
Chapter 5

Processing and Fabrication of Porous Ceramics with Tailored Pore Microstructure using Rice Husk and Sucrose

5.1. Introduction

Porous ceramics find wide spread industrial applications in diverse areas such as thermal insulations,¹⁰³ catalyst supports,¹⁰⁴ low as well as high temperature filtration of hot gases¹⁰⁵ and molten metals,¹⁰⁶ heat exchangers,¹⁰⁷ high efficiency combustion burners,¹⁰⁸ solid oxide fuel cells, bio-medical implants¹⁰⁹ etc. owing to their distinct properties such as low bulk density, high porosity, high surface area, high temperature resistance, high thermal shock resistance, high specific strength, low thermal mass, low thermal and electrical conductivity etc. Each individual application requires ceramic shapes with defined microstructure which suits the specific requirement.¹¹ Thus, depending on the requirements of the applications, porous ceramics with controlled microstructures i.e., varying porosity, pore size, pore sizes distribution, orientation of pores and pores' connectivity are being fabricated via different processing routes.¹¹⁰⁻¹¹²

Selection of fabrication process plays an important role in controlling the microstructure and resulting properties of porous ceramics. Among a variety of processes, one of the popular approach adopted for fabrication of porous ceramics with controlled porosity and pore size has been the use of pore forming additives which burn out during heat treatment leaving pores in the fired ceramics.^{11,112} A wide variety of pore formers such as starch, saw dust, cotton thread, wheat flour etc. have been successfully used in fabrication of porous ceramics.^{12,62-64} Ferreira et al. have reported use of starch both as a binder and pore former for fabrication of porous ceramics.¹² Ducman et al. have used saw dust and paper making sludge as pores forming agents for light weight clay bricks.⁶² Zhang et al. have fabricated porous ceramics with unidirectionally aligned continuous pores using cotton thread.⁶³ Prabhakaran et al. fabricated macroporous alumina ceramics employing wheat particles as gelling and pores forming agents.⁶⁴

Among various pore forming additives, natural pore formers are preferred due to the reason that these are low cost, non toxic and environmental friendly in nature.¹² One natural pore forming additive, rice husk, an agricultural discarded waste, has been reported by several authors for its use in fabrication of refractory bricks and porous ceramics. But the amount of porosity and pores' size was limited.⁶³ Torikai et al. reported preparation of porous ceramics containing Al or Al₂O₃ using rice husk.⁶⁸ The diameters of pores were 28 μm and 94 μm for (RH/Al) and (RH/Al₂O₃), respectively. Wei. et al. reported preparation of porous cordierite having porosity 42.4-45.02 vol%, using rice husk. The rice husk was used as a silica source as well as a pore forming agent.⁶⁵ Watari. et al. have reported fabrication of porous (10-30 μm pore size) SiO₂/C composite from rice husk.⁶⁶ Makovska et al. have used rice husk and waste aluminium oxide to fabricate porous mullite ceramics having 52.23-58.31 vol% porosity.⁶⁷ It is observed that porous ceramics fabricated using rice husk by other researchers, mentioned above, possess porosity and pores' size within a narrow range.

The present study demonstrates a cost effective way to fabricate porous ceramics with wide range of tailored microstructures using rice husk (RH) as pore former. This study was primarily focused on tailoring porosity and pores' size by varying the RH content as well as its particle size in the composition. Rice husk was chosen due to its easy availability, low cost and suitability to be used as a pore forming additive in processing and fabrication of porous ceramics.

Sucrose was preferred due to its dual role as a binder as well as a pore former in this fabrication process. Other advantages of using sucrose include room temperature solubility in aqueous solvent, comparatively low viscosity of resulting solution, reproducibility and consistency of binder solution, better homogeneity of the ceramic mixture etc. Additionally, sucrose is cheap and commercially available with controlled specification. It is important to mention here that though, sucrose has been used as a binder and rheology modifier in fabrication of ceramics through slurry processing and plastic forming,^{67,93} its use in dry processing has not been reported earlier. Thus, the combination of rice husk and sucrose as low cost additives, during fabrication of porous alumina ceramics, via dry processing is a

new method, in terms of unique composition, the standardized process steps, tailored microstructure and properties of the developed products.⁸⁷⁻⁸⁸ Also, the unique combination of rice husk and sucrose make the overall composition and process simple and cost effective. As the trend has been towards development of cost effective porous ceramics, the present fabrication process can be categorized as one of the low cost processes.

The experiments were carried out systematically to optimize the composition and tailor the microstructure with special emphasis on volume fractions of porosity, pore size and pore connectivity of the developed porous ceramics through variation of RH content and particle size of RH powder in the composition. Optimization of the processing parameters and establishment of a standard process flow chart was also done to end up with defect free compacts. Physical properties of both green and sintered porous alumina has been reported in this chapter. Although, the present research work is focused on alumina ceramics, we would like to emphasize that the developed methodology can be implemented easily to process samples for other ceramic materials.

5.2. Experimental Procedure

5.2.1. Processing and characterization of rice husk and sucrose

RH (unprocessed) was thoroughly cleaned using distilled water to ensure complete removal of dust, clay and sand adhered to the surface. Then, wet RH was dried in ambient atmosphere for 2 h followed by drying in a preheated oven at 150°C for 24 h. Drying temperature was chosen based on trial experiments related to grinding ability of the rice husk. This has been discussed in the next section. Fully dried RH was ground in a mixer machine (Kenstar Prince Royal, Videocon Industries Limited, India, 18,000 rpm) for 10 to 15 min. followed by sieving in a sieve shaker (Jayant Scientific Industries, India) for size classification. Five standard test sieves with mesh size 75, 180, 355, 420 and 600 μm (British Standard Specification) respectively were used during sieving. Accordingly, RH powder with size (< 75) μm , (75-180) μm , (180-355) μm , (355-420) μm and (420-600) μm were collected from each sieve and stored separately. RH powders of various size were used as the pore former. Sucrose (Merck Specialties Pvt. Limited, Mumbai) in the

form of solution (60 wt% aqueous solution based on maximum solubility at room temperature) was used as a binder.

Thermal degradation and loss on ignition of RH and sucrose was studied independently using TG analysis (Simultaneous Thermal Analyzers, Model Labsus, Setaram, France) by heating the sample in an alumina crucible at 1 °C/min up to 600°C in ambient atmosphere. An X-ray diffraction pattern of the residue left after burning RH powder at 800°C for 2 h was recorded and analyzed.¹¹³

5.2.2. Composition formulation, shape forming and post processing

High purity alumina powder (ALCOA ACC, CT3000SG, avg. particle size: 0.7 µm, surface area 7 m²/g) was used to process all the samples in this study. Alumina and RH powder mixtures with 5, 10, 15, 20, 30 and 40 wt% RH respectively were mixed separately using 20 wt% sucrose solution (12 wt% sucrose on dry weight basis) using a mortar and pestle. A general abbreviation Al_xRH_ySS₂₀ was used to express each mixture composition where Al, RH and SS represent alumina, rice husk and sucrose solution respectively. In this abbreviation, 'x' represents size in µm and 'y' represents RH content in wt%. Dry mixtures were pressed uniaxially in a rectangular steel die (60 mm x 20 mm x 20 mm) using a hydraulic press at a pressure of 100 MPa. Accordingly, a total of 35 compositions out of a large number of trial compositions were successfully dry pressed into green compacts having reasonable strength and without any visible defects. The list of successful compositions are given in Table 5.1.

Green compacts were dried in a preheated oven at 120°C for 24 h. Organic burnout of dried samples was carried out in ambient atmosphere in an electrically heated programmable furnace. An optimized and established burnout process, in which the rate of heating was 3 °C/min for each step of increment in temperature and 1 hour dwell time at each of 200, 300 and 500°C followed by bisque firing at 800°C for 1 h was followed for all samples. The organic burnout characteristics has been shown schematically in Fig. 5.1. Presintered samples were heat treated in an electrically heated furnace (Okay Furnace, Bysakh& Co. Kolkata, India), which uses Super Kanthal heating element (max. operating temp. 1800°C). All samples

Table 5.1 List of selected compositions (wt% basis) for fabrication of porous alumina ceramics using rice husk

RH size(μm)	$\text{Al}_x\text{RH}_y\text{SS}_{20}$							
	wt % RH							
	05	10	15	20	25	30	35	40
< 75	$\text{Al}_{<75}\text{RH}_{05}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{10}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{15}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{20}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{25}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{30}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{35}\text{SS}_{20}$	$\text{Al}_{<75}\text{RH}_{40}\text{SS}_{20}$
75-180	$\text{Al}_{75-180}\text{RH}_{05}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{10}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{15}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{20}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{25}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{30}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{35}\text{SS}_{20}$	$\text{Al}_{75-180}\text{RH}_{40}\text{SS}_{20}$
180-355	$\text{Al}_{180-355}\text{RH}_{05}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{10}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{15}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{20}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{25}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{30}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{35}\text{SS}_{20}$	$\text{Al}_{180-355}\text{RH}_{40}\text{SS}_{20}$
355-420	$\text{Al}_{355-420}\text{RH}_{05}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{10}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{15}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{20}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{25}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{30}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{35}\text{SS}_{20}$	$\text{Al}_{355-420}\text{RH}_{40}\text{SS}_{20}$
420-600	$\text{Al}_{420-600}\text{RH}_{05}\text{SS}_{20}$	$\text{Al}_{420-600}\text{RH}_{10}\text{SS}_{20}$	$\text{Al}_{420-600}\text{RH}_{15}\text{SS}_{20}$	$\text{Al}_{420-600}\text{RH}_{20}\text{SS}_{20}$	$\text{Al}_{420-600}\text{RH}_{25}\text{SS}_{20}$	# $\text{Al}_{420-600}\text{RH}_{30}\text{SS}_{20}$	# $\text{Al}_{420-600}\text{RH}_{35}\text{SS}_{20}$	# $\text{Al}_{420-600}\text{RH}_{40}\text{SS}_{20}$

Samples could not be dry pressed

Note: 20 wt% sucrose solution (SS_{20}) with 60 % concentration is equivalent to 12 g of sucrose

were heated in ambient air atmosphere in a single heating cycle which is as follows: room temperature up to 800°C at 4 °C/min followed by holding at 800°C for 2 h and then from 800°C to 1700°C at 5 °C/min with soaking time of 2 h at 1700°C.

Schematic of the sintering schedule has been presented in Fig. 5.2. The overall process flow chart for fabrication of porous alumina has been shown in Fig. 5.3. Sintered samples have been shown in Fig. 5.4.

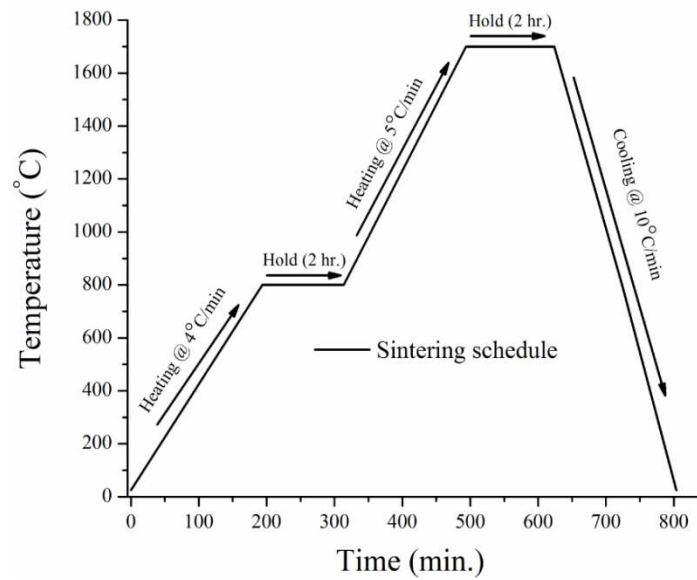


Fig. 5.1 Schematic diagram showing organic burnout schedule during heat treatment of samples

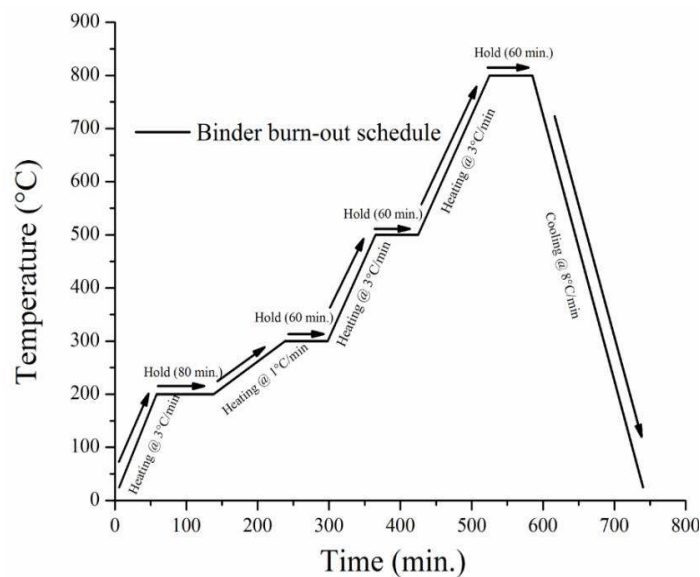


Fig. 5.2 Schematic diagram showing firing schedule of alumina samples

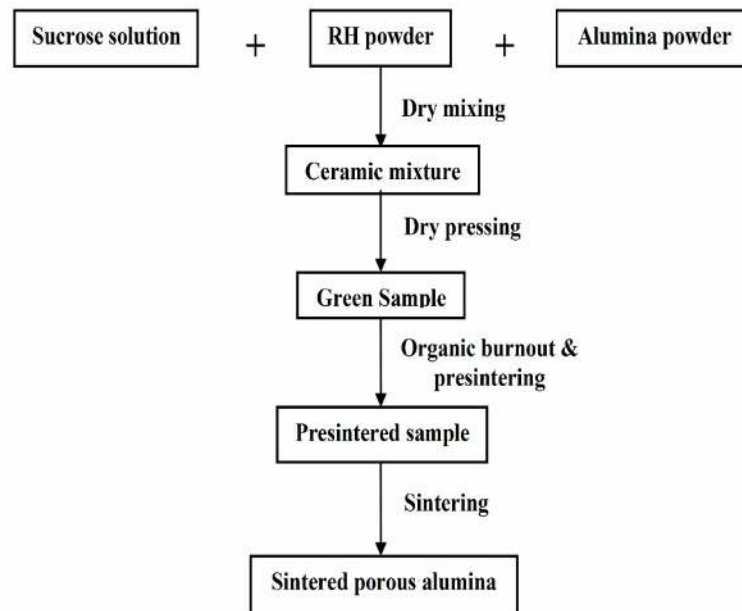


Fig. 5.3 Flow chart for fabrication of porous alumina

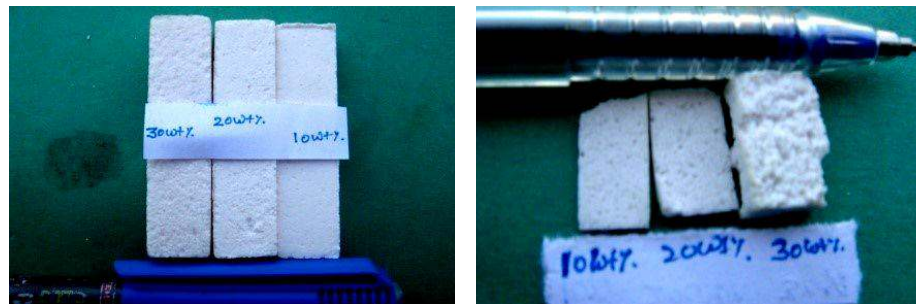


Fig. 5.4 Sintered samples fabricated with 10, 20 and 30 wt% rice husk

5.2.3. Physical characterization of green and sintered compacts

Shrinkage of alumina compacts after drying and sintering was expressed in terms of % linear drying shrinkage and % linear firing shrinkage respectively. Shrinkage was calculated by measuring the difference in length of the samples before and after heat treatment and then calculating the % change in length. Density of the green compacts (green density) was calculated simply by taking the mass/volume ratio for different samples. Density of the sintered samples was determined by water immersion method based on Archimedes' principle using the following equations (Eqn 5.1).¹¹⁴

$$\rho = \frac{m_{dry} \times \rho_{water}}{m_{wet} - m_{suspended} + m_{wire}} \dots\dots\dots(5.1)$$

where m_{dry} is the dry mass (in g) of the sample, $m_{suspended}$ is the mass of the sample suspended in water, m_{wet} is the mass of the sample after soaking in water, m_{wire} is the mass of the suspending system, ρ_{water} is the density (g/cc) of water. Theoretical density of 3.96 g/cc for fully dense Al_2O_3 ⁶³ was used as a reference to calculate % theoretical density of sintered porous alumina. Flexural strength of green samples was measured using a three point bend fixture with span length of 40 mm using a Universal Testing Machine (AGS-5KND, P/N 340-33309, Shimadzu Corporation, Japan). Machinability of green samples was studied through machining (drilling) of compacts using a drilling machine at 1440 rpm (Vijay Electronics, India, HP ¼, Volt 220/230. Sl. no. VE 0011, Single Phase) to introduce holes with different diameters into the samples. Drilling was carried out using drill bit of sizes 3/32, 9/64. Green machining gives an idea about the machinability of the sample to introduce additional features in the samples after shaping which were otherwise difficult to introduce during shape forming.

The phase compositions of the sintered porous alumina samples were determined using an X-ray diffractometer (Miniflex II, Desktop X-Ray Diffractor, Rigaku Corporation, Japan) with CuK_{α} radiation (wavelength= 1.542 Å) at 40 kV and 30 mA.

5.3. Results and Discussion

5.3.1. Analysis of properties of rice husk

The data of thermo gravimetric analysis carried out for rice husk and sucrose are shown in Fig. 5.5.

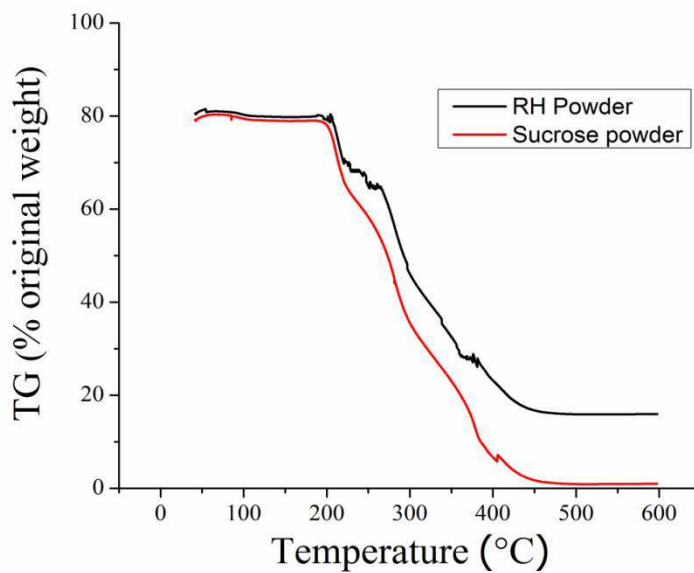


Fig. 5.5 TG analysis of RH powder and sucrose in air atmosphere

Decomposition of both RH and sucrose starts gradually from approximately 200°C and continues up to 450 to 500°C. Major weight loss takes place between 200°C to 500°C and beyond 500°C a very slow change in sample weight was observed for both RH and sucrose. However, ash content was almost nil for sucrose and approximately 15 wt% burnout residues, termed as rice husk ash (RHA), was obtained from RH sample. The RHA value in our case is within the range of values i.e., 13-29%, as reported by other researchers in the literature.¹¹⁵ The weight loss during thermal treatment of RH in air can be attributed to three stages such as drying (40-150°C) for removal of physically bonded water, burnout of volatile organic component (215-350°C), followed by degradation of carbonaceous phases cellulose and hemicellulose (>350°C).¹¹⁶ Similarly decomposition and burning of organic matrix in sucrose takes place between 180 to 480°C during thermolysis of sucrose in air.⁹⁴ Based on weight loss characteristics of RH and sucrose, organic burnout schedule of green compacts, as mentioned in the experimental, was established in order to achieve controlled burnout of RH and sucrose to get defect free samples.

Matori et al. have reported that RHA (burn out residue of RH) contains approximately 92-97% silica as major constituent and minor percentage of other oxides and depending on the heat treatment temperature, SiO₂ in RH/RHA is found

either in crystalline or in amorphous form.¹¹³ Analysis of X-ray diffraction pattern of RHA, in our case shows presence of a strong peak ($d= 4.06\text{\AA}$) corresponding to the crystalline phase of silica. i.e, α -cristobalite (Fig. 5.6).

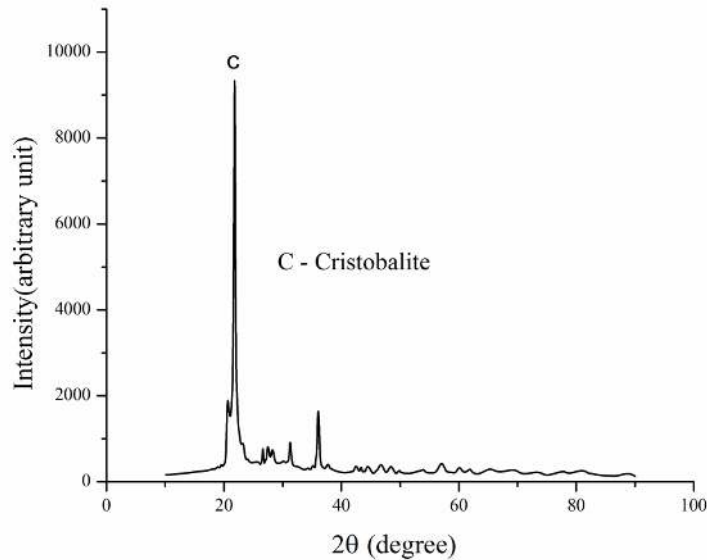


Fig. 5.6 X-ray diffraction pattern of residue (RHA) left after heat treatment of RH powder at 1000°C

Similar observation has also been reported by other researchers.¹¹⁶ It is important to note that presence of silica in RH is an additional advantage, as it reacts with alumina at high temperature to form a stable phase, mullite in the alumina matrix during firing of samples. It is important to mention here that in some ceramics like nitrides, carbides, borides etc. where the silica contributed by rice husk could be an undesirable impurity, in those cases acid treated RH (free from silica)¹¹⁷⁻¹¹⁸ can be used as the pore former for fabrication of porous compacts.

5.3.2. Processing and fabrication

During initial trials of size reduction of RH, it was observed that, RH sample dried at $110\text{--}120^{\circ}\text{C}/24\text{ h}$ was difficult to grind due to its fibrous nature. A series of experiments, therefore, were conducted to examine the grindability of RH. Samples of RH were dried at successive higher temperatures from $120\text{--}160^{\circ}\text{C}$ for 24 h prior to size reduction. Grindability of RH was measured in terms of maximum possible size reduction in order to get the smallest size RH powder i.e, $75\ \mu\text{m}$ in a reasonable quantity. The results of effect of drying conditions on grindability of RH showed

that 150 °C /24 h was the best drying condition to get required quantity of powder in each size range.

Homogeneous mixing and adequate binding of high density (3.96 g/cc) fine alumina powder with low density (0.86 to 1.14 g/cc) and comparatively coarse RH powder was a big challenge to optimize the process.¹¹⁹ PVA was not found suitable as a binder for shape forming of all mixture compositions displayed in Table 5.1, specifically the compositions with higher RH content and coarse RH powder. PVA was not a suitable binder due to its high viscosity (mol. wt. 31,000). This resulted in inhomogeneous mixing leading to defects in the pressed compacts and fired samples.¹²⁰ Loose corners and edges, loose packing, low green density, cracking and bursting of samples after drying and/or debinding step were the main defects. Sucrose in the form of aqueous solution was found as an alternative to overcome the problems mentioned above. Homogeneous and uniform mixing of alumina-RH mixture was possible due to relatively lower viscosity of sucrose solution. 20 wt% of 60% sucrose solution (60 wt% concentration) was found to be the best binder for all the compositions considered in this work. Keeping in view the major composition variables as RH content and RH size, binder percentage in the composition was established in order to achieve maximum strength, good packing and minimum pressing defect. This sucrose solution provided adequate strength to the green compacts in addition to improving plasticity and workability of Al^xRH_ySS₂₀ mixture. Defect free green compacts with coarse (avg. particle size up to 600 μm) RH content as high as 40 wt% were successfully fabricated using optimum binder addition. It is important to mention here that though, samples prepared from compositions Al³⁵⁵⁻⁴²⁰RH₃₀SS₂₀, Al⁴²⁰⁻⁶⁰⁰RH₃₀SS₂₀, Al¹⁸⁰⁻³⁵⁵RH₄₀SS₂₀, Al³⁵⁵⁻⁴²⁰RH₄₀SS₂₀ and Al⁴²⁰⁻⁶⁰⁰RH₄₀SS₂₀ (Table 5.1) were sufficiently strong for handling in the green stage and further processing without any shape distortion, the same samples underwent cracking and bursting during drying. This may be due to loose packing and non-uniformity in packing density especially for samples of all the five compositions mentioned above. For compositions having more than 40 wt% RH, in spite of the addition of largest possible quantity of binder, homogeneous mixing and consolidation into specific

shapes and dimensions was not possible even after adding a large quantity of binder solution. Addition of large amount of binder solution resulted in sticking of samples to the mold surface during pressing. Thus, fabrication of samples with any other composition than those displayed in Table 5.1, was not feasible using the materials and additives in the present form.

Binding of alumina powder particles due to sucrose in the composition is clearly seen only after the presintering cycle though no such difference was being observed in the green stage.

It was seen that samples with less amount of binder (10-15%) resulted in loose packing in few compositions. Also, samples with higher amount of RH (more than 20 wt%) resulted in fine cracks along the side faces of the sample and sticking problem to the mold surface. Some samples were loosely packed in spite of addition of higher amount of binder. 40 wt% RH samples and above could be pressed with smaller RH size (<75, 75-180) without formation of cracks during pressing, drying and pre-sintering stage. Samples with larger size RH in 40-50 wt% are cracking in different stages of processing (Fig. 5.7 a, b, c).



Fig. 5.7 (a) Cracking and bending in samples with 30 and 40 wt%, (b) Bursting of 30 wt% RH sample into powder after drying at 100 °C/24 h and (c) alumina samples with 10 and 20 wt% RH heated at 5 °C/min

5.3.3. Heat treatment

Drying related defects were not observed for any of the samples irrespective of sample composition. Cracking and bursting of dried samples was observed for samples with more than 30 wt% RH samples and for samples heated at fast heating rate (Fig. 5.7). Initial pre-heating conditions for organic removal at 3-5 °C/min

resulted in faster burnout of organics and thus resulted in cracking and bursting of samples with higher wt% RH and with RH size in the range 355-420 μm and more.

Thus a slow and step wise heating cycle which has been mentioned in the experimental part helped eliminating the cracking and bursting problem. Unlike presintering, no firing related defects were observed for all compositions. A few samples developed defects during firing, the origin of the defect was associated with improper packing, drying and presintering. Thus, irrespective of the variation in sample composition, a single drying, organic burnout and sintering cycle was established which was suitable for all compositions. This was valid for compositions having RH in the range of 5-30 wt% and RH size in the range 75-600 μm .

A single organic burnout schedule and firing schedule (Fig. 5.1 and Fig. 5.2), was suitable for all the compositions not only in terms of getting defect free samples after organic removal but also in simplifying the overall process. All the samples after sintering were free from defects. This was confirmed by study of the microstructure of samples which are presented in the next chapter.

5.3.4. Properties of green compacts

Green samples of all compositions were free from cracks and defects and had good surface finish. Drying shrinkage was almost negligible for all samples. Density of green samples was in the range 1.2-2.71 g/cc (30-68 % T.D). Density of green samples as a function of rice husk amount and size has been shown in Table 5.2 The decrease in green density of samples with increase in rice husk size for the same volume fraction RH, keeping other process parameters constant, can be attributed to loose packing for samples with larger size rice husk.

Table 5.2 Different mixture compositions and the corresponding bulk density of fabricated green alumina samples

Al ^x RH _v SS ₂₀		5 wt% RH	10 wt% RH	15 wt% RH	20 wt% RH	30 wt% RH	40 wt% RH
RH content (wt %)	RH powder size(μm)						
Bulk density (Green samples)	< 75	2.71	2.42	2.31	2.1	1.98	1.80
	75-180	2.49	2.35	2.2	1.91	1.74	1.6
	180-355	2.39	2.25	2	1.85	1.52	1.39
	355-420	2.31	2.02	1.96	1.78	1.45	1.2
	420-600	2.22	1.95	1.9	1.72	NA	NA

It has been observed during preliminary experiments that strength of dried samples prepared with RH is less in comparison to that of without RH. This is due to the fact that use of RH binders the tight packing of alumina particles due to the difference in particle size between RH (<75-600 μm) and fine alumina (0.7 μm). Also, replacement of high density alumina (3.96 g/cc) by low density RH (0.12 g/cc) decreases the overall density and strength of the compact. This variation in size and density between alumina and RH particles plays an important role in packing and strengthening during dry pressing compositions with 30 wt% and above RH.

Flexural strength for green RH based alumina samples was in the range 4.5-22.5 MPa (Fig. 5.8), being minimum for samples with composition $\text{Al}_{75}\text{-}^{180}\text{RH}_{40}\text{-SS}_{20}$ and maximum for the composition $\text{Al}_{75}\text{-}^{75}\text{RH}_{05}\text{-SS}_{20}$. It can be seen that strength of green samples is inversely related to the RH amount and size. Flexural strength is highest for 5 wt% RH sample with 75 μm size. Samples are strong enough for green machining (drilling) due to good packing and reinforcement action of RH particles in the alumina matrix. Fig. 5.9 (a) and Fig. 5.9 (b) shows strength and packing of samples after drilling and flexural strength measurement respectively which indicates good strength of the samples.

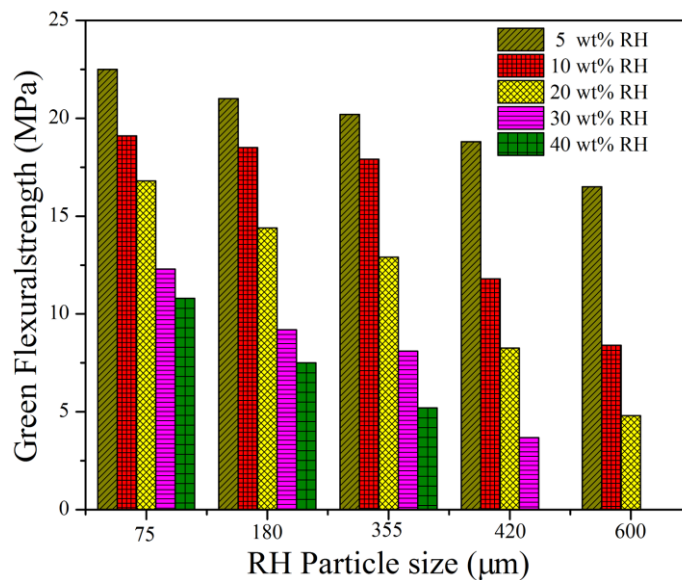


Fig. 5.8 Flexural strength of green samples

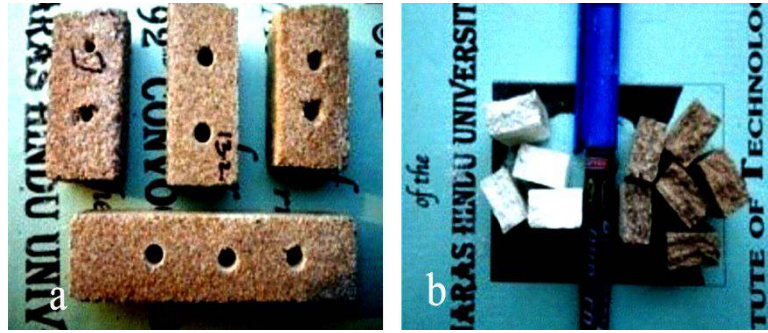


Fig. 5.9 (a) Drilling of green samples and (b) Fracture surface of samples after strength testing

5.3.5. Physical properties of sintered compacts

Shrinkage of samples after organic burnout/ presintering at 800°C was found to be in the range 0.5-2%. Firing shrinkage of samples prepared with higher wt% rice husk was more than those with lower wt% RH. Linear firing shrinkage of porous alumina samples was in the range of 11.9 to 18.3 % in the present work. Fig. 5.10 shows the sample Al₄₂₀₋₆₀₀ RH₁₀ before and after firing indicating a clear shrinkage.



Fig. 5.10 Sample Al₄₂₀₋₆₀₀ RH₁₀ before and after firing

The bulk density of sintered samples (Fig. 5.11) prepared with higher amount of RH was always less as compared to that of samples with lower RH content. the bulk density of sintered samples is directly related to the density of the green samples i.e, among a large number of samples, the samples with lower green density exhibit low sintered density in comparison to that of other samples under similar conditions of heat treatment. This is clear from Table 5.2 and Table 5.3.

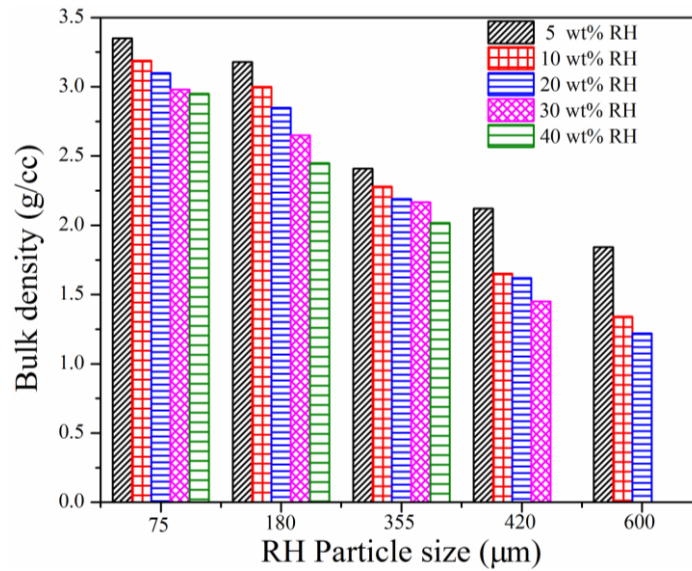


Fig. 5.11 Density of sintered samples as a function of size of rice husk in the composition

Also, a decreasing trend of sintered density was observed with increase in particle size of RH for the same total amount in the composition. Density of sintered samples measured was found in the range 3.16-1.34 g/cc (80-33.8 % T.D). The decrease in bulk density with incremental addition of RH can be attributed to the removal of higher percentage of organic additives and subsequent creation of pore phase during heat treatment.

Table 5.3 Different mixture compositions, the corresponding green density, % linear firing shrinkage and sintered density of fabricated porous alumina samples

Al _x RH _y SS ₂₀		% Theoretical density (Green)	Linear shrinkage (%)	% Theoretical density (Sintered)
RH content (wt %)	RH powder size(μm)			
5	< 75	78.2	13.3	80
	75-180	75.7	13	78
	180-355	74.4	12.8	76.28
	355-420	72.4	12.2	76.74
	420-600	69.4	11.9	72.73
10	< 75	73.9	13.6	78.3
	75-180	73	13.4	76.5
	180-355	72.72	13.2	74.75
	355-420	69.44	12.8	70.13
	420-600	65.15	12.5	65.1
15	< 75	67.92	14.16	76.25
	75-180	65.65	13.9	72
	180-355	59	13.36	68.05
	355-420	58	13.15	64
	420-600	54	13.33	60.83
20	< 75	65.15	14.9	59.85
	75-180	60.8	14.5	57.75
	180-355	56	14.2	54.3
	355-420	53	14	44.54
	420-600	45.45	13.6	39.75
30	< 75	53	15.6	53.53
	75-180	50.5	15	41.66
	180-355	49.2	14.33	38
40	< 75	47.97	18.33	46.46
	75-180	46.6	16.2	33.83

5.3.6. Phase analysis

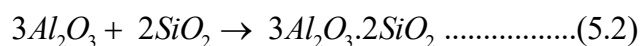
Fig. 5.12 shows an XRD pattern of a typical (Al₄₂₀₋₆₀₀RH₂₀SS₁₀ and Al₄₂₀₋₆₀₀RH₂₀SS₄₀) sintered porous alumina sample. Mullite (3Al₂O₃.2SiO₂) as well as α-alumina peaks are observed in the diffraction pattern. The crystal

structures and lattice parameters of mullite and α - Al_2O_3 are given in below Table 5.4.

Table 5.4 Crystal structures and lattice parameters of mullite and α - Al_2O_3

Phase	Crystal structure	Lattice parameters
Al_2O_3	Rhombohedral	$a= 4.76 \text{ \AA}$, $c= 12.990 \text{ \AA}$
Mullite	Orthorhombic	$a= 7.58 \text{ \AA}$, $b= 7.693 \text{ \AA}$, $c= 2.896 \text{ \AA}$

No crystalline peak due to crystalline silica (preferably cristobalite) was observed. It is important to mention here that presence of silica in alumina matrix is the burnout residue of rice husk and the volume fraction of silica is proportional to the volume fraction of RH in the sample. It is believed that this silica reacted with the surrounding alumina matrix to form a stable phase, mullite during sintering of the samples at 1700°C according to the following equation:



XRD patterns of other samples, were similar to the one shown in Fig. 5.12.

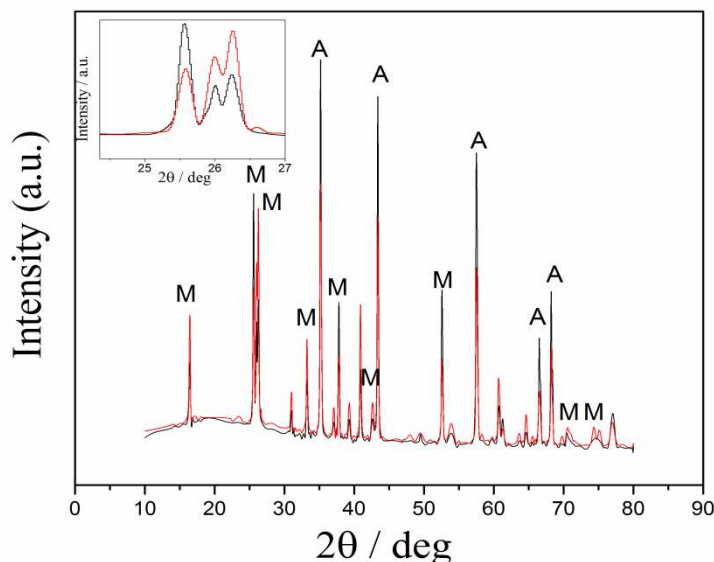


Fig. 5.12 XRD patterns of a porous alumina compacts $\text{Al}_{<75}\text{RH}_{20}\text{SS}_{20}$ and $\text{Al}_{180-355}\text{RH}_{40}\text{SS}_{20}$ fabricated using RH and sucrose and sintered at 1700°C .

Formation of mullite in alumina matrix in presence of RH/RHA has also been reported by other researchers.¹²¹⁻¹²³ It can be mentioned here that presence of mullite in alumina matrix is expected to improve the mechanical properties of the developed porous ceramics.¹²⁴

5.4. Fabrication of other Structures

Structures with functional distribution of dense and porous layers have also been fabricated using this process. Fig. 5.13 shows fractured surface and cut surface of two sandwich structures such as dense-porous-dense (Alumina_ alumina- RH_ Alumina) and porous-dense porous (Alumina-RH_ alumina_ alumina -RH). The porous layer has been developed using $Al_{420-600}RH_{20}SS_{20}$ mixture composition.

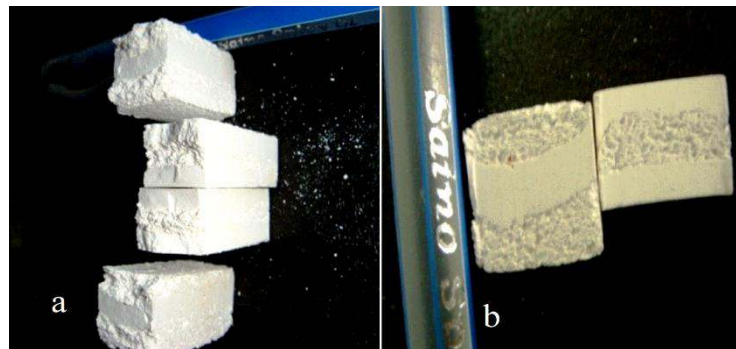


Fig. 5.13 (a) Fracture and (b) cut surface of sandwich structure

5.5. Summary

1. The present work reported a simple, cost effective method for producing porous alumina ceramics with various shapes and structures having tailored porosity and pore size, using rice husk as a pore former and sucrose as a binder as well as a pore former.
2. Sucrose was found suitable due to the fact that, it not only helped in adequate binding and compaction of ceramic mixture to form defect free green samples with high packing density but also contributed to additional porosity in the sintered compact.

3. The drying shrinkage of the samples was almost negligible, linear presintering shrinkage was 0.5-2% and linear firing shrinkage was 11.9 to 18.3 %.
4. Porous alumina ceramics with isolated and/or interconnected pores with bulk density in the range 3.16-1.34 g/cc (80-33.8 %T.D) were successfully fabricated using this process.
5. Sintered samples are strong enough for machining (drilling).
6. Rice husk in combination with sucrose in the selected composition range along with optimized processing conditions resulted in successful fabrication of defect free porous alumina ceramics with tailored microstructure and properties.
7. The developed porous ceramics can be used in various applications such as thermal insulation, electrical insulation, gas permeability, low and high temperature filtration etc.
8. This process opens up an opportunity for utilization of rice husk, an agricultural waste material, for fabrication of porous shapes having wide range of microstructure and properties using other ceramic materials suitable for technical and engineering applications.