PREPARATION AND CHARACTERIZATION OF POROUS CERAMIC BODY USING BALL CLAY

Thesis submitted for the degree of

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CERTIFICATE

This is to certify that the thesis entitled **"Preparation and Characterization of Porous Ceramics body using Ball Clay,"** submitted by **Mr. Rahimuddin Khan** for the degree of **Master of Technology (Dual)** in **Ceramic Engineering** to the National Institute of Technology, Rourkela is a record of bonafide project work has been done by him under our supervision and guidance. His thesis, in our opinion, is worthy of consideration for the award of degree of Master of Technology (Dual) in accordance with the regulations of the institute.

The results embodied in this thesis have not been submitted to any other university or institute for the award of a Degree.

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Abstract

In the past few years, porous ceramic materials having improved microstructure has become very popular due to its wide application in different fields. Now a days there are many techniques such as Polymeric Sponge Replica Technique, Starch consolidation method, Gel Casting method etc. have been developed for the preparation of porous ceramic body with controlled microstructure such as porosity, pore size, pore connectivity etc. In this project work, an effort has been made to prepare porous ceramic body (using Ball clay as raw material) by Polymeric Sponge Replica Technique. Ball clay used as major raw material with some amount of dispersant (sodium silicate) and some samples also prepared with some amount of PVA as binder and also observed the effect of binder on porosity. The optimal viscosity of the slurry for the Sponge replica technique was observed in the range 0.02-1.15 Pa.s. By the sponge replica technique, macroporous ceramic having pore size in the range 400 nm to 4 mm and the porosity 20% to 97% could be obtained. This macroporous body prepared by sponge replica technique can be used in different areas such as molten metal filtration, hot gases filtration etc. Solid loading is the main factor of the slurry was found for the preparation of porous ceramic body of different pore morphology by sponge replica technique. The porosity of the porous samples were measured by vacuum method, the porosity obtained in the range 70-85% and the strength of the samples was found 0.02-1.5 MPa. The microstructure such as pore size, pore connectivity has been analyzed by the FESEM.

Key words: Porosity, Sponge replica, viscosity, microstructure.

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Chapter 1
INTRODUCTION

1. INTRODUCTION

1.1 Overview of Porous Ceramics

Porous ceramics has been very popular in the recent years, because of its improved microstructure such as porosity and pore size distribution, adequate strength, low thermal conductivity and high permeability etc. These porous ceramics have a lot of applications in technical field namely filtration of metal and hot gases; ion exchangers, burner etc. Porous ceramics also found wide application in medical, mining, oil & gas exploration, chemical processing, pharmaceutical industries etc. Application area of porous ceramic depends on the composition and morphology of the porous structure, namely pore size, shape and its distribution together with the pore connectivity.

Pores present in a porous material are of two types i) Open pore and ii) Closed pore. The porous ceramic body having open pores are used for filters and catalysts while the closed pores are required for thermal insulation.

Pores also classified into the following categories based on their sizes:

1) Microporous(<2 nm)
2) Mesoporous(2-50 nm)
3) Macroporous(>50 nm).

Meso and microporous can be utilized in molecular sieves [1] and in catalysis [2]. Macroporous can be used in whitewares like roof tiles and also in advanced ceramics such as medicines and automobile engines [3].

The advancement of the porous filters fulfilled the necessities like the recuperation of the methane from mines, expulsion of carbon dioxide and hydrogen sulfide from natural gas, recuperation of hydrogen in petroleum refinery operation. In the foundry business, porous filters are utilized for molten metal filtration [4]. Porous ceramics can also be utilized in sensors, battery materials as well as in the field of biomedical [5]. Types of porous ceramics based on pore structure and their uses are given in the table 1.

Table.1.Types of porous ceramics based on pore structure and their uses [6]

Pore Structure	**Uses**
Microporous and Mesoporous body	Coatings Sensors and Actuators Catalytic support Desiccant materials
Foam and Honeycomb pore structural body	Flue gas filters Molten metal filtration Burners Electrodes of fuel cells Porous scaffolds which is used in tissue engineering Kiln furniture
Multilayer ceramic body	Ultra filtration membranes Nano filtration membranes Hot gas filtration membranes Dense membranes Zeolite membranes

1.2 Fabrication Technique of Porous Ceramics

Different techniques have been developed in order to get porous ceramic body of desired morphology and properties. The techniques are sacrificial template technique, paste extrusion method, freeze casting method [7], direct foaming method, sponge replica method, rapid prototyping technique etc.

1.3 Sponge Replica Technique

Pore size in the range of 400 nm to 4 mm could be realized in a porous ceramics fabricated by sponge replica technique. In the sponge replica technique, commercial polymeric sponge were used as template. The procedure includes coating of open-cell polymeric sponge with stabilized slurry and then sintering of that coated sponge which yields an imitation of porous ceramic. This technique produces ceramic body with a

greater part of open cell sponge microstructure. The pore morphology of ceramic body fabricated by this technique could be tailored by controlling the consistency of the slurry and the polymeric sponge qualities (strut thickness, pores size, shape and its distribution). The strut thickness, and pore morphology depends on the thickness of ceramic slurry coating on sponge strut.

In the present study ball clay has been chosen as the matrix of porous ceramic. Precursor ball clay is characterized for its physical and thermal behavior. The amount of electrolyte require to make a stable ball clay slurry was optimized. Slurry was prepared with different amount of ball clay loading with taking optimized amount of sodium silicate and the effect of solid loading on viscosity was studied. Effect of PVA addition on the properties of porous scaffolds has also been studied.

The organization of the present thesis is as follows. Chapter 1 (this chapter) describes a brief introduction on porous ceramics, and a back ground of the present wok. Chapter 2 details the literature available on the porous ceramic fabricated by different techniques. This chapter has three parts. Parts first contains the different fabrications techniques and its applications, overview of importance of porous ceramics. In second part the analysis of stabilization of slurry which is used in the preparation of porous ceramic through sponge replica technique. The third section has the detailed study of literature based on present work.

Chapter 3 describes the aim and objective of current work. Chapter 4 contains the experimental part of current project, which is composed of four section i) characterization of raw material (ball clay) ii) optimization of dispersant (sodium silicate) iii) characterization of prepared samples iv) effect of binder on properties of porous ceramic. Chapter 5 contains the result and discussion part of my project which is composed of different part. Chapter 5 describes the conclusion of the present work.

Chapter 2

LITERATURE REVIEW

2. LITERATURE REVIEW

Porous ceramic is a class of highly porous materials with variety of pore structure like honey comb structure, interconnected rod, hollow sphere etc. The advancement of the porous filters fulfilled the necessities like the recuperation of the methane from mines, expulsion of carbon dioxide and hydrogen sulfide from natural gas, recuperation of hydrogen in petroleum refinery operation. In the foundry business, porous filters are utilized for molten metal filtration [8]. Porous ceramics can also be utilized in sensors, battery materials as well as in the field of biomedical [9].

2.1 Fabrication Techniques of Porous Ceramic Body

There are many techniques for the fabrication of porous ceramic body such as sponge replica technique, direct foaming method, paste extrusion, rapid prototyping method. Highest porosity in the range of 40-95% can be achieved and of 200μm to 3mm pore by sponge replica technique size. For the use of filtration high interconnectivity in the structure are required and high interconnectivity is achieved by replica technique but this technique gives very less mechanical strength, this is the main disadvantage of this technique. Many techniques such as repeated coating were used to remove this problem. Techniques such as starch consolidation, gel casting, freeze casting are comes in the category of sacrificial template techniques. In this technique, porosity comes in the range of 25-90% and with a pore size of range 1-100μm. direct foaming techniques gives porosity of 42-90% and having a pore range of 35mm to 1.25mm. Paste extrusion method gives honeycomb structures. More typical structure with a proper pore distribution can be obtained by rapid prototyping technique. High preparation cost make it less popular.

Major raw material is ball clay were used in making slurry. Ball clay is the finest clay having highest plasticity. Ball clays are the secondary clay made up of kaolinitic sedimentary rocks. Ball clays mainly contains 20 to 82% kaolinite, 10 to 23% mica, and 5 to 5.5% quartz along with some impurities such iron oxide, calcium oxide etc.

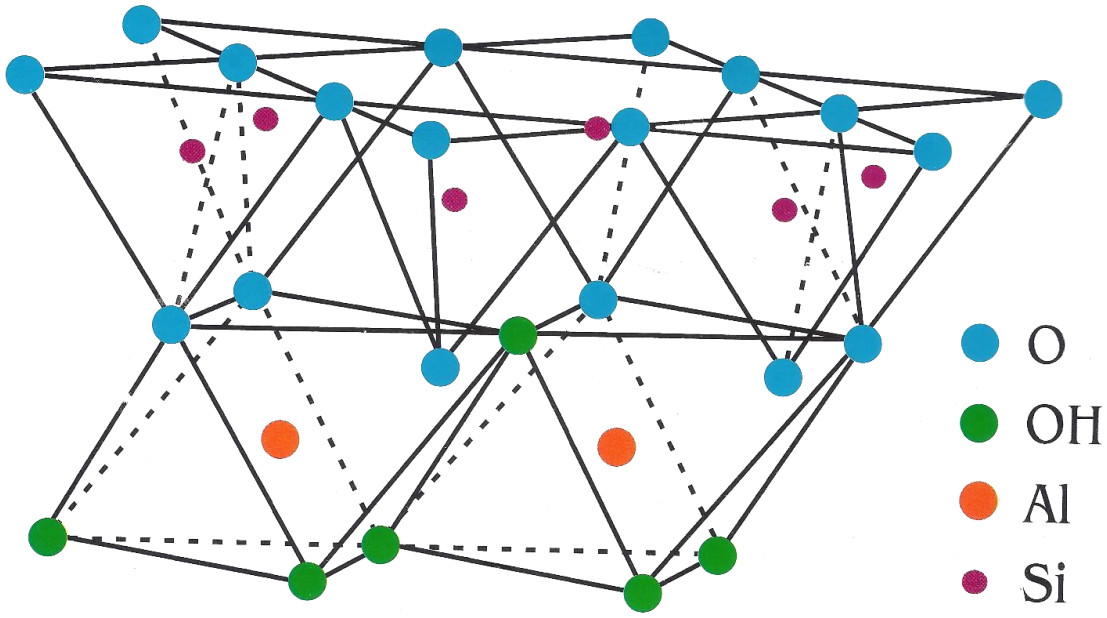


Figure.1.Structure of clay [10]

2.3 Sponge Replica Technique

Porous ceramic bodies are the category of large porosity materials and they are widely used in different areas. In the sponge replica technique, commercial polymeric sponge were used and these foam as template were dipped into stabilized slurry and then put for drying into oven and then sintering at high possible temperature. The properties of ceramic body created by this technique could be balanced by fluctuating the consistency of the slurry and the polymeric sponge qualities, for example, thickness, pores size, shape and its distribution. The nature of ceramic coating on the polymeric sponge is unequivocally subject to the thickness of the slurry and the thickness of the sponge. The procedure includes coating of open-cell polymeric sponge with stabilized slurry and then sintering of that coated sponge which yields an imitation of porous ceramic. This technique produces ceramic body with a greater part of open cell sponge microstructure.

The impact of the firing temperatures on the quality of the ball clay samples made by utilizing the polymeric sponge replica technique has been analyzed [11]. It had been accounted for that the porosity of the specimens reduced from 89 to 85.75%, and strength enhanced from 0.27MPa to 0.527MPa when the sintering temperature expanded from 1400^{o}C to 1500^{o}C. The increment in the strength of samples were not considerable with the enhancement in the temperature from 1500^{o}C to 1550^{o}C, but there was an

appreciable increase in the grain size which increase the strength. The further increment in the sintering temperature up to 1500 ^{o}C brought about an uncommon increment in the grain size prompting the decline in strength of the ball clay samples. Subsequently, the present work proposed that the sintering temperature of 1550^{o}C is required to obtain the good strength of ball clay samples.

Xiumin Yao et. al analyzed the impact of the recoating slurry viscosity on the properties of the porous SiC ceramic [12]. It has been analyzed that for the recoating of polymeric sponge high viscous slurry with the thixotropic loops are needed. With the increase in solid loading viscosity increases and due to this pore size of SiC porous ceramic made by replica technique decreases but the strut thickness increases. The reduction of pore size and increment in the strut thickness credits to increment in the solid loading. The compressive strength of the porous ceramic samples varied in the range from 0.782MPa to 1.591MPa as the recoating viscosity of slurry increased from 0.071Pa.s to 1.441Pa.s. With the help of surface topology it has been observed that both small and some big pores are present in the porous ceramic sample. The tiny pores were formed by firing while the big pores were caused by entrapped air. Extra slurry were removed by Roller technique which also helps in removing air bubbles. There is another technique called centrifugal technique to remove the excess slurry but this could not eliminate the air bubbles so this increased the porosity of samples.

Santanu Dhara and Parag Bhargava have studied about the direct foaming and casting method. They made porous ceramic body with the slurry composed of ovalbumin. They also add some amount of acid and analyzed that it increase the volume shrinkage of samples. Porous ceramic formed by ovalbumin gives many advantages as compare to others. Ovalbumin played two important roles first it hold the particles together and second provides foam formation. With the use of 20 vol% or lower alumina solid loading, porous body of porosity more 90% could be formed. Pores connectivity enhanced with lowering in solid loading [13].

Guangyao Meng et.al studied the preparation of porous ceramic body by gelcasting method. This technique is not appropriate for the preparation of porous ceramic with larger pore size. This technique is used to prepare porous ceramic body with high density. Slurry are made with low solid loading along with organic monomers for this gelcasting technique. They prepared the slurry by using ceramic powder poured into organic monomer with some amount of water. Ammonium bisulphate $(NH_4)_2 S_2 O_8$ as

initiator mixed with the slurry and then cast these into a mold. This cast put into drier and then dried gelcast was fired at appropriate temperature. Green porous body of density 2.291 g/cm^3 was obtained by this alumina powder using gelcasting technique. Porosity of the porous ceramic body prepared by this technique has been obtained in the range of 47.41% to 41.11% at the firing temperature of 1450 to 1500^{o}C. Pore size of samples are big enough hence it has a wide application range. There was a little 5.95% volume shrinkage in the sample fired at 1550^{o}C. gelcasting technique also used for the preparation of porous multi-component oxides ceramic. Highly packed porous body (54%) as well as low firing shrinkage(5.95%) has been obtained for Al_2O_3 powder fired at 1550^{o}C [14].

Zuzana Zivcova et. al prepared a porous ceramic samples with the help of a new pore forming agents. They made slurry with alumina powder poured in distilled water, some amount of dispersant and pore former. Pore forming agent were used in the range of 5-10vol% with respect to alumina. There are many types of natural biopolymer which can we used as pore former. Slurry were prepared in the plastic bottle with some alumina balls in it and then put for homogenization on the shaker (milling) machine. The prepared slurry were cast into mold. There are two types of casting methods first is simple casting in which slurry are poured into POP mold and the second one is starch consolidation method in which slurry are poured into metal mold. They found the porosity of samples (made by starch consolidation technique) in the range of 24-54% while in the Traditional slip casting method porosity in the range of 23-28% were obtained with the varying amount of starch from 10 to 50 vol%. They used different types of biopolymers as pore former and observed the porosity of prepared porous sample. Rice starch, potato starch, corn starch, lycopodium, poppy seed, and coffee were used as pore forming agent and analyzed the porosity. Starch rice, corn starch, and potato starch were taken 10, 30, 50 vol% with respect to alumina and porosity observed in the range of 22.81 to 27.82%, 28.12 to 47.71%, and 25.81 to 53.92% respectively [15].

C. W. Pernell et. al studied the properties of whey and egg white protein foams. They used the varying amount (2-20 w/v%) protein of egg white and whey and compare their properties. They found that the egg white large yield stress developed with the small protein concentration. They observed the effect of protein concentration on the yield stress and they found the average yield stress developed in foam in due to whey protein

and due to egg white were totally different. High concentration (10-20 w/w%) of whey protein is required for foam formation with long time of whipping while low concentration of egg white (2-10 w/w%) with less whipping time is needed for the preparation of foam. The yield stress developed in the foam made from egg white protein is more and stable than yield stress developed in foam made from whey protein. They also analyzed the impact of whipping time on the stability of stress developed in the foam [16].

Rui Xie et. al prepared alumina ceramic by gel casting method and observed its strength. They used alumina powder having particles of size 0.5µm and water soluble as well as less toxic epoxy resin as raw materials. Slurry were made with 50 vol% solid loading followed by milling in the ball mill with 10-15 wt.% aqueous solution of epoxy resin. Slurry was put in vacuum chamber for degassing and then poured into polydimethylsiloxane. Then dried the samples in two stages first was put at 40^oC for 4 hrs and second stage was put sample at 80^oC for 2 hrs and then fired at 1550^oC. They analyzed the effect of epoxy resin on the viscosity and found that the on increasing the concentration of epoxy resin, viscosity increases. They also observed the impact of epoxy resin on green strength and relative density and found that on increasing the concentration of epoxy resin the green strength and relative density increases. The concentration of epoxy resin greatly affect the green strength and density of samples. If they used 15 wt.% epoxy resin, the strength and relative density obtained 43.41 MPa and 52.2% [17].

Sarama Bhattacharjee et. al studied the effect of additives (albumin and starch) on the gel strength, rheological behavior of alumina slurry and microstructure of porous scaffold prepared by combine method of gelling and foaming. At room temperature starch is insoluble in water, hence it increases the viscosity of alumina slurry. So, higher the content of starch, high would be the viscosity. The overall porosity of porous scaffold depends on the viscosity of slurry, albumin makes very little open porosity while starch is a pore former, increase the connectivity of pore [18].

Fengqiu Tang et. al studied the pore size and porosity of a porous material prepared by hetero coagulation template method. They used PMMA (polymethyl methacrylate) polymer as template and Al_2O_3 powder. The polymer size affect the pore size and the porosity could be manipulated by adjusting the volume ratio of polymer/ceramic constituents [19].

R.M. Khattab et. al studied the effect of temperature on the properties of porous sample such as microstructure, resistivity etc. prepared by starch consolidation method. They used corn starch as pore former and obtained lower open porosity at low corn concentration. They fired the samples at different temperature 1500, 1600, and 1700. They obtained the bulk density in the range of 1.4 – 2.05 gm/cm^3 and porosity in the range of 46 to 64% having pore size 1.79- 4.28µ [20].

S.A. Silva et. al prepared and characterized reticulated ceramic with the help of vegetal sponge as template. In this technique the sponge were dipped into the suspension of clay 50%, feldsper 35%, sand 15% (w/w) and this composition gives ideal plasticity. They found the reticulated ceramic in millimeter (5-10mm) and the morphology of reticulated ceramic is same as vegetal sponge. They found the optimum firing time and temperature was 1175^{o}C for 2hours [21].

Hassna Rehman Ramay et. at prepared a macroporous hydroxyapatite body by a combine method of sponge replica and gel casting technique. They observed the better microstructure and strength in the sample prepared by this new technique. They used monomer, deflocclant (ammonium polymethacrylate), hydroxyapatite powder, in the preparation of porous scaffolds. A compressive modulus of 8GPa and yield strength of 5MPa was obtained using hydroxyapatite 50 wt.%. The pore size in the range of 200-400µm were obtained [22].

Iis Sopyan et. al prepared the porous hydroxyapatite by sponge replica technique and characterized their properties. They analyzed the effect of sintering time and temperature, stirring time and hydroxyapatite concentration on strength, porosity, and crystallinity of porous scaffold. Hydroxyapatite composition did not change for all sample after sintering of green samples. They observed both micro and macro pores having size of 0.2-1µm and 100-200µm respectively. The average strength of porous scaffolds were found in the range from 1.8 to 10.5 MPa and porosity in the range of 59.8 to 34.3% [23].

Marcelo Strozi Cilla et. al prepared a macroporous ceramic scaffolds with nonaligned pore structure using fire clay by freeze casting technique. The properties of porous scaffolds were controlled by parameters like types of fire clay and amount of gelatin. Gelatin was used as an additives which modify the pore structure. They obtained the maximum porosity of 74% with a porosity as high as 70 vol% and having a spherical pore size [24].

Pat Sooksaen et. al were prepared a porous ceramic by a low cost polymeric sponge technique using a clay (Surat Thani clay and Ranong) from southern Thailand along with alumina as raw materials. They used polyurethane as sponge as template having different pore size. They sintered the green porous scaffold at two different temperature 1150 and 1200^{o}C and obtained the total porosity of greater than 70% with a total shrinkage in the range 8.25 to 12.5 %. Surat thani clay is acted as a ball clay and gave high shrinkage as well as densification while ranong clay was act as a kaolinitic clay gave good strength due to formation of mullite phase when fired at 1200^{o}C [25].

Li Zhu et. al were synthesized porous ceramic membrane using mullite whiskers with improved porosity, permeance as well as good strength. They used (MoO3and AlF3) as a binder which formed whiskers-interlocked structure. MoO_3 5% and AlF_3 4% were used which gave 48.6± 0.5% open porosity, 81.2±3.2 MPa strength at 1200^{o}C as well as high permeance [26].

A. Esharghawi et. al were prepared the pure porous mullite from kaolinite with the addition of some amount of Al and Mg metal powder and hot pressed in oxidized atmosphere. The thermal behavior of porous mullite were observed by XRD, SEM, DSC-TG, dilatometry etc. The samples were fired at 1550^{o}C. It was observed that porosity increases with increasing the amount of Mg metal powder [27].

J.-G. Kim et. al introduced a new method for the preparation of porous samples. (Ba, Sr) powder has been taken for the preparation of porous sample and corn-starch used as a pore former. They observed the effect of concentration of corn-starch on the porosity and grain size. If the corn-starch concentration was 5 wt.% then the porosity and grain

size were 21.1% and 3.6μm respectively, while when the concentration of corn-starch was 20 wt.% then the porosity and grain size were 44% and 3.1 μm respectively [28].

Xinwen Zhu et.al prepared the silicon carbide reticulated porous ceramic by replica technique. Polyurethane sponge having pore size of nearly 11 pore per inch has been used as template. The powders (SiC, Al2O3, bentonite) were mixed with some amount of deflocculant in water using silica sol as a binder was studied by zeta potential and viscosity. They optimized the PH value 10 for this mixture. They optimized the slurry behavior which is good for impregnating the polymeric sponge [28].

Chapter 3

OBJECTIVE OF THE PRESENT WORK

3. OBJECTIVE OF THE PRESENT WORK

The main aim of this project is to prepare a highly porous ceramic body using ball clay by one of the most suitable method. The properties of ball clay porous ceramic body prepared by sponge replica technique are greatly affected with the factors like Ball clay loading, viscosity (rheology) of slurry. Particle size of ball clay also affect the porous samples. The firing temperature influenced the cold crushing strength and porosity of porous samples. The samples fired at low temperature have high porosity and low strength while the samples (made from same slurry) have low porosity and high strength. We can also make samples (which is fired at high temperature) having high porosity by increasing the amount of pore former. For e.g. in case of sponge replica techniques, sponge is used as pore former so we can make samples (which is fired at high temperature) of high porosity by using appropriate sponge. There are many method to induced porosity in porous body. The pore developed due to large quantity of pore forming agent with fired at low temperature can have equal porosity of sample which have low pore quantity of former with fired at high temperature. If we prepared sample which is fired at low temperature could also have same porosity with the sample which is formed with some amount of sintering additives in it maintaining the pore forming agent unchanged.

Objective of the project are given:

Preparation of porous ceramic body using ball clay by sponge replica technique (SRT).

1. Optimization of slurry with the help of zeta potential, sedimentation height, and viscosity.
2. Observation of the effect of solid loading on the properties of porous ceramic body such as porosity, strength, connectivity of pore.
3. Observation of the effect of binder on the porosity, strength, and microstructure of porous scaffold.

Chapter 4

EXPERIMENTAL PROCEDURE

4. EXPERIMENTAL PROCEDURE

4.1 Optimization of deflocculant for the formation of stable ball clay slurry

Sodium silicate has been used as deflocculant in this present work. Slurry has been prepared with different amount of sodium silicate varying from 0.1 to 0.9 wt.% with a fixed solid loading of 20 wt.%. the stability of slurry has been calculated by measuring the zeta potential, sedimentation height and viscosity of the slurries. Sedimentation height was measured by pouring of slurry in a 100ml measuring cylinder. Slurry was filled with a height of 80ml and measured the sedimentation height at different interval of time up to 24 hours of settling.

4.2 Optimization of binder for slurry of desired viscosity

PVA (polyvinyl alcohol) has been used as binder. Slurry has been prepared with a fixed solid loading of 20 wt.% along with a varying amount of PVA from 2 to 8 wt.% with the help of Rheometer, viscosity was measured.

4.3 Rheological Behaviour of Ball Clay with Deflocculant

Clay slurries were made up by utilizing ball clay and sodium silicate as a deflocculant with varying weight proportion. Slurries were prepared with solid loading of 30 wt.%, 40 wt.%, 50 wt.% and 50 wt.% along with 0.4 wt.% sodium silicate as deflocculant. All these compositions of slurries were milled in a pot mill for 12 hours with some alumina balls used as grinding media. Total weight of all compositions are 100gm.

Table 2 Batch Calculation

BATCH COMPOSITION				
Solid loading (wt.%)	Wt of water (gm)	Quantity of clay (gm)	Quantity of deflocculant (gm)	
30	70	30	0.4 wt.%	0.12
40	50	40	0.4 wt.%	0.15
50	50	50	0.4 wt.%	0.20
50	40	50	0.4 wt.%	0.25

4.4 Slurry preparation with PVA

Clay slurries were made up by utilizing ball clay and optimized value of sodium silicate as a deflocculant and with optimized wt.% of PVA as binder. The quantity of PVA added was 5 wt.%, and with varying amount Ball clay. Slurry was made with 30 wt.%, 40 wt.%, 45 wt.%, and 50 wt.% solid loading of Ball clay along with optimized value of binder and deflocculant. All these compositions were wet milled in pot mill for 8 hours with some alumina balls used as grinding media.

Table 3 Batch Calculation containing binder

BATCH COMPOSITION						
Solid Loading (wt.%)	Quantity of water (gm)	Quantity of Ball clay (gm)	Amount of deflocculant (gm)		Amount of PVA (5w.t% PVA solution) (ml)	
30	30	30	0.4 wt.%	0.12	5 wt.%	30
40	20	40	0.4 wt.%	0.15	5 wt.%	40
45	10	45	0.4 wt.%	0.17	5 wt.%	45
50	0	50	0.4 wt.%	0.20	5 wt.%	50

4.5 Different Techniques for the Preparation of Porous Ceramic Body

Porous Ceramic body can be made by three method.

1) Starch consolidation method (SSM)
2) Sponge replica technique (SRT)
3) Combination of SSM and SRT

Porous ceramic body has been fabricated by sponge replica technique.

4.6 Sponge replica technique (SRT)

Ball clay slurry having different clay content in the range 30 to 50 wt.% with 0.4 wt.% sodium silicate as deflocculant has been prepared. Poly Vinyl Alcohol (PVA) 5wt.% as binder also used in other batch of slurry to keep the proper viscosity of slurry. Cubic sponge of size 2.5×2.5×2.5 cm were immersed into the prepared Ball clay slurry and the soaked samples of sponge were dried at 80^{o}C for 12 hours and then the dried samples

were fired at 1300^{o}C and the fired samples were characterized by porosity, cold crushing strength, and microstructure.

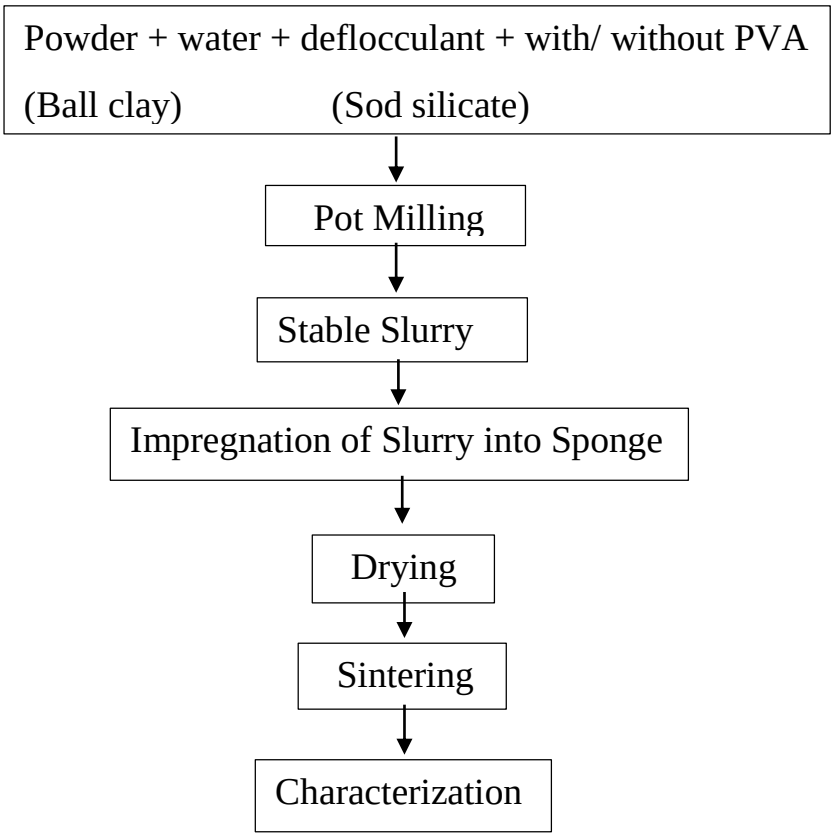


Fig. 2 Flowchart of sample preparation by Sponge Replica Technique

4.7 Characterizations of Porous Sample

4.7.1 Rheological Analysis

The rheological behavior of stable Ball clay slurries has been calculated by Anton Parr Rheometer. The experiments were performed with an increasing shear rate (1-200 s^{-1}) at 25^{o}C. With the help of this Anton Parr Rheometer viscosity, shear stress were calculated.

4.7.2 Porosity Calculation

The porosity of porous ceramic body prepared by sponge replica technique has been calculated by vacuum method. In this method first of all dry weight of samples were taken and then the samples put into a glass beaker filled with kerosene. The beaker then put in a vacuum desiccator for about 2 hours inside vacuum and then the soaked weight and suspended weight were measured by balance. Apparent porosity and bulk density of samples were calculated by the help of given formulae

$$Apparent\ Porosity = \frac{Soaked\ Weight - Dry\ Weight}{Soaked\ Weight - Suspended\ Weight}$$

$$Bulk\ Density = \frac{Dry\ Weight \times Density\ of\ Kerosene}{Soaked\ Weight - Suspended\ Weight}$$

$$Relative\ Density = \frac{Bulk\ Density}{Theortical\ Density} \times 100$$

The theoretical density of Ball clay has been taken as 2.51gm/cc.

4.8 Measurement of Strength of Samples

The strength of the porous scaffold prepared by Sponge Replica Technique was measured by (). Force-deflection curve was plotted and the ultimate tensile strength was measured.

4.9 Microstructural Analysis

Microstructural analysis of porous samples has been done by a typical electron microscope i.e. Field Emission scanning Electron Microscope (FESEM) in which images of the surface of samples were taken by using electron beams. In this technique the significant information about the samples microstructure were obtained by the interaction of secondary electrons (SE), backscattered electron (BSE), as well as characteristic X-rays with the surface of porous body. The microstructure of porous samples were observed by using scanning electron microscope (Nova Nano SEM/FEI). The porous samples were coated to avoid charging.

Chapter 5
RESULTS AND DISCUSSIONS

5. RESULTS AND DISSCUSSIONS

5.1 Raw Materials Characterization

5.1.1 Particle Size Distribution of Clay

The particle size distribution of ball clay powder as measured by Zeta sizer is given in Figure 3. From the figure, it could be observed that maximum particles are of the size in the range of 200-750nm. It could be seen that the graph is almost symmetric on both side of its maxima. The maximum particles size was found to be 400nm. The nature of the curve shows a mono modal particle size distribution. Thus the study indicates that the ball clay used in the present study has a mono modal particles size distribution with a peak nearly about 400 nm.

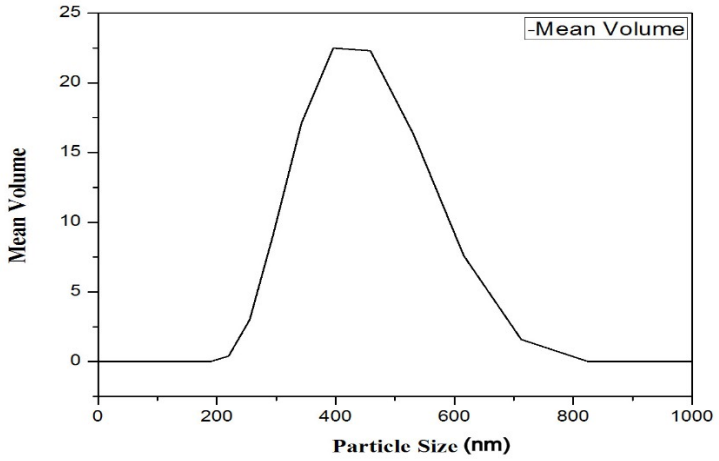


Figure 3 Particle Size Distribution of clay

5.1.2 DSC-TG of Ball Clay

In the figure 4, the DSC –TG curve of ball clay powder has been shown. At about 100 ^{o}C, there is a peak in the TG curve which is may be due to the disturbance in the machine at the time of starting the experiment.

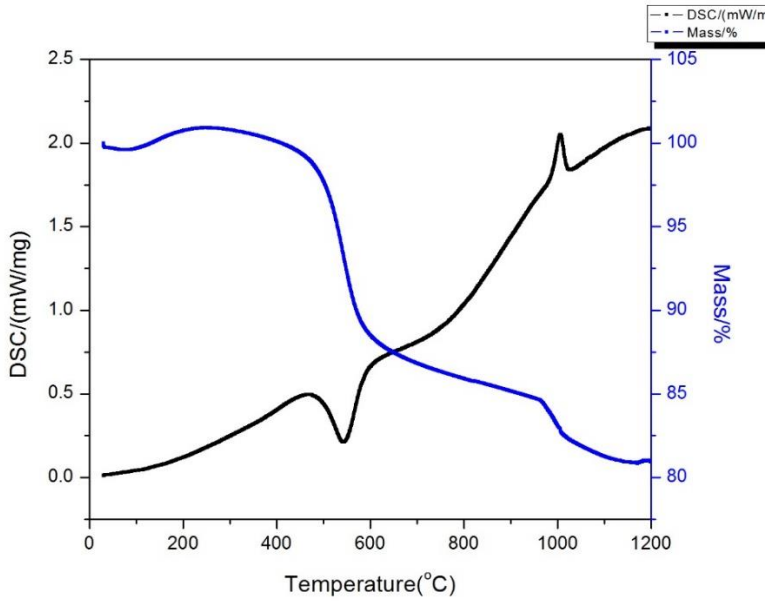


Figure 4. DSC-TG of ball clay

On heating ball clay physically adsorbed water goes out at a temperature of about 150 ^{o}C. At about 450^{o}C, the endothermic peak due to the dehydration of Ball clay(crystalline water goes out). At about 1050^{o}C mullite formed and this is an exothermic reaction.

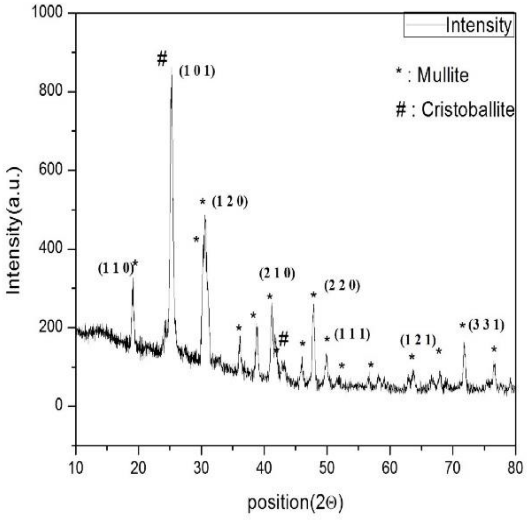
$$Al_2O_3 . 2\ SiO_2 . 2H_2O \longrightarrow Al_2O_3 . 2\ SiO_2 + 2H_2O$$

Due to the removal of crystalline water at around 450^{o}C, there is a weight loss of about 8% and again during mullite formation at around 1050^{o}C, some weight loss observed which is about 2-3%. The graph showing some weight loss during mullite formation which can't be expalined because no weight loss occur during mullite formation

$$Al_2O_3 . 2\ SiO_2 \longrightarrow 3Al_2O_3 . 2\ SiO_2 \text{ (mullite)}$$

5.1.3 XRD of Ball Clay powder

The figure (5, 6) represent the XRD pattern of (6) ball clay as received and (5) ball clay fired at 1300^{o}C for 2hours. It could be seen from the figure that the major phase kaolinite present in received ball clay. The major phase obtained was kaolinite (hyderated aluminium silicate) having JCPDS file no. 83-0971. It was found that kaolinite have a anorthic structure. The major peaks were observed at planes (0 0 1), (-1 1 0), (-1 1 1), (0 -2 1), (0 0 2).



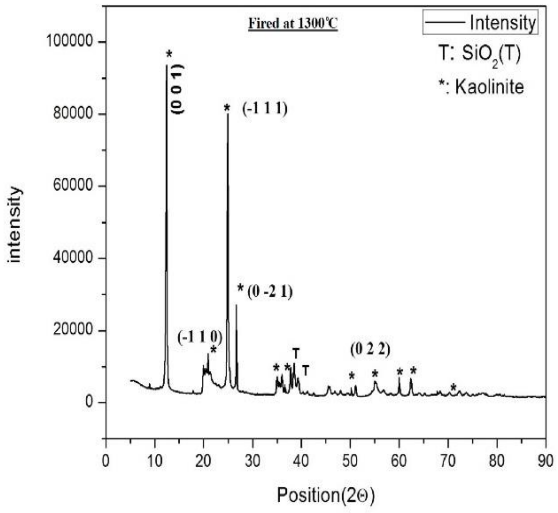


Fig. 5 XRD pattern of fired (1300°C) ball clay

Fig. 6 XRD pattern of as received ball clay

It could also be observed that the ball clay fired at 1300°C for 2 hours have majore peak of mullite and cristoballite. The mullite peaks are identified with JCPDS file no.79-1455 whereas the cristoballite has been identified with JCPDS file no. 82-0512. The crystal structure of mullite was found as orthorhombbhic and with space group Pbam. The major peaks of mullite were obtained at the planes (1 1 0), (1 2 0), (2 1 0), (2 2 0), (1 1 1), (1 2 1), (3 3 1). and having a tetragonal structure with a space group P41212. Only one major peak of cristoballite was obtained at the crystal plane (1 0 1). The hydration reaction of Al_2O_3. $2SiO_2$. $2H_2O$ (kaolinite) undergoes dehydration reaction at 450°C as disscuss earlier in section no. 5.1.3. the dehydrated metakaoline formed mullite and cristoballite at temperature of 1050°C. Thus the phases observed in the fired sample are quit obvious.

5.1.4 Effect of Temperature on Firing Shrinkage and Porosity of Ball Clay Sample

Figure 7 shows the firing shrinkage and porosity of ball clay as a function of sintering temperature.

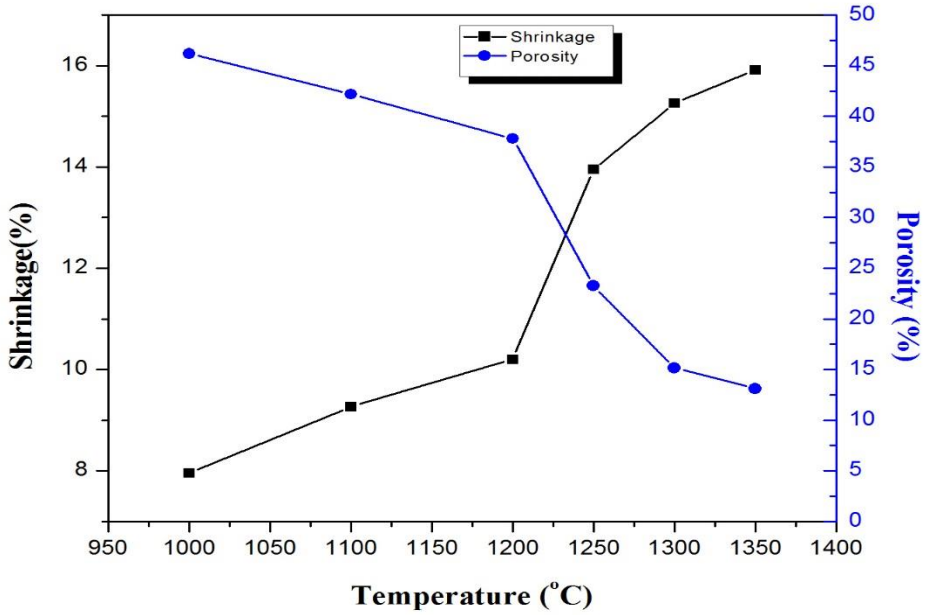


Figure 7 Effect of temperature on Porosity and Shrinkage

From the figure (7) it could be observed that from the temperature 1000 to 1200^{o}C, porosity decreases gradually but from the temperature 1200 to 1350^{o}C, the porosity decrease rapidly. This rapid change in porosity is due to the formation of liquid phase during sintering. This liquid phase formed due to the presence of impurity in the materials. Thus, the samples of high solid loading have high packing density and low loading samples have low packing density hence high porosity.

5.2. Optimization of slurry

5.2.1 Effect of Deflocculant on Zeta Potential

The effect of deflocculant (sodium silicate) on the Zeta Potential of ball clay slurry is shown in fig.8. From the given Fig. it could be said that on increasing the quantity of deflocculant (sodium silicate) the value of zeta potential decreases but on further increasing the quantity of dispersant the value of zeta potential increases. On adding dispersant in the slurry, charges were developed due to this zeta potential increases but on further increasing the amount of dispersant, zeta potential decreases due to overcrowding of charges.

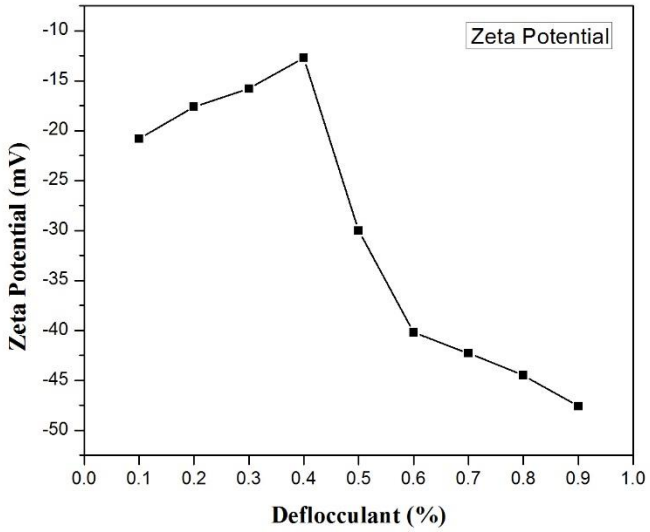


Figure 8. Effect of deflocculant on Zeta Potential of Ball clay slurry

It could be observed that the nature of graph in case of viscosity and sedimentation height were same but in case of zeta potential it came opposite because zeta potential are related to the effect of charge and viscosity and sedimentation height are dependent of different type of forces particles such as gravitational force, bouncy force, repulsive force etc.

5.2.2 Effect of Deflocculant on Sedimentation height

The stability of ball clay slurry was estimated by measuring the sedimentation height of the powder into the slurry as a function of deflocculant content and time. Figure (9, 10) shows the sedimentation behavior of the ball clay slurry. Wherein Figure (9) shows the sedimentation behavior as a function of time and Figure (10) represent the same as a function of deflocculant content.

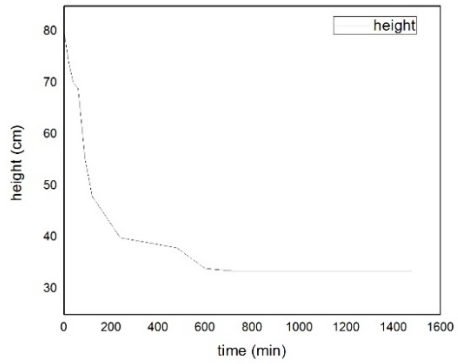


Figure 9. Rate of settling of particles.

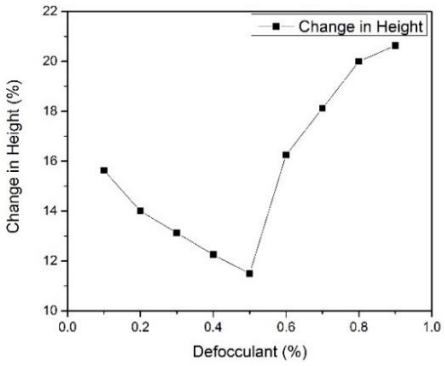


Figure 10. Effect of deflocculant on Sedimentation height

From the above fig. it could seen that the sedimentatin height increases as the time increases. The increase in sedimentation height is related to the gravitational settling of the particles. The slurry contains ball clay with some amount of sodium silicate as deflocculant into the water. The sodium silicate because of higher settling of particles. After a long time about 24hrs later, change in sedimentation height become negligible so we can say that no significant change in height. In the fig. 5.5 represents the effect of sedimentation height of ball clay with deflocculant (sodium silicate). From the fig. it could be observed that sedimentation height first decreases up to 0.4 wt. % and then increases from 0.4 wt.% to 0.9 wt.% of sodium silicate and found that settling minimum at 0.4 at.% and is consider as the stability of slurry. As the deflocculant (sodium silicate) quantity increases repulsive force between ball clay particles increases and due to this repulsion settling velocity of particles decreases so sedimentation height decreases. But on increasing the quantity of deflocculant sedimentation height increases due to overcrowding as well as overlapping of the electric double layer due to this there is an increase in the Van der Waal's force of attraction which increases the sedimentation height of ball clay slurry.

5.2.3 Effect of Deflocculant on Viscosity of slurry

Sodium silicate was used as deflocculant in the present clay based system. The effect of deflocculant (sodium silicate) on the viscosity of Ball clay slurry is shown in Figure 11

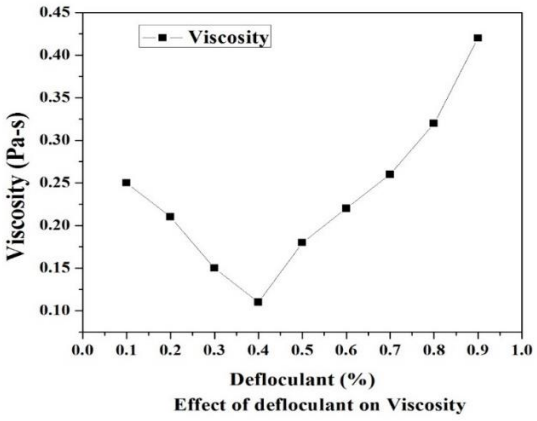


Figure 11 Effect of Deflocculant on Viscosity

From the Figure (11), it could be observed that the viscosity of Ball clay slurry first decreases with increasing deflocculant addition and then increases. The viscosity of the slurry decreases from 0.1 to 0.4 wt. % sodium silicate after that it increases from 0.4 to 0.9 wt. % of sodium silicate addition. Clay surfaces become negatively charged when exposed to water. The sodium silicate ionizes to Na^+ when dissolved in water. This Na^+ ions from deflocculant (sodium silicate) get adsorbed onto the clay surfaces. An electrical double layer is formed by the adsorption of Na^+ ions on clay surface and charge balance by the counter ions. The double thickness increases with increasing the deflocculant concentration up to a certain level. Thereafter the double layer interacts each other due to over crowding effect of the electolyte and the double layer thickness decreases. Viscosity decreases due to repulsion between particles having electrical double layer. This repulsive force acting between the adjacent double layer is responsible for lowering the viscosity of the slurry. The increase in viscosity is correlated to the overcrowding effect of the deflocculant.

5.3 Characterization of Porous Sample

5.3.1 Effect of solid loading on viscosity

Figure (12) shows the effect of solid loading on viscosity. From the figure, it could be observed that on increasing the solid loading viscosity increases nearly exponentially.

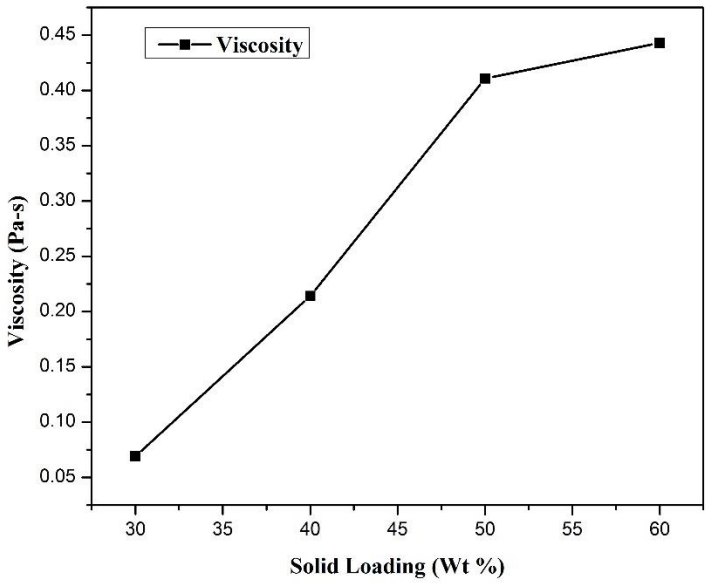


Figure 12. Effect of solid loading on viscosity

On increasing the solid loading, the water content in the slurry decreases and with the decrease in water content the slurry became thick. Hence the viscosity increases.

5.3.2 Effect of Solid Loading on Porosity

5.3.2 (a) Effect of solid loading on porosity without PVA

Figure (13) showed that the influence of ball clay solid loading on porosity. It could be analyzed that the porosity decreases with increase in solid loading of ball clay. On increasing the solid loading, the water content in the slurry decreases. With the decreasing water content in the slurry, the thickness of strut coating increases and pores filling of sponge also increases during fabrication.

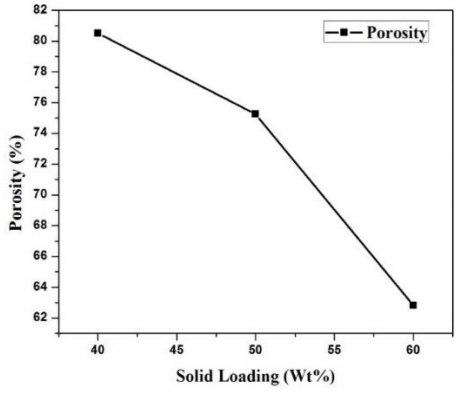


Figure 13 Variation of porosity with solid loading

The decrease in porosity with increasing solid loading is thus correlated to the water content in the slurry, the green strut thickness and pores filling of sponge. Hence the sample prepared with high solid loading showed lower porosity.

5.3.2 Effect of Solid loading on CCS

The figure (14, 15) shows the effect of solid loading on the strength of porous ceramic body. It could observed that on increasing the solid loading the cold crushing strength of porous scaffold increases.

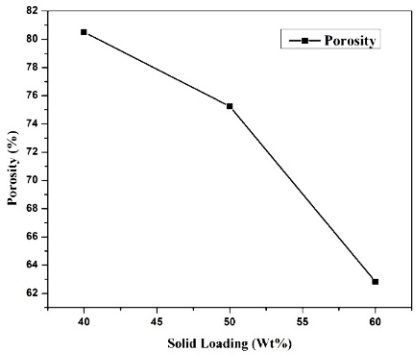


Figure14. Effect of solid Loading on porosity

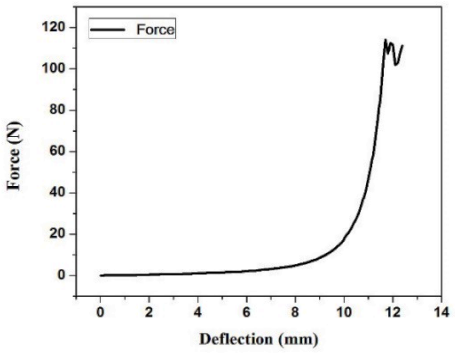


Figure15. Load – Deflection curve of porous sample

Figure 2. Variation of CCS with solid loading

With the increasing solid loading, water content in the slurry decreases as a result the coating strut thickness increases and the more pore filling of the sponge occurs. On firing the porous the porous scaffold is likely to have more fills by ball clay. The increase in strut thickness and the pore filling of sintered scaffolds are correlated to the increase in strength with solid loading of the starting slurry. Here on varying solid loading from 40 to 50 wt. % the CCS value obtained in between 0.1 to 0.5 MPa. Fig showed the deflection behavior of porous scaffold with force. As the force increases, the deformation in the samples goes on increasing up to the fracture point.

5.3.4 Effect of solid loading on microsturcture

Figure (16, 17) are the microstructure of the porous scaffolds prepared with 40% and 50% without any binder (PVA). It could be seen from the figure that the scaffold prepared with 40% solid loading slurry is more porous and less pore filled as compared to that observed with scaffold prepared with 50% solid loading slurry.

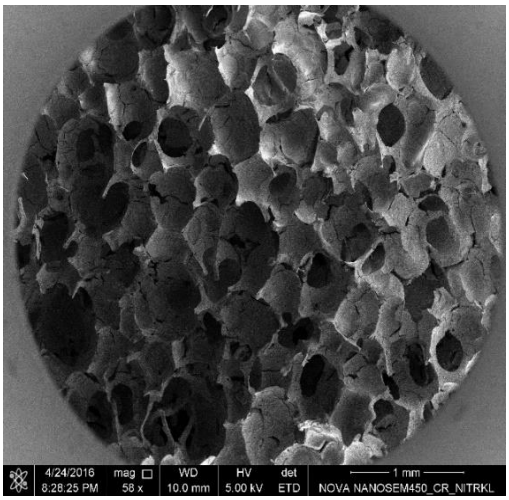


Figure16. Microstructure of sample having 40 wt. % solid loading

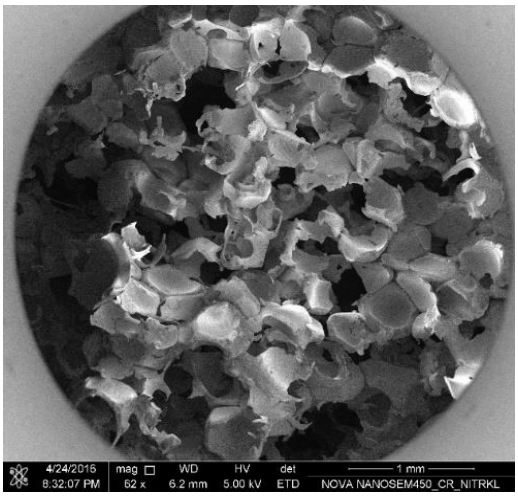


Figure17. Microstructure of sample having 60 wt. % solid loading

Microstructure of porous scaffolds fabricated by sponge replica technique depends on the sponge morphology, viscosity and solid loading of the slurry. For the same sponge morphology, lower the solid loading lesser will be the strut coating thickness and more will be the porosity. Thus the sample prepared with 40 wt.% solid loading slurry will have more porous structure and that prepared with 60 wt.% solid loading will have thick strut thickness and more pore filling.

5.4 Effect of Solid Loading and Binder on the Properties of Porous Scaffolds

5.4.1 Effect of Solid Loading on Porosity with Binder (PVA 5 wt.%)

The effect of ball clay solid loading with some amount of binder (PVA 5 wt.%) has been shown in figure (18). It could be observed that on increasing the ball clay solid loading keeping the binder content constant, the porosity decreases.

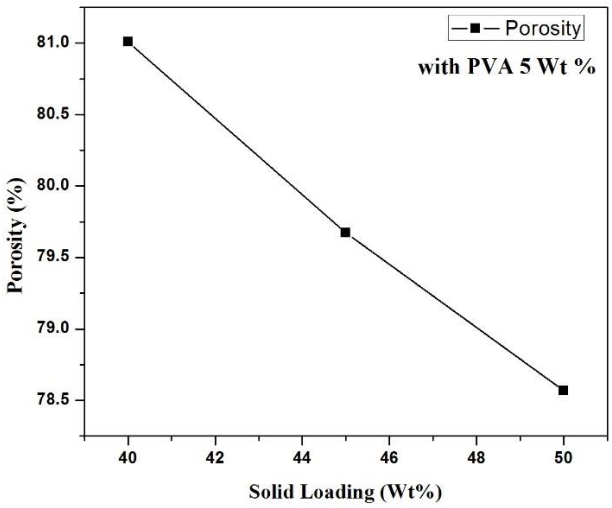


Figure18. Effect of solid loading on porosity

As the solid loading increases, the water content in the slurry decreases and with the decrease in water content the thickness of coating strut increases and more pore filling in the sponge occurs as explain earlier. Presence of PVA also helps in increasing the strut coating thickness and also enhanced the pore filling of the sponge. 10 wt.% solid loading changed can cause a porosity change of only 2.5%. Thus this change in porosity is correlated with thickness of strut coating, pore filling.

5.4.3 Effect of Solid Loading on CCS (with Binder 5 Wt.%)

Figure (19) displayed the influence of solid loading on the strength of the porous scaffold and figure (20) shows the load deflection curve of porous scaffolds. It could be observed that the Cold crushing strength of porous ceramic (made up of ball clay with 5 wt. %) increases with the increasing of solid loading. On increasing the solid loading, water content in the slurry decreases. The decrease in water content and with the presence of binder, the thickness of strut coating and pore filling increases.

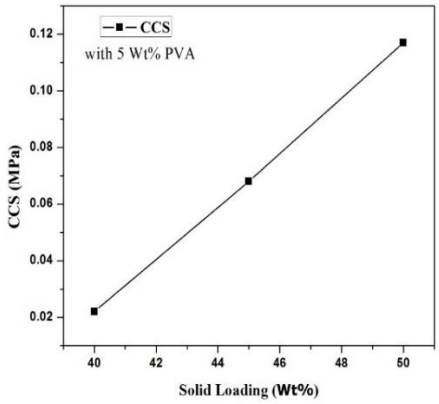


Figure19. Variation of CCS with Solid loading

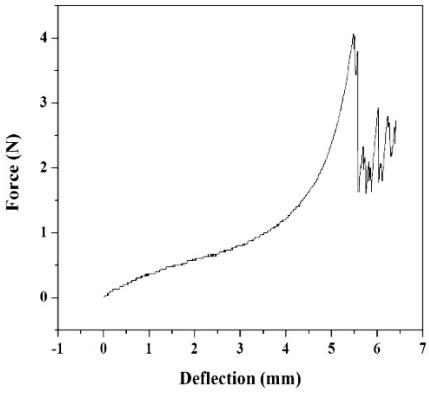


Figure 20. Load – Deflection curve of Porous sample

Thus the sample containing high ball clay solid loading have lower strength. The increase in strength with increase in solid loading is thus associated with the water content in the slurry, PVA in the slurry, the green strut thickness and pore filling of sponge.

5.4.4 Effect of binder on microstructure of porous scaffold

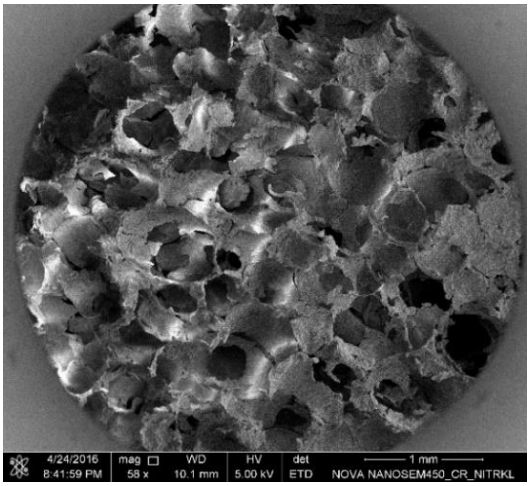


Figure 21 .Microstructure of sample having 40 wt.% solid loading

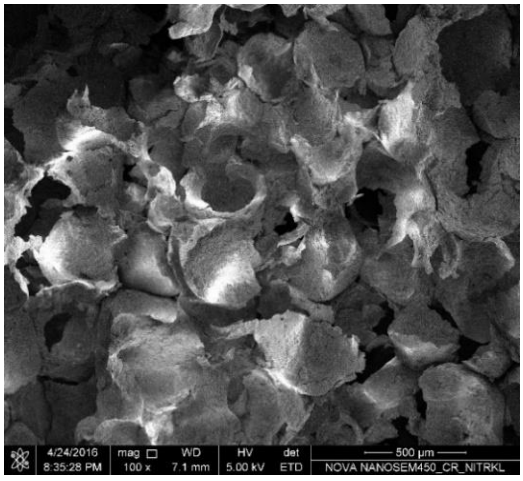


Figure22 .Microstructure of sample having 50 wt.% solid loading

Figure (21, 22) shows the effect of binder on Microstructure of porous scaffolds fabricated by sponge replica technique. The sponge morphology, viscosity and solid loading of the slurry mainly affect the microstructure of porous scaffolds. For the same sponge morphology, lower the solid loading lesser will be the strut coating thickness and

more will be the porosity. Thus the sample prepared with 40 wt.% solid loading slurry with 5 wt.% binder will have more porous structure then that which prepared with 50 wt.% solid loading with 5 wt.% binder will have thick strut thickness and more pore filling.

5.5 Effect of binder (PVA) on CCS and porosity

Table 4 Value of CCS and Porosity

Solid Loading (wt. %)	CCS (MPa)	CCS (MPa) (with 5 wt.% PVA)	Porosity (%)	Porosity (%) (with PVA 5 wt.%)
40	0.1123	0.0228	80.5073	81.0101
50	0.2474	0.2182	75.2489	79.5551

From the table, it could be observed that there was no considerable effect of binder (binder) on the porosity and strength of porous scaffold. The value of porosity and strength of porous sample in both the case was nearly same because the plasticity of ball clay is high enough so that the effect of binder has been negligible. Thus the porosity and strength of sample having PVA have same numerical value with the sample without PVA.

Chapter 6
CONCLUSION

6. CONCLUSION

- Ball clay used in present work have the maximum particles in the range of 250 - 800 nm. Hence the ball clay contains fine particles and fine in nature. From the XRD, it was found that the kaolinite is the major phase present in ball clay and mullite is the major phase in the ball clay which is fired at 1300 for 2hrs.
- With the help of Zeta Potential, Sedimentation height, and Viscosity, It was observed that irrespective of solid loading of the slurry 0.4wt.% sodium silicate was sufficient to obtain a stable and dispersed slurry.
- The porosity and strength of the samples could be varied from 60-85% and 0.02 - 0.12MPa respectively with varying the solid loading from 40 – 60 wt.% in this technique.
- No considerable effect of PVA was observed on the properties of porous scaffolds.

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