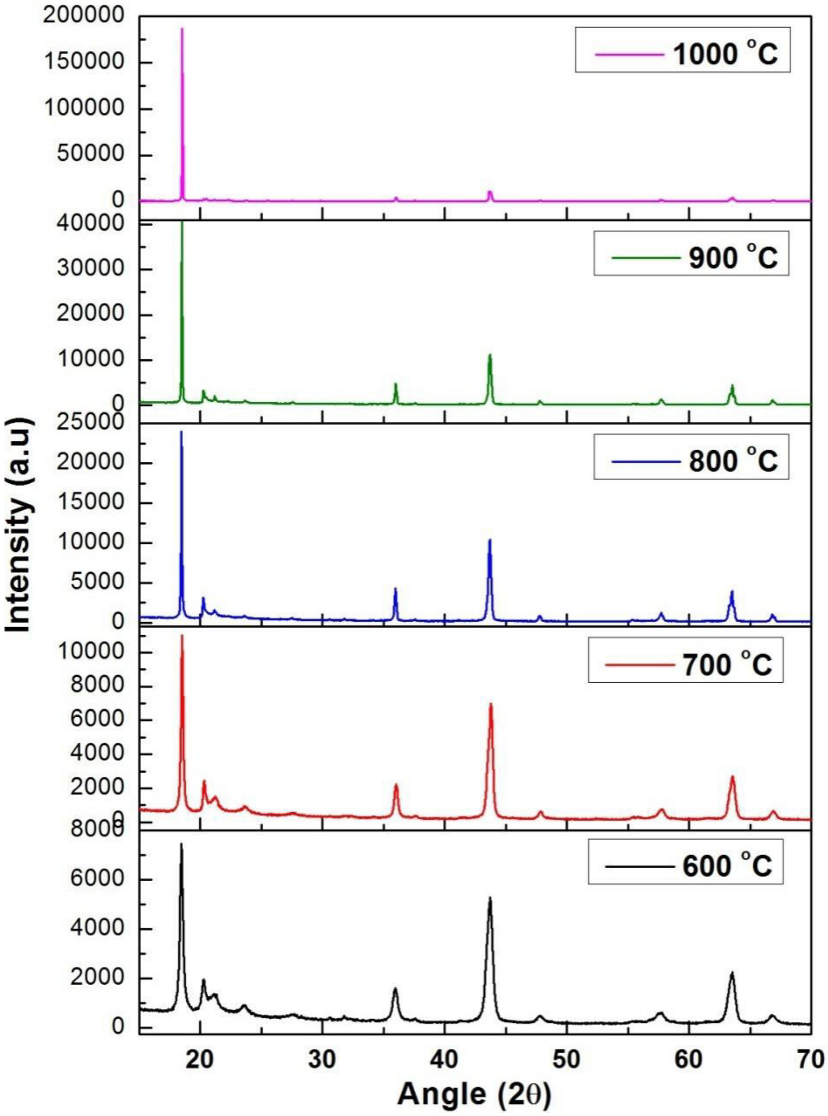

FIG. 3. XRD patterns of Li2TiO3 powder calcined at different temperatures

3.2 Thermal properties of Li_2TiO_3:

Measurement of thermal conductivity by the laser flash method: Thermal conductivity is one of the important property of material. The thermal conductivity of lithium ceramic materials is very low, and the effective thermal conductivity of lithium ceramic pebble beds is even lower than that of the individual pellets. Therefore, the thermal performance of these pebble beds plays an important role in the design of fusion blankets designs. Thermal diffusivity ofLi_2TiO_3 pellets is measured using the laser flash technique in the temperature range from room temperature to 800C. Using the thermal diffusivity, specific heat, and density values, the thermal conductivity of Li_2TiO_3 is calculated. Some modeling of the thermal diffusivity using finite element analysis is performed to simulate the transient thermal measurements of Li_2TiO_3 pellets.

In the laser flash method according to ASTM E1461 [5], a sample is placed within a furnace under a controlled atmosphere and subjected to a finite pulse of radiant energy (Nd:YAG laser having a wavelength of1064 nm, maximum output energy of 25 J/pulse, and pulse width of 10 ms) on its front surface. Before putting the sample in the laser flash apparatus as shown in Fig. 4 the Li_2TiO_3 pellets (12.6 - 12.7 mm diameter and 2-3 mm thick) were coated with graphite to enhance the absorbance of flash energy. The transport of heat through the sample resulting from the laser pulse causes a transient temperature rise on the rear surface of the specimen. This temperature rise is measured by an infrared (IR) detector placed above the rear (back) sample surface.

FIG. 4. Laser flash system (Model: LFA 1000) an the graphite coated Li_2TiO_3 pellets

FIG. 5 shows the schematic of laser flash method and a typical transient temperature curve of the rear surface after laser pulse heating, where, ΔT_{max} is the maximum temperature rise and $t_{1/2}$ is the time taken for the temperature to rise half way between the initial (ambient starting) temperature and the final temperature [i.e., to $(\Delta T_{max})/2$]. Then, the thermal diffusivity a is calculated using the half-rise temperature method as follows [6]:

$$\alpha = \frac{1.38L^2}{\pi^2 t_{1/2}}$$

Where, L is the sample thickness (m), $t_{1/2}$ is the time required to reach half of the maximum temperature rise at the rear surface of the sample (s) and where α is in meters squared per second.

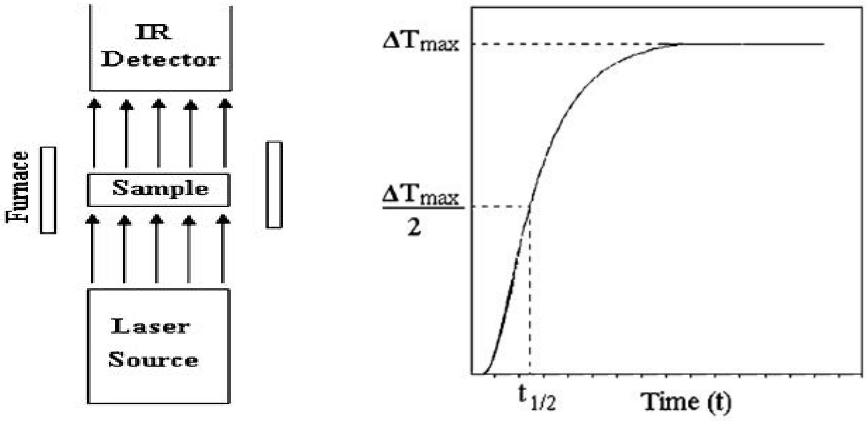

FIG. 5. Schematic of Laser Flash method and Transient temperature curve of the rear surface of the sample after laser pulse heating.

During the experiment the sample was held in thermal equilibrium at the measurement temperature, and the flat surface of the front side of the sample was subjected to a laser pulse of uniform energy density. This incident pulse was absorbed by the sample surface in a very short time, resulting in a temperature rise of the incident surface. Because of the temperature gradient across the sample thickness, a transient condition was observed, and the heat was conducted through the thickness. The temperature rise on the rear face of the sample was recorded as a transient signal using an IR detector. FIG. 6 shows the experimentally obtained simultaneously measured temperature dependent thermal diffusivity and specific heat of Li_2TiO_3 samples at their different densities. Based on these experimentally obtained data, the thermal conductivity was calculated using the following equation: $\lambda = \alpha \cdot C_p \cdot \rho$, where, C_p is the specific heat capacity of the material and ρ is the density of the material. Finite element analysis using ANSYS software was also has been performed to simulate the transient thermal measurements to compared with those results obtained by the laser flash method. The experimental and ANSYS simulation results were found to be in good agreement [7].

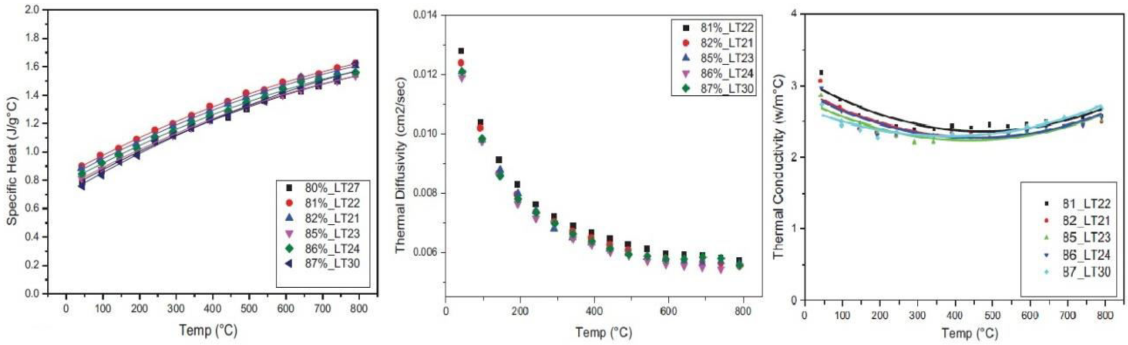

FIG. 6. Measurements of Specific value, Diffusivity and Thermal Conductivity of Li_2TiO_3 samples

3.3 Mechanical Properties

Contact strength of the pebbles is of concern, since they might get crushed in the blanketunder thermo-mechanical load [8]. Crush load tests were performed to characterize the load bearing capacity of single ceramic pebble to evaluate their strength. In these tests single pebble was crushed at room temperature by using by a pair of parallel plates where the pebble is placed. The lower plate is fixed and the upper plate is moving. The approach velocity of the upper plate was kept constant. The displacement of the upper plate and the reaction force were recorded during loading. As a ceramic material, the failure of pebbles is spontaneous and the crush load can be easily identified. The crush load has big scattered values due to the ceramic characteristic of the pebbles. In order to derive the complete crush load test information, maximum, minimum, standard deviation as well as distribution plots was obtained as shown in FIG. 7. They give the optimal strength which can be attributed to the proper sintering of the pebbles. In each experiment, minimum 50 pebbles of size 1.00 ± 0.15 mm have been used for the crush load test majority of the pebbles have the crush load more than 45N. .Post-irradiation studies needs to be done in order to check strength of the pebbles at working conditions.

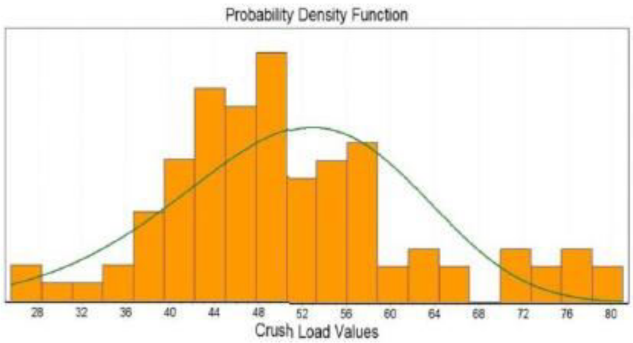

FIG. 7.Measurements of Crush load different sample frequencies

3.4 Pebble Bed Characterizations

The thermal properties of the lithium ceramic pebble beds have a significant impact on blanket's temperature profile and the heat extraction process. So, the effective thermal conductivity of Li_2TiO_3 pebble beds is an important design parameter for the temperature control in the pebble beds. Experimental setup has been developed for the measurement of thermal conductivity of pebble beds using steady state and Hot Wire method.

Steady state-axial heat flow method: In this method, steady state values of heat flux and temperatures across the Li_2TiO_3 pebble bed are measured to calculate k_{eff} using the Fourier's law of one dimensional heat conduction. The experimental system mainly consists of heater disc, heat flux smoother, measuring cell, heat flux and multi level temperature sensors, heat sink unit, data acquisition unit, PID temperature controller, vacuum feedthroughs, vacuum components, thermal insulation materials, etc. The Li_2TiO_3 pebble bed has pebbles of 1 ± 0.15 mm in diameter having packing fraction of 63%. The schematic diagram and the experimental set-up is shown in FIG. 8. Experiments were performed on uncompressed Li_2TiO_3 pebble bed in stagnant helium gas filled at different pressure but above the atmospheric pressure. Dependence of the k_{eff} on the bed temperature and gas pressure has been observed. The k_{eff} of Li_2TiO_3 pebble bed has been measured from room temperature to 400C as shown in FIGV 9. Upgdation of the system to measure above 400C is in progress.

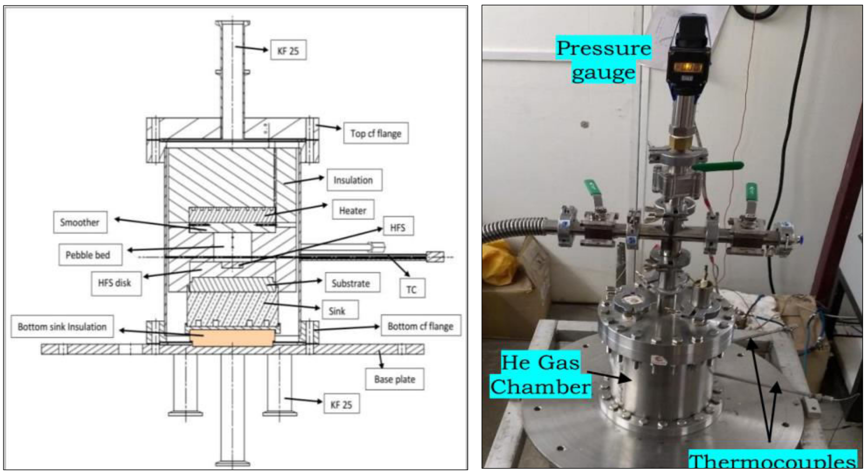

FIG. 8. Schematic and Experimental set up for the measurement of effective thermal conductivity of Li_2TiO_3 pebble bed using Steady State method

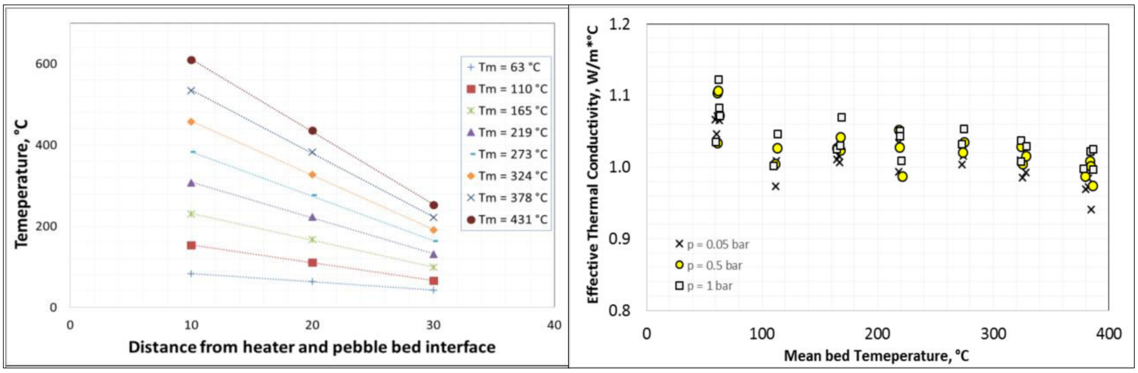

FIG. 9. Temperature distribution and effective thermal conductivity of Li_2TiO_3 pebble bed (Steady Sate method)

Transient hot wire technique: In this method, a constant electrical current is passed through a pure platinum wire placed inside the Li_2TiO_3 pebble bed. The rate at which the hot wire heats is dependent upon how rapidly heat flows from the hot wire into Li_2TiO_3 pebble bed maintained at constant temperature. The hot wire temperature changes with time is accurately calculated by measuring its change in electrical resistance in the same way a resistor temperature detectors (RTD) works. A Fourier equation is then used to calculate k_{eff} by using the rate of temperature increase of the wire and power input. Schematic and the experimental facility is of transient hot wire technique is shown in FIG. 10. Main components of the hot wire test facility are: temperature controllers, data acquisition unit, test section with Li_2TiO_3 pebbles, platinum wire, thermal insulation, thermocouples, etc.

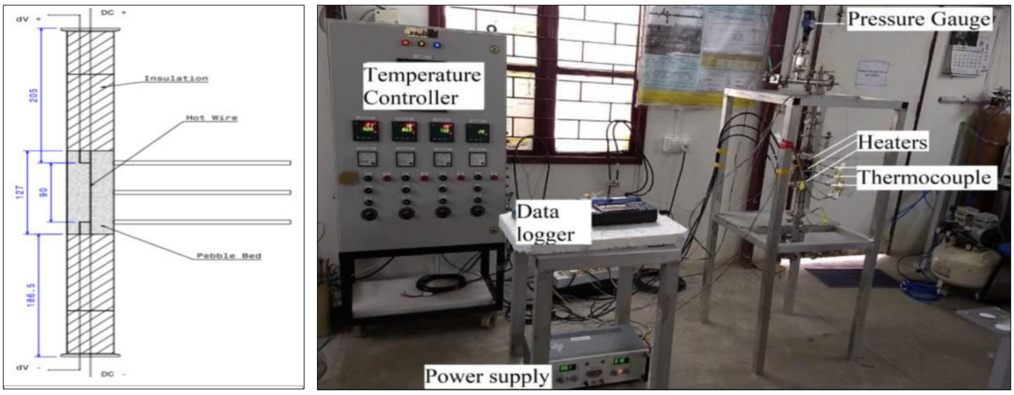

FIG. 10 Schematic and Experimental set up for the measurement of effective thermal conductivity of Li_2TiO_3 pebble bed using Steady State method

Experiments have been performed with the filled mass of Li_2TiO_3 pebbles in the volume of 147 cc is 270 gm having packing fraction of pebble bed is estimated by 63 %. A temperature response of hot wire embedded in pebble bed is shown in FIG. 11. Clear dependence of helium gas pressure has been observed on k_{eff} of Li_2TiO_3 pebble bed which is in agreement with the Smoluchowski effect.

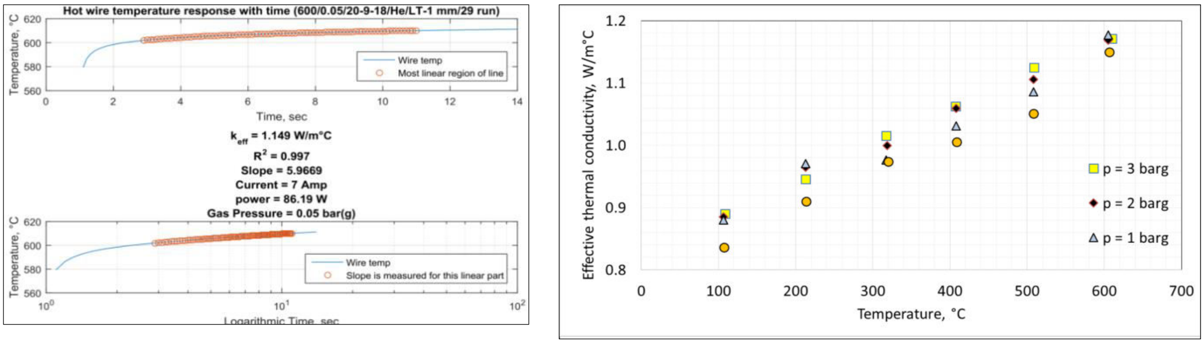

FIG. 11. Temperature distribution and effective thermal conductivity of Li_2TiO_3 pebble bed (Hot Wire Method)

Discrete Element Method (DEM) simulations have been used to study the packing process of the pebbles in a canister and its flow characteristics. DEM is also used to study the pebble bed in uniaxial compression or oedometric compression are carried out to study stress-strain responses, changes in pebble bed parameters, contact force distributions, correlation between external loadings and internal contact forces, force map and cyclic loadings of pebble beds. It has been observed that the pebble bed with constant value of radius and young's modulus has much stiffer stress-strain response compare to the pebble bed with distribution in radius and young's modulus.

4. SUMMARY AND DISCUSSIONS

Li_2TiO_3 powder was synthesized by solid state method and phase purity was maintained in sintered samples. Various characterizations have been performed to get the desired properties of Li2TiO3 powder, pellets and pebbles. Experimental facility has been setup for the measurement of pebble bed thermal conductivity using steady state axial heat transfer method & hot wire method. approach has been applied to study mechanical behaviors of ceramic breeder pebble beds.

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