

2.1 Introduction

Recently, the utilization of wastes in several ceramic sectors, including both traditional and advanced fields has acquired more attention from many researchers. This chapter introduces a brief description about the synthesis of ceramics like refractories, whitewares, glass-ceramics, oxide, and non-oxide ceramics by utilizing of waste RHA, FA, ES, seashell, river silt and refractory grog.

Silica (SiO_2) is one the most important ingredient for the ceramic industries. It is believed to be the backbone of the ceramic industries (Carter and Norton, 2013). However, most of the manufacturers are collected silica from the natural sources (Table 1.1). With the use of these sources, our problem remains the same, i.e., a loss of virgin raw materials. Therefore, the whole world is looking for the alternate sources of silica through waste utilization. RHA is found to be the most promising waste to serve as a potential silica source. River silt is retained silica as a major compound, which can also be used as another silica source. FA is a source of alumina silicate with fine particle size and nearly spherical in shape. Therefore, it can be used as a source of silica and alumina.

Calcium oxide (CaO) is another important ingredient for making different ceramics like glasses, whitewares, high temperature cements and several oxide ceramics like hydroxyapatite (HAp), wollastonite, etc. Commonly, limestone is used as a CaO sources (Table 1.1). Some wastes such as ES and seashell have also been retained as high purity CaO sources. Therefore, researchers are looking to utilize these wastes for making ceramics.

2.2 Rice husk ash utilization

Rice is the second most widely consumed food item globally, with rice paddy production about ~758 million metric tons in 2017. This number will increase gradually due to the projected demand of the world population (Lokare, 2017). The statistics for the rice paddy production in different countries according to the production volume in 2017 is shown in Figure 2.1 (Shahbandeh, 2018). China and India leading countries for rice paddy production around 48.87 wt.% of the total volume of rice paddy production. Rice husk (RH)

is a by-product of the industrial processing of the rice and approximately 20 wt.% of the bulk grain weight. The main constituents of the RH are 70-80% organic substances, such as cellulose, lignin, etc. and the remaining 20-30% comprises mineralogical components such as silica, alkalis and trace elements (Sarangi *et al.*, 2009). Due to its high calorific value (16,720kJ/kg), it can be used as fuel in boilers for the energy production through direct combustion or by gasification process (Della *et al.*, 2002). This burning generates new waste, designated as rice husk ash (RHA), which is roughly 25% of the initial husk weight. It also creates environmental pollution as well as disposal problems (Kishore *et al.*, 2011). The properties of RHA depend on the ecological circumstances of its origin as well as the process applied for burning the husk (Gonzalves *et al.*, 2007). Generally, 1000 kg of paddy grain produces about 200 kg (20%) of RH. When it is burnt to generate energy, about 50 kg (25%) of RHA is generated, and it contains around 45 kg (85-95 %) of amorphous silica. This silica has broad applicability in ceramic industries, as graphically illustrated in the [Figure 2.2](#). Researchers have been motivated to incorporate the RHA in the following various fields to developed different ceramics.

2.2.1 Refractory

RHA has low thermal conductivity (κ), it can be used as an ingredient for the manufacturing of insulation refractories. The κ of the refractory materials is ascribed to the vibrating atoms caused by phonons (low temperature) and photon conductivity (high temperature) in crystalline materials (Pal *et al.*, 2012). RHA containing silica is amorphous in nature; however, it acts as a non-heat conducting ingredient in the refractories. RHA insulation refractories are fabricated by the mixing of different flux contents (as binder), plasticizers (due to the lack of plasticity of RHA) and pore-forming agents (to increase the porosity of the final products) (Gonzalves and Bergmann, 2007; Bhardwaj *et al.*, 2017; Sobrosa *et al.*, 2017). Air is entrapped in the pores of the refractories, a characteristic which is attributed to lower values of κ , because entrapped air acts as a barrier to the flow of heat. These insulating refractories may be used as a second lining of furnaces or kilns in the ferrous

or non-ferrous industries. RHA is also used in steel industries for the insulation of ladles, tundishes, and trough (Ugheoke *et al.* 2006; Ahmed *et al.*, 2008). The insulation of RHA increases the thermal shock resistance of the refractories. The low σ of RHA leads to a slow reduction of molten iron temperature during casting and helps to maintain uniform solidification. Besides this, several researchers are trying to use RHA in the production of advanced refractories, such as cordierite (Sembiring *et al.*, 2016; Sembiring *et al.*, 2017), forsterite (Hossain *et al.*, 2017) and mullite refractories (Sultana *et al.*, 2011; Serra *et al.*, 2016).

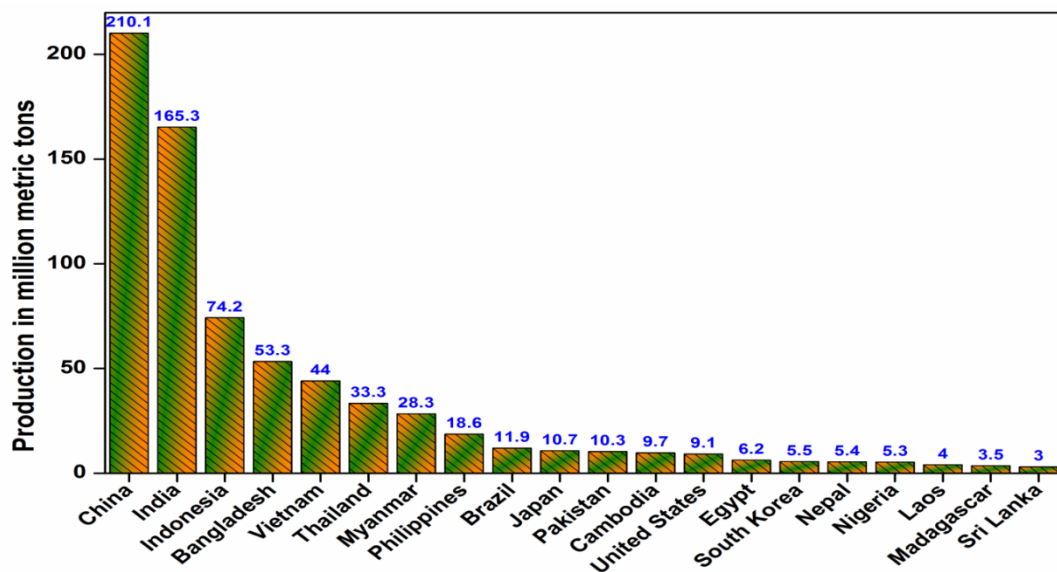


Figure 2.1: Statistic of rice paddy production of different country in 2017 [Shahbandeh, 2018].



Figure 2.2: Schematic representation of the fabrication process of RHA and their application for the preparation of ceramics.

2.2.2 Whiteware

Silva and Surangi (2017) have studied the effect of RHA addition for partial replacement of clay in the composition of clay roof tiles used in roofing buildings. Their study conclude that 10 wt.% RHA addition shows around ~45.97% increment in the breaking load, whereas, density is reduced by ~3.04% and the thermal properties are also improved (indoor temperature decreases ~4°C). In whiteware bodies, the substitution of a conventional RHA silica source influences the vitrification temperature around 50 to 100°C in the bodies (Prasad *et al.*, 2001; Jamo and Maharaz, 2015). Consequently, thermal expansion is reduced and the mechanical strength is improved at lower temperature in the mature bodies (Prasad *et al.*, 2003). Bondioli *et al.* (2007, 2010) have analyzed the feasibility of using RHA in place of quartz in pigment and frit development. In the case of pigments, RHA is used to replace silica in Pr-ZrSiO₄ solid solution for synthesis of yellow-colored ceramic pigments. The obtained pigment shows the development of a stable, intense yellow color, which is similar to that of a composition containing pure quartz. Similarly, RHA is also applicable for frit manufacturing in the application of tiles and glazes.

2.2.3 Oxide ceramics

Cordierite is a magnesium aluminosilicate (Mg₂Al₄Si₅O₁₈) system, and RHA can therefore be used as a silica source for cordierite. A few researchers have conducted studies in this area in the past two decades. Simbering *et al.* (2016) have used an alkali extraction method for extraction of silica from RHA followed by solid-state mixing of the raw materials for the development of cordierite. For the later step, i.e., development of cordierite, they have mixed all the raw materials in an alcohol medium with an appropriate ratio of MgO:Al₂O₃:SiO₂ i.e., 2:2:5. Mixing is conducted using a magnetic stirrer for 6 h in an alcohol medium. Upon completion of the mixing process, the mixed mass is filtered and dried at 110°C for 8 h to absorb residual alcohol. The dried mass is palletized using uniaxial hydraulic pressing and sintered at temperatures of 1050-1350°C. Figure 2.3 shows the X-ray diffraction (XRD) analysis of these sintered samples. At 1050°C sintered sample is retained with spinel,

crystalite and μ -cordierite phases. μ -cordierite to α -cordierite transformation is started at 1100°C. The cristobalite and spinel phases are vanished almost completely with increasing temperature from 1230 to 1350°C and ascribed to only α -cordierite phase. Similarly, [Kurama and Kurama \(2008\)](#) have used solid-state mixing of raw materials for the development of cordierite phase. They have used RHA in place of kaolinite for the development of cordierite. The milling is conducted in a planetary ball mill in water medium. A sample is palletized at 1.96 MPa and sintered at 950-1350°C. The ramp rate for the temperatures up to 1000°C is 5°C/min and 2.5°C/min for higher temperatures with a holding time of 1 h. [Naskar and Chatterjee \(2004\)](#) have used the sol-gel method for the development of cordierite. They have first prepared separate sols of silica and then mixed it along with other ingredients. The mixtures are dried at 90°C, followed by calcination at 400-1400°C. In all the above studies, formation of α -cordierite is occurred at temperatures above 1200°C. μ -cordierite is formed at lower temperatures, i.e., below 1200°C, but the transition from μ -cordierite to α -cordierite is occurred only at above 1200°C. The formation of μ -cordierite at lower temperatures indicates that a diffusion reaction between cristobalite and spinel (MgAl_2O_4) starts at this temperature ([Janackovič et al., 1997](#)). Moreover, at high temperatures $>1200^\circ\text{C}$, this μ -cordierite starts converting into α -cordierite, due to the formation of an Mg-O-Al-O-Si bond during phase transformation ([Simbering et al., 2016](#); [Naskar and Chatterjee, 2004](#); [Janackovič et al., 1997](#)). It can therefore be observed that active silica present in RHA promotes the conversion of μ -cordierite to α -cordierite at low temperatures (1300°C) compared to other conventional sources (1400°C) due to its high surface area and fluxing properties. Besides this, application of RHA leads to a decrease in the activation energy required for the crystallization of α -cordierite ([Kurama and Kurama, 2008](#)).

[Sembiring et al. \(2014\)](#) have synthesized mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) using RHA derived silica and aluminum nitrate hydrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$]. They have concluded that the mullite phase is started to form at around 1150°C. The mullite amount rapidly increases with the

increasing heat-treatment temperature from 1150 to 1350°C. [Serra *et al.* \(2016\)](#) have also investigated the mullite formation ability of RHA as a conventional silica source. The stoichiometric ($3\text{Al}_2\text{O}_3:2\text{SiO}_2$) amount of RHA (~94.74 wt.% SiO_2) and calcined alumina (Al_2O_3) containing dry pressed body is started mullite formation at 1400°C and completed after at 1600°C.

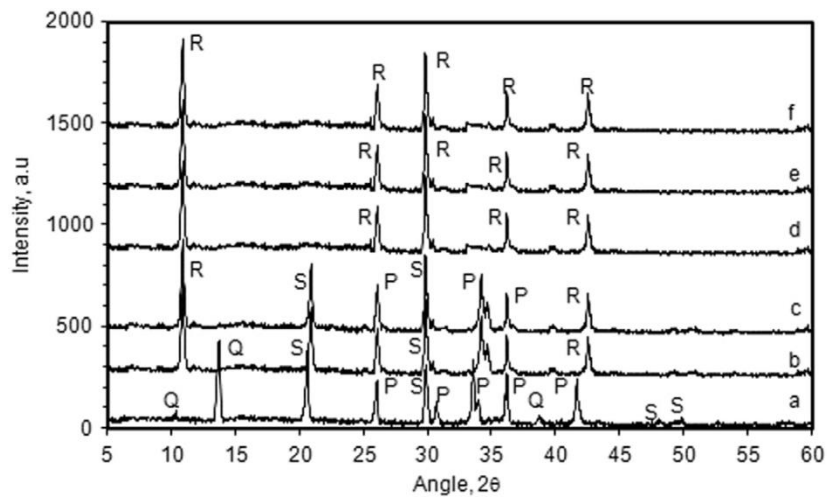


Figure 2.3: X-ray diffraction patterns of the sintered samples at different temperatures (a) 1050°C, (b) 1110°C, (c) 1170°C, (d) 1230°C, (e) 1290°C and (f) 1350°C. P: spinel, Q: m-cordierite, R: α -cordierite, S: cristobalite. Copyright with the permission from Ref. [[Simbering *et al.* \(2016\)](#)].

2.2.4 Non-oxide ceramics

Recently, [Li *et al.* \(2018a\)](#) have developed a process for synthesizing of SiC nanowires from RHA without catalysts or protective atmosphere. RHA and phenolic resin are mixed in a high-speed planetary mill with a stoichiometry amount of SiC. The mixed mass is then placed in a graphite crucible with a graphite cover, and the crucible is placed in an alumina container, as shown in [Figure 2.4](#). The residual space in the alumina container is packed with graphite dust, and the container is locked with an alumina plate. This environment does not allow any oxidation of the mass. Calcination of the mixed mass is conducted at 1600°C for 3 h without a protective atmosphere. Afterwards, light-green β -SiC nanowires are acquired from the graphite crucible.

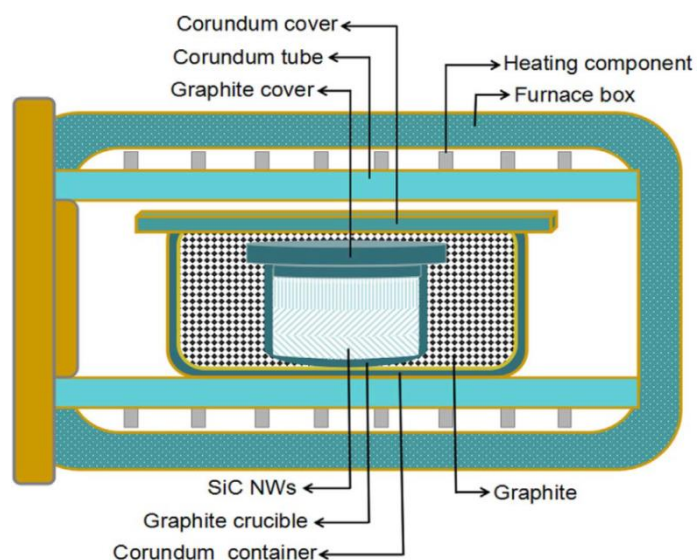


Figure 2.4: Schematic diagram of the fabrication process of β -SiC from RHA. Copyright with the permission from Ref. [Li *et al.* (2018a)].

Abdulhameed *et al.* (2018) have fabricated Si_3N_4 through hydrothermal reactions route at 100, 150, 200 and 300°C using RHA as source of SiO_2 , sugarcane bagasse ash as C source, NH_4OH , and HCl. The obtained powder at 100°C/ 24 h is contained ~92 wt.% Si_3N_4 , a mixture of α and β phases. Soltani *et al.* (2017) have prepared Si_3N_4 coating using RHA derived silica via a chemical vapor deposition method.

2.2.5 Silica aerogel

Silica aerogel (SA) is a synthetic nano-porous, ultra-light, structure-controllable, solid material, which possesses excellent characteristics such as super-low bulk density (0.03-0.5 g/cm^3), huge porosity (80-99%), a high specific surface area (500-1500 m^2/g), low κ and a low dielectric constant (Rajanna *et al.*, 2015; Pan *et al.*, 2017; Śłosarczyk, 2017). It has a wide range of technological applications, such as insulation materials for buildings, membranes, pollutant absorbents, microelectronics, catalytic supports, drug carriers and dielectric materials (Dorcheh and Abbasi, 2008; Gurav *et al.*, 2010). Many reports are found to prepare silica aerogel from RHA through the sol-gel route. In every case, SiO_2 is first extracted from RHA in the form of a sodium silicate (water glass) solution using a sodium hydroxide solution. The sodium ions are then removed by the cation exchange resin method (Feng *et al.*, 2018; Cui *et al.*, 2015) or by neutralizing the water glass solution using acid (Li and Wang,

2008; Nayak and Bera, 2009; Tadjarodi *et al.*, 2012) to form silica hydrosol. A small quantity of tetraethyl orthosilicate (TEOS) is added to form a gel, and washing is conducted with water and ethanol. The pretreated gel is dried at atmospheric pressure (Li and Wang, 2008; Nayak and Bera, 2009; Tadjarodi *et al.*, 2012) or supercritical drying (Cui *et al.*, 2015) to attain silica aerogel. RHA-derived SA exhibits a porosity of about 80-85%, a pore volume of about 0.7-3 cm³/g, a specific surface area of about 950-270 m²/g and bulk density of about 0.3-0.7 g/cm³.

In summary, amorphous silica containing RHA has high potential as a replacement for conventional silica (e.g., quartz) sources for making of different ceramics such as refractories, glasses, whiteware, SiC, mullite, cordierite and silica aerogel.

2.3 Fly ash utilization

The coal ignition by-product is classified as fly ash (FA) in the form of solid. It pollutes the environment through air pollution and damages cultivated land/ponds (Duan *et al.*, 2016). According to a survey, FA is produced approximately ~196 MT per annum (2017-2018) in India as a waste by-product and continuously it increases from the present level. Out of which, ~67% of the FA is used for making cement, concrete, bricks, and agriculture, etc (Ram, 2018). Rest FA is still unused, which causes various health problems, environmental issues and serious ecological difficulties (Haque, 2013). To protect the environment, the unused FA has to be reused. The composition of the FA is complex, and it depends on the type of raw coal and the combustion circumstances (Lü *et al.* 2014). However, FA mainly silicoaluminium minerals contains some minor constituents such as CaO, MgO, Fe₂O₃ and another oxides. It is considered as an inexpensive, finely granular with low particle size distributed material that makes it suitable to use as a source of geo-polymerisation reaction (Fan *et al.*, 2018; Mucsi *et al.*, 2018). Recently this waste can also be used as an ingredient to fabricate different ceramics as shown in Table 2.1. Investigators have shown with interest to incorporate FA to develop various following ceramics.

Table 2.1: Fly ash derived ceramics.

Products	Amount (wt.%)	Firing temperature (°C)	Properties	References
Insulation refractory	75	1000	$\kappa \sim 0.163$ W/m·K at 600°C, porosity ~ 71.16 %, compressive strength ~ 5.05 MPa	Otero <i>et al.</i> , 2004
Insulation refractory	10	1350	$\kappa \sim 4$ at 800°C (W/m·°C), compressive strength ~ 0.92 MPa	Bragança <i>et al.</i> , 2008
Wall tile	50	950	Full-fill the Indian standards	Chandra <i>et al.</i> , 2008
Wall tile	10	1020	-	Olgun <i>et al.</i> , 2005
Tile	60	1200	Porosity ~ 1.1 %, water absorption ~ 0.47 %, flexural strength ~ 51.28 MPa	Ji <i>et al.</i> , 2016
Tile	70	1300	Porosity ~ 0.13 %, flexural strength ~ 67 MPa	Wang <i>et al.</i> , 2017
Tile	100	1300	Porosity ~ 0.68 %, water absorption ~ 0.10 %, flexural strength ~ 109.67 MPa	Luo <i>et al.</i> , 2018b
Mullite membrane	-	1300	Open porosity ~ 50 %, flexural strength ~ 69 MPa,	Cao <i>et al.</i> , 2014
Mullite membrane	-	1450	Porosity ~ 45 %, flexural strength ~ 45 MPa, bulk density ~ 1.73 g/cc,	Dong <i>et al.</i> , 2009
Mullite powder	-	1200	Particle size < 0.3 μm	Li <i>et al.</i> (2018b)
Mullite body	-	1600	Porosity ~ 1.2 %, bulk density ~ 2.78 g/cc, compressive strength ~ 169 MPa	Lin <i>et al.</i> , 2015
Cordierite	-	1300	α -cordierite with small amount spinel	Hajjou <i>et al.</i> , 2017

2.3.1 Refractory

Otero *et al.* (2004) and Sukkae *et al.* (2018) have prepared the insulation refractory bricks by utilizing the FA and local clay. The lower κ , linear shrinkage, and bulk density are obtained with the incorporation of FA in the composition. Bragança *et al.* (2008) have synthesized the insulation bricks using coal combustion ashes. During the coal combustion, two types of ashes are generated, i.e., FA (fine particle size) and bottom ash (coarser particle size). FA is used in place of kaolin clay up to 10 wt.% for the insulation refractory bricks fabrication and bottom ash (10 wt.%) is used as a replacement of chamote in the composition of commercial bricks. The presence of ashes in the compositions (10 wt.%) decreases the density and κ of the bricks. Conversely, it is slightly diluted the mechanical strength of the bricks compared with the commercially available insulation bricks. Mandal *et al.* (2017) have synthesized insulation bricks by utilizing the aluminum plant wastes (FA and red mud) along

with sawdust. FA (0 to 100 wt.%), red mud (100 to 0 wt.%) and sawdust (0 to 10 wt.%) are mixed with an adequate amount of water and pressed with an uniaxial pressure of 15 MPa. The bricks are fired at 1000, 1100 and 1200°C. 60:40 weight ratios of FA and red mud along with 7.5 wt% sawdust containing fired bricks (1100°C) meets the required properties as per standard IS:2042 for Type-A insulation bricks.

2.3.2 Whiteware

The use of FA is rapidly extended for the preparing of ceramic tiles. [Chandra *et al.* \(2008\)](#) have prepared low temperature firing wall tiles by addition of low alkali pyrophyllite and sodium hexa-meta phosphate (SHMP) with FA and fired in the temperature range 950 to 1050°C. [Olgun *et al.* \(2005\)](#) have developed wall tiles by replacement of K-feldspar with FA and tincal waste (boron process waste) in the range of 2 to 10 wt.%. [Ji *et al.* \(2016\)](#) and [Wang *et al.* \(2017\)](#) have fabricated tiles using high alumina containing FA as main raw material, and they have introduced 60 wt.% and 70 wt. % of FA in the composition, respectively. While [Luo *et al.* \(2018b\)](#) have produced fully FA based mullite containing ceramic tiles, as shown in [Figure 2.5](#). These works are significant to verify the possibility of using FA as a substitution of traditional natural materials for ceramic tile fabrication. Additionally, the consumption of FA is also favorable to enable the improvement of ceramic properties. In particular, [Wang *et al.* \(2018\)](#) have made dense/foam bi-layered thermally insulation ceramic tiles using high-alumina FA and waste glass by a single pressing and a single-firing process.



Figure 2.5: Photographs of fly ash containing mullite-based tiles sintered at different temperatures. Copyright with the permission from Ref. [[Luo *et al.* \(2018b\)](#)].

2.3.3 Glass and glass-ceramics

Erol *et al.* (2007) have developed glasses by melting of three different types of FA at 1500°C and annealed at 600°C. Sheng *et al.* (2003) have also made glass using FA with 10 wt.% of Na₂O. Melting and annealing are done at 1200°C and 520°C, respectively. Chen *et al.* (2012) have studied the foam glass-forming ability of FA with sodium borate (Na₂B₄O₇) and calcium carbonate (CaCO₃) as a flux agent and foaming agent, respectively. 70 wt.% FA containing and 800°C fired samples exhibit excellent comprehensive properties like porosity (52%), bulk density (0.876 gm/cc), and compressive strength (2.09 MPa).

Wang *et al.* (2014) have presented an overview of the fabrication of glass-ceramics (GC) using coal FA as an ingredient. Detail description about the acquired methodologies for the preparation of GC from FA along with the major crystal phases, corresponding properties, and probable application of those materials are described. Class C type FA (SiO₂+Al₂O₃+Fe₂O₃ ≥ 70 wt.%) is much more appropriate for making CaO-Al₂O₃-SiO₂ system GC. This system is retained usually anorthite (CaAl₂Si₂O₈), gehlenite (Ca₂Al₂SiO₇), wollastonite (CaSiO₃) and diopside (CaMgSi₂O₆) as main phases and it has a huge application on constriction as decoration or insulation material. Generally, class F type FA (SiO₂+Al₂O₃+Fe₂O₃ ~50-70 wt.%) can be used to prepare MgO-Al₂O₃-SiO₂ system based GC. It retains phases like mullite (2Al₂O₃·SiO₂) and cordierite (2MgO·2Al₂O₃·5SiO₂) mainly. The GC derived from F class FA is suitable as a wide range of infrared drying and heating material.

2.3.4 Oxide ceramics

Coal FA has much potential as an ingredient for making the mullite due to its abundant availability and chemical composition. FA contains around ~54 wt.% and 35 wt.% of SiO₂ and Al₂O₃, respectively. Therefore, bauxite (Li *et al.*, 2009; Cao *et al.*, 2014), pure Al₂O₃ (Lee *et al.*, 2013; Zhu and Yan, 2017), Al(OH)₃ (Chen *et al.*, 2008), AlF₃ (Cao *et al.*, 2014; Zhu *et al.*, 2015) and other sources of Al₂O₃ have been added into FA to maintain the

stoichiometry weight ratio of Al/Si (~2.55) for mullitization. [Cao *et al.* \(2014\)](#) have developed low-cost mullite membrane using coal FA with natural bauxite (extra alumina source), V_2O_5 (sintering additive) and AlF_3 (pore-forming agent and alumina source). [Figure 2.6\(a\)](#) displays the XRD pattern of 4 wt.% AlF_3 and 3 wt.% V_2O_5 containing membrane specimen. They have concluded that this composition is completed secondary mullitization reaction at $1300^\circ C$ with 86.75% mullite content. [Figure 2.6\(b\)](#) shows SEM micrograph of $1300^\circ C$ fired sample, and displays the interlocking microstructure of anisotropically developed mullite whiskers with open pores (~50 %). [Li *et al.* \(2018b\)](#) have synthesized mullite powder from FA through mullitization and hydrothermal process. Boehmite sol is mixed with the pre-calcined FA powder and again calcined at $900-1300^\circ C$. Composition with 12 wt.% boehmite sol and calcination at $1200^\circ C$, shows 63.80 wt.% of mullite. The amount can be increased up to 96.4 wt.% through the proper alkali and acid treatment (hydrothermal process). Recently, high alumina containing FA is attained more interest for the formation of the mullite, because it contains more than > 45 wt.% of alumina. The combustion temperature of the coal-fired boiler is approximately $1300^\circ C$. It is nearest to the secondary mullite formation temperature. Thus, a large quantity of mullite is generated in the high alumina FA through the reaction between FA containing alumina and silica. [Lin *et al.* \(2015\)](#) have synthesized mullite using only pre-treated high alumina FA. The alkali (20% NaOH solution) and acid (15% HCl solution) treatment of high alumina FA can be increased the alumina content above 65 wt%. The pre-treated high alumina FA contents above 88 wt.% of mullite after sintering at $1600^\circ C$.

[Hajjou *et al.* \(2017\)](#) have developed cordierite ceramics using FA along with magnesium chloride and silica gel to maintain the stoichiometry of the cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$). They have concluded that cordierite is started to form at $1200^\circ C$ and the pure phase is obtained at $1300^\circ C$ with a small amount of spinel. [Liu *et al.* \(2015\)](#) and [Długosz *et al.* \(2016\)](#) have also used FA to fabricate the cordierite ceramics.

In summary, fly ash is a fine solid waste, which contains mostly silico-aluminium mineral. It is suitable to use as a raw material for the manufacturing of value-added ceramics for practical applications.

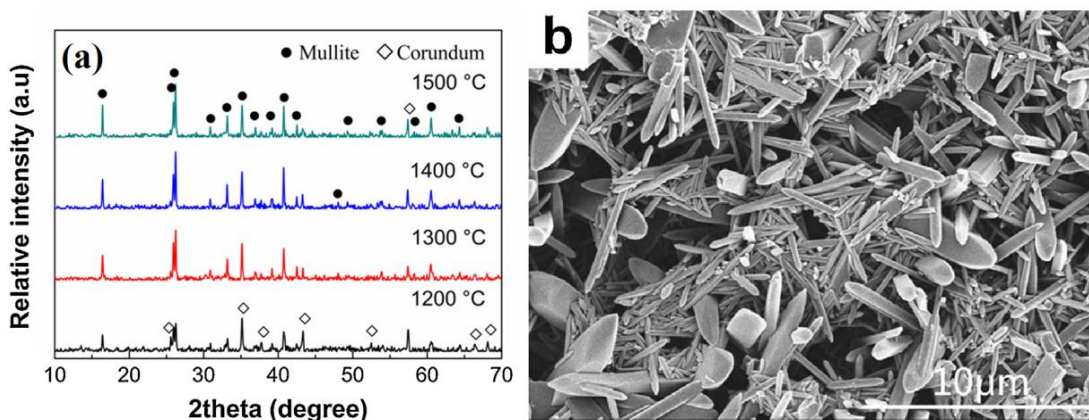


Figure 2.6: (a) XRD patterns and (b) SEM micrograph of 4 wt.% AlF_3 and 3 wt.% V_2O_5 containing sample. Copyright with the permission from Ref. [Cao *et al.* (2014)].

2.4 Eggshell utilization

ES are available as waste from the food-processing industry. They are disposed of immense amounts on a daily basis causing serious pollution and public health problems. It is therefore important to recycle this waste to preserve the environment. Avian eggs contain ~11 wt.% of ES waste to the total weight of the egg and this waste contains around 94 wt.% CaCO_3 , 1 wt.% MgCO_3 , 1 wt.% $\text{Ca}_3(\text{PO}_4)_2$ and 4 wt.% organic matter (Tsai *et al.*, 2006; Naga *et al.*, 2015). When ES are calcined at above 700°C , however, all phases except CaO are removed (Witoon, 2011).

Chaudhuri *et al.* (2013) have synthesized hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) nanoparticles using calcined ES powder and di-potassium phosphate (K_2HPO_4) as a source of calcium and phosphate, respectively. ES derived CaO and K_2HPO_4 are mixed with maintaining Ca/P ratio around 1.67 in water and NH_4OH solution is added to the mixture for adjusting the pH value of the solution around 12. The solution is left for 7 days at 37°C for allowing self-reaction and HAp is formed according to the following reaction (equation no. 2.1, 2.2):

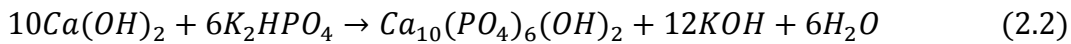
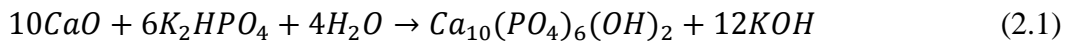


Figure 2.7 shows the XRD spectrum of HAp, which is formed with different soaking time of ES derived CaO powder in K_2HPO_4 . No remarkable alteration is detected in the XRD pattern with respect to the peak intensity and positions for different reaction time (1–7 days). It is designated that the HAp formation reaction is completed almost within first days. The white HAp particles are separated from the solution and dried at 37°C . The particle size of the formed HAp is around 41 nm. Wu *et al.*, (2015); Ummartyotin and Tangnorawich, (2015); Ronan and Kannan, (2017) and Bernalte *et al.*, (2019) have also used ES to derived HAp. Choudhary *et al.* (2015) have synthesized bio-active calcium magnesium silicate and Leite *et al.* (2017) have prepared calcium silicate insulation material by utilizing ES. Puntharod *et al.*, (2013) have prepared wollastonite utilizing egg shell and diatomite through hydrothermal technique. This method is performed at 100, 150, and 200°C for 24 h using 1:1 molar ratio of calcined egg shell and diatomite. Later, the powder is calcined at 1000°C for 24 h and formed wollastonite with particle size less than $1\ \mu\text{m}$. Vichaphund *et al.*, (2011) have produced single phase wollastonite powder using ES and SiO_2 as starting materials through microwave heating at 1100°C for 10 min. Noor *et al.*, (2015) have prepared wollastonite glass-ceramic by utilizing ES and waste glass.

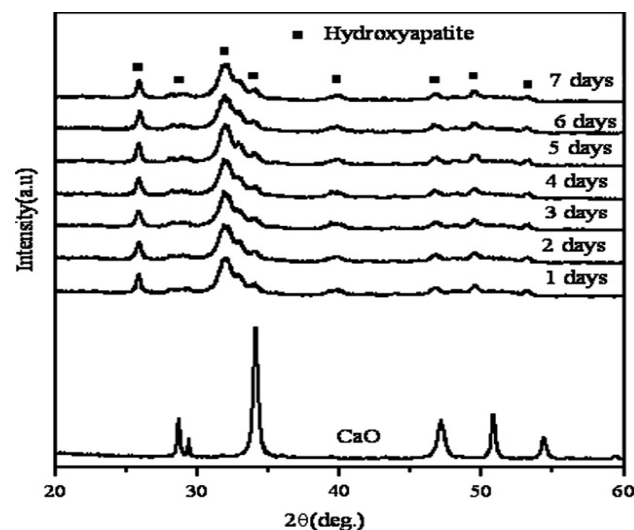


Figure 2.7: XRD analysis of the CaO powder obtained from the ES and those of the HAp prepared from this CaO powder soaked in K₂HPO₄ solution for different days. Copyright with the permission from Ref. [Chaudhuri *et al.* (2013)].

2.5 Seashell utilization

The seafood (other than fish) is highly delicacy in a different country like USA, Europe, China, Japan, Korea, etc. Therefore, several types of empty seashells, i.e., mollusks of oyster, bivalves, clam, gastropods, mussel, and scallops shells mainly are found abundantly outside the different fishery industries along coastal areas (Olivia *et al.*, 2015). These untreated shells spread odors and breeding of flies and mosquitoes. It would harmfully affect the living environment and local health. A seashell is a solid, hard, protective outer layer or exoskeleton of an animal having an absence of a backbone, i.e., an invertebrate that exists in the ocean. This solid consist of around ~ 30 wt.% of an animal's body weight (Li *et al.*, 2015). This fishery waste has no significant uses except landfill as a solid waste. The ground seashells contain around 90-99 wt.% of CaCO₃ that is suitable for the replacement of conventional sources of CaO (Mo *et al.*, 2016).

Shavandi *et al.*, (2015) have synthesized nano HAp through rapid microwave method utilizing waste mussel shells. 900°C calcined shells with 2.8 gm are mixed in 0.1 M EDTA (C₁₀H₁₆N₂O₈) solution and make a 50 ml Ca-EDTA complex solution. Later 50 mL of 0.06 M Na₂HPO₄ solution is added with continues stirring and pH is maintained around 13. Then, the solution is treated in microwave (2.45 GHz, 1100 W) with 50% of its power capacity until the solution is dried. The obtained solid is washed through deionised water and dried at 80°C in a vacuum oven. Finally, 30-70 nm rods like particles of HAp are formed, as shown in Figure 2.8. Jones *et al.*, (2011) and Kumar *et al.*, (2017) have also used waste mussel shells to derived HAp. Shavandi *et al.*, (2016) have utilized kina shells to prepare porous HAp followed by pyrolysis and chemical route. Oyster shell (Rujitanapanich *et al.*, 2014; Wu *et al.*, 2017) and abalone shell (Chen *et al.*, 2015) derived CaO is also used for synthesizing HAp powder.

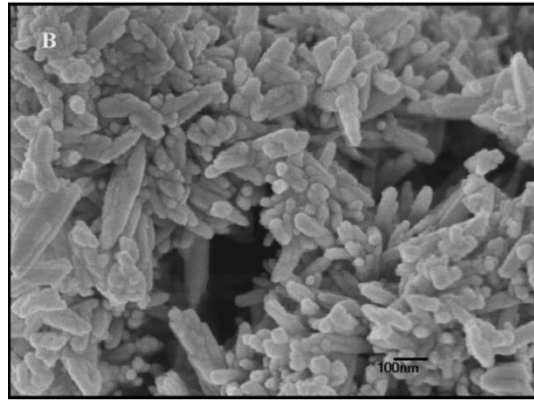


Figure 2.8: SEM images of HAp powders derived from mussel shells. Copyright with the permission from Ref. [Shavandi *et al.*, (2015)].

Teixeira *et al.* (2017) have used oyster shell as a pore forming agent for synthesizing of vitrocrySTALLINE foams. The mixture of waste glass bottles and oyster shells (1–15 wt.%) are uniaxially pressed (20 MPa) and fired at 800–950°C for 30–120 min. The composition containing 9 wt.% oyster shells and 91% glass bottles shows optimized properties of produced vitrocrySTALLINE foams. Figure 2.9 shows the SEM micrograph of 9 wt.% oyster shells containing foam specimen fired in the different temperature. The obtained porosity, κ , and compressive strength of 900°C fired foam sample is varied from 81- 91%, 0.057-0.077 W/m-K and 1.00-2.33 MPa, respectively, with holding times of 30–120 min. Heriyanto *et al.*, (2018) have utilized waste shell with waste glass for synthesizing of calcium silicate insulation material.

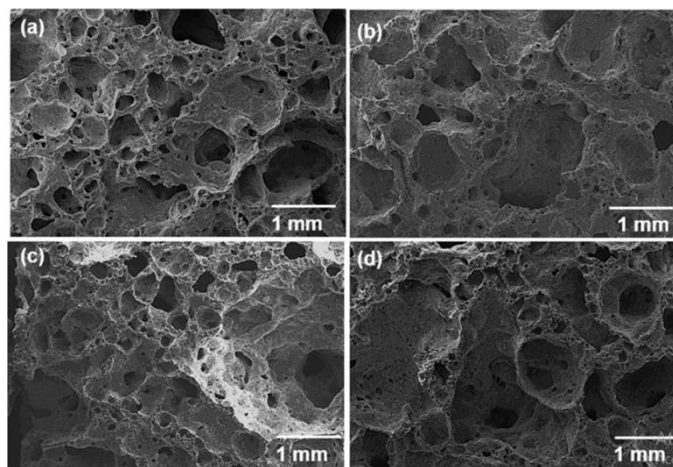


Figure 2.9: SEM micrographs of 9 wt% shells containing foam samples fired at (a) 800°C, (b) 850°C, (c) 900°C (c) and 950°C. Copyright with the permission from Ref. [Teixeira *et al.* (2017)].

2.6 Kosi river silt utilization

Kosi River originates from Tibet in China. It lies in the middle of 85° and 89°E Longitude, and 25° 20' and 29°N latitude. Figure 2.10 shows the course of Kosi river in India. As it comes from the mountainous region of Nepal, it brings an enormous amount of sedimentation about 80 million m³/yr. with its flow and causes an alteration in the morphological characteristic of the river (Regmi, 2013). This huge sedimentation minimizes the volume of the river to carry extreme flows, results in a flood in the plains along the banks and drives the river to find another path. It flows on the Bihar plain land and settles down the silt, which damages the agriculture land. It causes wide spread human sufferings by excessive damage to life and destruction of property. For this reasons, Kosi River is also known as the “Sorrow of Bihar” (Thapa, 2004). If this silt can be used in any productive purpose, it can bring salvation from floods in Bihar. However, no such area, is found till now, where Kosi river silt can be used in huge amount.

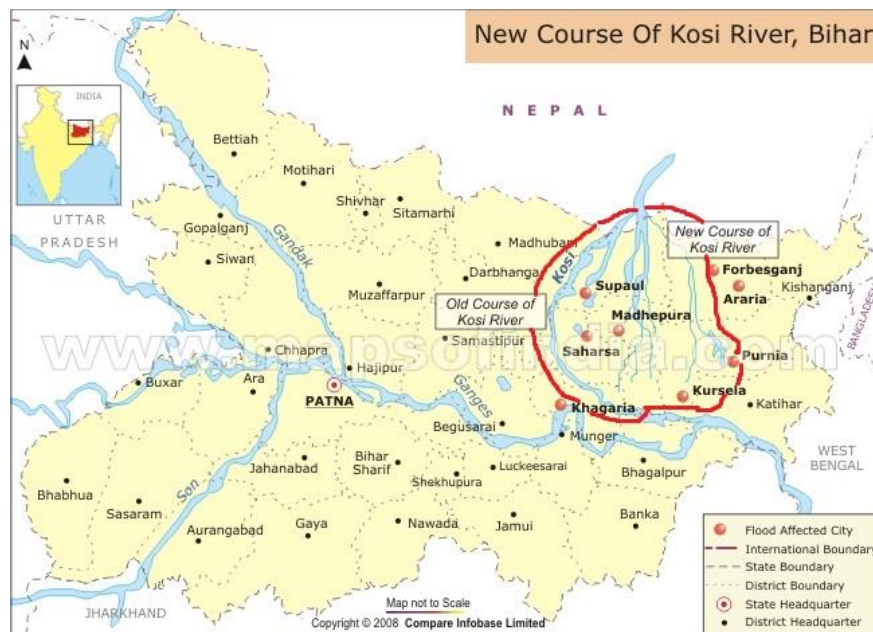


Figure 2.10: The course of Kosi river in India (source: <https://www.mapsofindia.com>).

2.7 Refractory grog utilization

Waste refractory grog is generated during the shorting (separation of defect products) and transportation of fired refractories, and repair of kilns or furnaces. This ceramic waste has no proper uses rather than disposal. However, some studies are found to attempt the reuse of

this waste for production of building bricks and as an aggregates in the concrete. [Vieira and Monteiro \(2007\)](#) and [Patel and Modi \(2017\)](#) have incorporated fired refractory grog in the composition of clay bricks up to 20 wt.% and 25 wt.%, respectively. [Kavas et al. \(2006\)](#) have used as aggregates for the production of concrete along with ordinary portland cement (OPC) and sand.

2.8 Summary of literature review

Today, the production of toxic and hazardous wastes from various sources is continuously increased, and at the same time, it is created difficulties in the form of dumping and pollution to the environment. The valorization of these wastes and up-grading as a substitute of primary natural resources can present numerous benefits, i.e., reduced the extraction volume of natural ingredients (resource conservation), less energy consumption throughout the subsequent processing (cost-effective), and lower pollutant releasing rates (improvement of society's health and safety). In view of the environment, ecological and economic issues, science and technology developers are engaged to find the appropriate route of utilizing wastes for the production of value-added products. In these aspects, researchers are also investigated to recycle the industrial by-products or wastes to fabricate ceramics. Therefore, numerous research studies are published in the last two decades regarding the utilization of RHA, FA, ES, seashell and grog for the fabrication of ceramics. Within this background of the literature review, the following important outcomes can be drawn:

- ❖ RHA can be used for the preparation of insulating refractories due to its low thermal conductivity. It is contained huge amount of amorphous silica, which has potential applications in glass formation. Silica acts as a “network former” in glass. The network formation is easily achieved in case of amorphous silica due to its high reactivity. This reason also makes it suitable for use in the preparation of silica aerogel. RHA can reduce the vitrification temperature of the ceramic bodies and it allows to use in whiteware bodies up to a certain percent. The activation energy required for crystallization has been

reduced by application of RHA, which assists in formation of mullite and cordierite ceramics.

- ❖ FA can be found the most promising waste for development of the ceramics. It can be used to fabricate insulation refractories and ceramic tiles. Different type of FA has potential to prepare different properties GC for different types of application. FA is also a good candidate to synthesis mullite ceramics through the incorporation of other Al_2O_3 sources by maintaining the stoichiometry weight ratio of Al/Si (~2.55). Alkali and acid treated high alumina containing FA is able to generate mullite without addition of Al_2O_3 sources.
- ❖ ES is the most promising bio-waste as a source of CaO for preparing of HAp. Other high CaO containing shell like oyster shell, mussel shells, abalone shell, and kina shells also can be used to derive synthetic HAp.
- ❖ No prominent application field has been discovering till now where river silt can be used in huge amount for fabrication of ceramics.
- ❖ Waste refractory grog can be used as a replacement of non-plastic ingredient (quartz and sand) for the production of ceramics.

However, industrially produced ceramics from waste ingredients are not yet widely matured. Some tile industries are started to use wastes for the production of tiles ([Rambaldi, 2018](#); [Julie and Paul, 2019](#)) but these numbers are very less. The recycling of the wastes for the production of ceramics is beneficial because it consumes a huge amount of natural raw materials. Even if, a small amount of waste incorporation is possible in the high production ceramics, it will effect into significant absorption of wastes. Therefore, the more deep investigation is required in technological transfer from the academic to industry for commercialization the waste-derived ceramics. The technology transfer is becoming a confront from different perspectives, like ethics, knowledge, and risks of unsustainability. Therefore, more encouragement is required to industrial manufacture for recycling the wastes.

The government may also lead to an increase the interest through making laws and policies. Sustainable production not only helps the ceramic industry but also saves the environment and society from pollution.

2.9 Objectives of the work

The objective of the present study is the valorization of wastes, like RHA, FA, ES and seashell with reference to ceramics. Facile, eco-efficient and economical routes are developed for the synthesizing of sustainable ceramics like sol and nano silica, foam of silica and mullite, castable refractory, wollastonite, ceramic board and insulation brick. Focus is given to incorporate the maximum amount of wastes in the composition of ceramic and investigates the importance characteristics of the respective ceramics.

In this investigation, RHA is the main waste, which is common for all the respective ceramics. FA, ES, seashell and other waste like river silt and refractory grog are also incorporated to increase the waste amount in the composition.

The wastes derived ceramics and different effect on their properties will be studied by the following sub-objectives:

- ❖ To synthesize high purity nano silica and silica sol from the waste RHA and utilize to prepare silica foam, mullite foam and castable refractory.
- ❖ To synthesize low cost synthetic wollastonite from waste RHA along with ES, and study the physico-mechanical and dielectric properties. Also, investigate the fluxing properties of the waste derived wollastonite with river silt in the tile body.
- ❖ To fabricate ceramic board using RHA, RH, FA and seashell through simple room temperature curing process.
- ❖ To prepare insulation refractory by waste RHA, FA, refractory grog with incorporation of RH as a pore former.