4.0 EXPERIMENTAL

4.1 Synthesis of hydroxide hydrogel of zirconium and aluminium

Zirconium oxychloride of Riedel quality and aluminium nitrate of analar BDH quality were selected for the synthesis of the mixed hydroxide hydrogel. Liquor ammonia used for coprecipitation was also of BDH quality. Synthesis of the mixed hydroxide hydrogel was carried out at three different molar ratios of ZrO₂ : Al₂O₃ i.e. 1:1, 1:2 and 1:4 respectively, by following the wet interaction technique in aqueous phase. For this purpose molar solutions of each ingredient were prepared in deionised water, and analysed for the cationic constituents.

Required volume of the ingredient solutions were taken in a glass jar of 10 litre capacity, and diluted to 5% w/v concentration with deionised water. Then the ingredients were mixed thoroughly. 1:2 ammonia solution was added slowly with constant stirring. The viscosity of the mixed solution gradually increased with the formation of mixed hydroxide gel manifested by the turbid appearance. This was continued and the pH was kept at 9 whereby enormous gel formation occured with complete engulfment of the dispersion liquid.

The formed hydrogel was allowed to age at room temperature (25°C) for a period of 24 hours, whereby syndesis took place indicating the true nature of the gel. Then the gel was thoroughly dispersed in large bulk of deionised water and allowed to settle. The gel particles settled at the bottom with separation of clear supernatant liquid. The clear liquid containing water soluble impurities was siphoned off carefully followed by addition of fresh water. This process of alternate settling the colloid particles and siphoning the top liquid was repeated until the bulk of the impurities was removed as indicated by the dispersing tendency of the settled mass. This was then filtered through Buchner funnel(s), washed thoroughly with hot water until free from chloride. The filtered
cake was then subjected to normal dialysis to remove the last traces of ionic impurities. Finally the purified gel was dried at 60°C in an electrically operated air oven.

4.2 Characterisation of synthetic hydrogel

4.2.1 Chemical analysis

Chemical analysis of precursor powder was carried out gravimetrically. For this purpose 0.15 g of the finely agitated sample was digested with 1:2 HCl solution, whereby it completely dissolved. This was made up to 100 ml. with deionised water. From this 25 ml was taken, and to it an excess 10% NaOH was added. This was boiled for total conversion of Al³⁺ into NaAlO₂. The precipitated Zr(OH)₄ was filtered, washed with hot water, ignited and weighed. The filtrate was acidified and Al(OH)₃ was precipitated with NH₄OH - NH₄Cl buffer. This was also estimated gravimetrically. From the analytical results molar ratio of ZrO₂ : Al₂O₃ was calculated.

4.2.2 Particle size analysis

Particle size analyser instrument of model CIS-1, Galai of Israel was used. Distilled water was taken in the cavette and few drops of prepared sample along with 1 - 2 drops of sodium hexametaphosphate as dispersing agent was added. The cavette was shaken thoroughly, and placed in the machine where particles were imparted a continuous dynamic motion with magnetic stirrer. This obstructed the path of the laser beam resulting in the formation of image of these particles on the photo sensor. The image in turn was converted into sizes of the particles in microns with the application of time transition theory.

Number, area and volume distribution of the particles along with statistical parameters like mean, medium, standard deviation etc. were computed with the help of an application software dedicated to the instrument.
4.2.3 Loose bulk density

Loose bulk density of the precursor powders was determined by taking the weight and corresponding volume of the sample quantity. About 0.5 g of the loose powder was taken in a 10 cc test tube which was graduated earlier. The test tube was then subjected to 3-4 strokes at the bottom from a height of about 15 cm to get compactness of the mass. The volume occupied by the mass was noted, and loose bulk density was determined by dividing weight of the mass in gram with the volume occupied in cubic centimeter.

4.2.4 Surface area determination

The specific surface area of the zirconia-alumina powders was determined using Surface Area Analyser Model 1750 of M/s. Carlo Erba Strumentazione, Italy. The test is conducted as per BET method. From BET equation,

\[
\frac{P}{V(P - P)} = \frac{1}{V_m} + \frac{(C-1) \times P}{V_m C \cdot P_s}
\]

where, 
- \( P \) = Pressure of gas
- \( P_s \) = Saturation gas pressure
- \( V \) = Volume of gas adsorbed
- \( V_m \) = Volume of monomolecular gas adsorbed
- \( C \) = Constant

For this purpose about 5 grams of sample was taken in a sample tube degassed at 110\(^\circ\)C in vacuum upto 3 mbar. The sample tube was then closed by a stop cock, cooled and placed in a liquid nitrogen bath. Grade I nitrogen gas was then allowed to absorb on the surface of the sample at liquid nitrogen temperature. The instrument determined the amount of gas absorbed for developing a monolayer on the sample surface. The measured total surface area was displayed by a digital indicator. The surface area per unit gram of the sample taken was calculated and reported as metre square/gram.
4.2.5. **Infrared analysis of precursor powder**

Infrared spectrophotometer of Parkin Elmer Model 287 was used. Spectra were recorded over the range 4000 to 400 cm\(^{-1}\) range to produce adequate characterisation of ZrO\(_2\) - Al\(_2\)O\(_3\) hydrogel. Such coverage ensures most of the useful vibrations active in the infrared.

A small amount of the sample (0.2 g) was thoroughly mixed with ground Br in an agate mortar, and the disc (2.5 mm dia.) was prepared by vacuum pressing at a pressure of 33 kg/cm\(^2\). The sample disc was placed in the sample holder, and spectrogram was taken.

4.2.6 **Differential thermal analysis**

NETZSCH Simultaneous Thermal Analyzer STA 409 instrument was used. 0.2 to 0.3 g of sample taken in the crucible was placed inside a closed tubular furnace. The temperature of the furnace was raised at the rate of 10\(^0\)C/min., to a maximum temperature of 1400\(^0\)C. Both DTA and TGA curves were recorded in the chart, from which exothermic and endothermic peaks were identified with their corresponding peak temperatures.

4.2.7 **X-ray diffraction analysis of precursor powder and sintered material**

The identification of different crystalline phases of zirconia and alumina was carried out by powder X-ray diffraction study. The precursor powders were analysed in X-ray diffractometer of D 500 model of Siemens make, with a scanning speed of 2\(^0\) (2\(\theta\)) per minute using Mo as target. The X-diffractographs were recorded within the angle range 8\(^0\) < \(\theta\) < 32\(^0\), where \(\theta\) = Bragg's angle. XRD measurements of the sintered samples were taken on the consolidated form in order to restrict the stress induced conversion of ZrO\(_2\) from tetragonal to monoclinic form. X-ray diffractometers of PM
9920/03 and PW (1710) models of Philips make, with Cu anode were used. The X-
diffractographs were recorded within angle range $10^0 < 2\theta < 60^0$.

4.3. *Equilibrium dehydration -rehydration*

The sample was equilibrated at a specified temperature and the loss in weight was
recorded. A definite weight of the hydrogel ( 2g in each case ) was placed in porcelain
 crucible and heated in an electrically heated muffle furnace at the selected temperatures
up to the point of equilibrium. The temperatures of heat treatment were 100, 200, 300,
400, 500, 600, 700 and 800°C respectively.

After determining the weight loss, the heat treated samples were successively
equilibrated at relative humidities of 35, 55, 75 and 100 % respectively, weighed after each
stage, and finally placed in the thermostat (32 ± 1°C). The materials thus obtained have
been referred to as final thermostated material.

4.4 *Kinetics of dehydration*

The kinetics of thermal dehydration was investigated with the powder samples.
The rate study was performed by carrying out isothermal experiments in a
thermogravimetric apparatus. This consists of thermobalance from one arm of which a
platinum crucible ( cylindrical in shape, 1.5 cm diameter, total capacity of 5 ml.) was
suspended into the uniform temperature firing zone of a tubular furnace. The tip of the
thermocouple of the temperature indicator was placed closed to the crucible. Temperature
of the furnace was raised and controlled by means of an adjustable variac. The control of
temperature was within ±0.5°C. 0.4 g of sample was used for each experiment i.e. for
three different compositions, and at five different temperatures of 250, 275, 300, 325
and 350°C. The crucible with the loose powder was equilibrated in incubator at 36 ± 1°C,
and then placed carefully in the firing zone of the furnace which was previously raised to
the desired temperature. The weight losses were recorded by the thermobalance at suitable time intervals, the initial weight corresponding to the zero time being taken from the instance of suspension of the crucible (with the sample) inside the furnace. This obviated the need for buoyancy correction for the weights of isothermal dehydration.

4.5 Fabrication of pellets / bars

For fabrication of pellets, moulds of cavity size around 12 mm. was prepared from high carbon steel of special quality. About 0.5 g of the precursor powder was weighed and put into the cavity. This weight was kept almost fixed for all the pellets. Pellets were fabricated in a laboratory Carver Press at a pressure of 1800 kg/cm² by uniaxial pressing. After reaching the desired pressure, it was held for 10-15 sec. in each case. No additional binding agent was used except about 10% of the uncalcined hydrogel with the calcined ones. The pellets were found to be sufficiently strong to be handled for next operation.

For fabrication of bar, mould of size 60x6x6 mm was prepared from high carbon steel of special quality and samples were made in the same process as done for pellets.

For making Y₂O₃ doped samples, Y₂O₃ was mixed with precursor powder by wet process using acetone as solvent. After thorough mixing for 4 hours, the samples were dried in a drier, and then used for pellet and bar making.

4.5.1 Sintering of the pressed pellets and bars

The pressed pellets and bars after proper drying were placed on alumina plate in a high temperature electrically heated muffle furnace with superkanthal heating elements. The temperature was raised at a rate of 10⁰C/min up to 1000⁰C, and then at 5⁰C/min. to the final temperature of heat treatment. The soaking period was kept fixed at 2 hours. The selected temperatures of heat treatment were 1400⁰, 1450⁰, 1500⁰, 1550⁰ and 1600⁰ C respectively. Heating was performed in normal furnace atmosphere. The thermal regime
of the furnace was controlled through a programmer cum controller of "Eurotherm" within ± 2°C. After firing, the furnace was allowed to cool in a natural way, which took about 20 hours.

4.6 Characterisation of sintered material

4.6.1 Volume shrinkage

This was measured through dimensional changes. The diameter and the thickness of the pellets were measured with the help of a screw gauge after calcining the pellets at 1000°C for 2 hours, and then at the desired temperatures for 2 hours, from which the shrinkage was calculated.

4.6.2 Apparent Porosity and Bulk density

The bulk density of the sintered samples were determined using the Archimedes principle. Sintered pellets were weighed in dry condition (W_d) and then kept in boiled water for about two hours to ensure that water completely filled the open pores. The weight of the samples when suspended in water was measured and noted as (W_{sus}). The samples were finally weighed in fully soaked condition in air (W_s). Bulk density and apparent porosity were estimated from the following formula.

a) Bulk density (g/cc) = W_d / (W_s - W_{sus})

b) Apparent porosity (%) = (W_s - W_d) / (W_s - W_{sus}) x 100

4.6.3 Thermal expansion

This was carried out in a high temperature Dilatometer of NETZSCH model no.402. The initial length of the sample (size: 40-45 mm length and 5 mm φ) was
measured accurately, and placed inside the tubular furnace. The temperature of the furnace was raised at $5^\circ C/\text{min}$ up to $1400^\circ C$. The cooling rate was also maintained at $5^\circ C/\text{min}$ up to $700^\circ C$. The difference in dilation of the test sample, the push rod and the tube sample support resulted in a displacement of the iron core of a differential reactor. The displacement in this changed the balance in the bridge circuit. A change in voltage took place, which was converted into a proportional direct voltage by a carrier frequency measuring amplifier, and registered by a 6 channel compensated potentiometer recorder. This recorder registered simultaneously the sample temperature measured by the sample thermocouple, and the time gradient of the difference in dilation. The recording continued during cooling of the sample up to $700^\circ C$.

4.6.4 True density

True density of the powder samples was measured by a Pycnometer. Samples were ground to pass completely through a 200 mesh BS sieve, and dried at $110^\circ C$ for 2 hours.

The pycnometer was weighed (a), dried sample was introduced into it and weighed (b). About 10 to 15 ml. of kerosene of boiling range 180-220$^\circ C$ was introduced into the bottle slowly, and was evacuated at a pressure of 5 mm Hg for 2 hours. The bottle was then completely filled with kerosene and weighed (c). Then the bottle was made empty, cleaned, dried and filled with kerosene completely and weighed (d). The true density was calculated as

If the specific gravity of the kerosine = $G$

The true density ($\rho$) of the powder sample = $(b - a) \times G / (d - a) - (c - b)$
4.6.5 Flexural strength at ambient temperature

Measurement of flexural strength at ambient temperature was done in a three point bending fixture at Instron Universal Testing Machine Model No 1185. The span was 40 mm and the crosshead speed was maintained at 0.5 mm/min. The rectangular bars of 55 x 5 x 5 mm were ground on diamond discs of 180 and 20µ in a polishing machine, Planopol 3 of Struers make. The bars were finally polished with diamond paste of 16, 8 and 1µ. The tensile edges were chamfered. Flexural strength was calculated from the following equation:

\[
\text{Modulus of Rupture or Flexural strength} = \frac{3WL}{2bd^2}
\]

Where \( W \) = Fracture load
\( L \) = Span of the bar between the two supporting edges.
\( b \) = Width of the sample.
\( d \) = Depth of the sample at the fracture plane.

4.6.6 Flexural strength at elevated temperature

Flexural strength at elevated temperature was determined in a three point bending strength tester. The test was carried out on a span of 40 mm under 3 point loading. The temperature of the furnace within which the whole assembly was placed was raised at a rate of 5°C/minute. Samples were kept at the maximum temperature of 1200°C for 30 minutes. Loading rate was maintained at 50 kg per minute. The load was transmitted through the load cell transducer and displayed by digital indicator. Flexural strength was calculated as per the formula given in 4.6.5.
4.6.7 Thermal shock resistance

Rapid fluctuations of temperature generate stresses within a material. Resistance to initiation or propagation of crack under stresses generated due to thermal fluctuations is known as thermal shock resistance.

Thermal shock resistance was measured as resistance to weakening or fracture under stresses generated due to temperature fluctuations. Bars of 55 x 5 x 5 mm dimension were heated to 1200°C and soaked for 30 minutes. Subsequently, heated bars were quenched in water at room temperature. Quenched samples were tested in an Instron Universal Testing Machine for retained fracture strength. The span maintained at 40 mm and the cross head speed at 0.5 mm/min.

4.6.8 Microstructure analysis

Phase assemblage in the sintered materials with and without dopant was analysed in a scanning electron microscope (SEM). Scanning electron microscope of S-440, LEO model of Cambridge make, U.K was used to study the microstructural features of samples, as it has much greater resolution as compared to optical microscope. In SEM a hot tungsten filament electron gun under vacuum emits electrons which pass through a series of electromagnetic lenses. The sample is then bombarded with a fine beam of electrons. A part of the beam is reflected back as back scattered electrons. Images formed from the secondary electron beam were studied in the extrinsic mode of SEM. In the reflective mode of SEM where image is created by back scattered electrons, difference in atomic numbers result in increasing contrast.

Sample surfaces were ground with the help of a series of diamond grinding pad from 400 μm to 20 μm on a Planopol polishing machine. The samples were polished with 8 μm diamond paste on a glass plate. Final polishing was done with 5, 2 and 1 μm
diamond paste to create a mirror finish on a lapping machine. Then the samples were mounted on metal stub using adhesive tape on both sides and thinly coated with gold under vacuum of 0.01 Torr in a vacuum evaporator to make the surface conducting. In order to make the full sample conductive a silver line was drawn from top of the surface to the metallic stub by means of silver paint. Samples were then put into the microscope chamber and subjected to evacuation and electron beam scanning. Photographs were taken on a black and white 100 ASA film (Ilford Pan).