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Review
Processing, properties and applications of reactive silica from rice husk—an overview

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Rice husk is an abundantly available waste material in all rice producing countries. In certain regions, it is sometimes used as a fuel for parboiling paddy in the rice mills. The partially burnt rice husk in turn contributes to more environmental pollution. There have been efforts not only to overcome this but also to find value addition to these wastes using them as secondary source of materials. Rice husk contains nearly 20% silica, which is present in hydrated amorphous form. On thermal treatment, the silica converts to crystobalite, which is a crystalline form of silica. However, under controlled burning conditions, amorphous silica with high reactivity, ultra fine size and large surface area is produced. This micro silica can be a source for preparing advanced materials like SiC, Si_3N_4, elemental Si and Mg_2Si. Due to the high pozzolanic activity, this rice husk silica also finds application in high strength concrete as a substitute for silica fume. Possibility of using this silica as filler in polymers is also studied. The present paper is an attempt to consolidate and critically analyse the research work carried out so far on the processing, properties and application of rice husk silica in various laboratories and also highlighting some results on the processing and characterization of RHA and reactive silica obtained from it in the authors' laboratory.

1. Introduction

Developing countries like India possess abundantly available agro based resources and their by-products from industries, many of which are under utilised along with a variety of low value products. On the other hand, developed countries have accepted and followed the concept of "no waste" and all such materials are termed as "new resources" for new material development through value addition. Rice husk (RH) is one of the by products of rice, a major food material of most of the developing countries including India. It is one of the agricultural 'waste' materials available in plenty in rice producing countries, which is amenable for value addition. It is reported that for every ton of rice produced, ∼0.23 tons of RH is formed and accordingly, during 1997–98, the production of RH in India is reported to be nearly 26 million tons [1]. If this can be used profitably through value addition, economic benefits will accrue to the producers and thus to the national economy. Value addition of any material including 'wastes' is based on the clear understanding of its structure and properties. Chemical composition is one such property, which determines the end use of any material. This is also important for pre-treatment to be given to RH for further processing. The chemical composition of RH is found to vary from sample to sample. The differences in the type of paddy, crop year, climatic and geographical conditions, in addition to the sample preparation and method of analysis, could be the reason for this variation. A number of studies have reported [2–8] chemical composition of RH obtained in different parts of the world. It is interesting to note that most of them report the organic content in RH as 72% of the husk by weight, but with wide variation of the constituents such as cellulose, moisture content and ash as expected with any natural material. Govindarao, in an extensive review [2] has analysed all the reported data on the chemical composition of rice husk from various countries including western world and Asia and gives an average composition on dry basis as ash 20%, lignin 22%, cellulose 38%, pentosans 18% and other organic matter 2%. As can be seen from this work, there is significant variation in the silica percentage. Even in India itself, the samples from two southern places Trivandrum and Hyderabad, appear to be high in Mg, Al and Fe content. The use of chemical fertilisers in the paddy field may

TABLE I Organic constituents in rice husk [3]

Constituent	Amount present in rice husk (wt%)
α-cellulose	43.30
Lignin	22.00
D-xylose	17.52
l-arabinose	6.53
Methylglucuronic acid	3.27
D-galactose	2.37
Total	94.99

TABLE II Analysis of rice husk ash [5]

	Weight % of ash from			
Component	USA[a]	Jorhat, India[b]	Trivandrum	Hyderabad
Si as SiO_2	94.5	94.5	91.4	89.4
Ca as CaO	0.25	0.48	0.17	2.55
Mg as MgO	0.23	0.23	1.30	1.30
Al	Trace	0.21	1.57	3.81
Fe	Trace	0.54	0.62	1.95
Mn	Trace	1.09	0.11	0.03
K as K_2O	1.1	Trace	Not examined	
Na as Na_2O	0.78	Trace	Not examined	
P as P_2O_5	0.53	Trace	Not examined	
S as SO_4	1.13	Trace	Not examined	

[a] Hough and Barr (1956).
[b] Borthakur *et al.* (1980).

be contributing to this, in addition to the difference in the soil chemistry. When the RH silica is used in concrete and polymers the traces of other elements may not be of much significance. However, these elements act as impurities in the preparation of nitrides, carbides and other inorganic materials where RH ash is used as the source for silica. Later, Sharma *et al.* [3] have analysed the organic constituents in rice husk after excluding silica and Table I gives the details. The presence of silica in RH has been known since 1938 [4]. The chemical compositions of selected RH samples have been reported by Rama Rao *et al.* [5] and are given in Table II.

The silica is in hydrated amorphous form, either opal or silica gel [6, 7]. RH on burning gives ash containing >90% silica, which is normally in the crystalline form. However, under controlled burning conditions it gives amorphous silica, which is highly reactive due to its ultra fine size and high surface area (a form of micro silica with special properties). It is also interesting to note that the above studies present a wide range of chemical composition of RH clearly bringing out its dependence on location, climate, etc. Based on the above knowledge, a number of end uses have been derived for both RH and RHA and accordingly utilized. There have been excellent reviews on these aspects since nineteen forties [2].

In certain regions of India, rice husk is mainly used as a cheap source of energy for par boiling paddy in rice mills. The product of combustion is the partially burnt RH, which is not only a waste material but also contributes to environmental pollution. However, the cost of RH has gone up since many countries took up R&D projects. During 1970–85, many rice producing countries such as India, Pakistan, Bangladesh, Sri Lanka, Australia, Thailand, Indonesia and USA had projects on the utilisation of RH supported by government and other organisations. However, in many countries including India, most of such projects have been closed down now without establishing real concrete programs. The actual value addition achieved as well as the utilization of the energy on burning this agro waste needs critical evaluation. It will be highly beneficial, if RHA with superior properties is produced by fully utilising the fuel value of the husk keeping in view of the environmental considerations.

Extensive research has been carried out [2–20] on the preparation, properties and applications of RHA during the last three decades and many papers and patents have been published on this subject. Govindarao, in the review, has mentioned various uses of RH of which the most promising included manufacture of industrial chemicals such as silica, sodium silicate, zeolite, activated carbon and refractory materials such as SiC and Si_3N_4 [2]. It has been clearly pointed out that a pure form of silica with minimum impurities and amorphous nature is essential for the preparation of inorganic materials. The organic part in RH can be profitably converted to chemicals like xylose, furfural, xylitol, ethanol, acetic acid and lignosulphonic acid. Once the organic part is extracted, the inorganic residue may be relatively pure, forming a better source for silica. Karera *et al.* [9], while discussing the use of rice husk for the production of a variety of inorganic materials mentioned above, have given account of inorganic constituents of RH from different countries, its structure and pre treatments adopted to make it suitable for different applications. This included materials for thermal insulating, building materials and polymer composites. It is relevant that processes for the optimal utilization of RH with respect to maximum value addition, energy efficiency, cost and environmental aspects should be given more attention.

The present paper gives an overview of the work carried out so far with an attempt to consolidate the research findings of various aspects dealt by different laboratories. Also, included briefly are the efforts made in Regional Research Laboratory, Thiruvananthapuram (RRL-T) to study the nature and reactivity of rice husk silica/RHA as well as the feasibility to produce reactive silica from RH as possible substitute for condensed silica fume in the preparation of high strength concrete.

2. Preparation/processing of reactive silica from rice husk

Rice husk on burning gives ash, which contains a very high percentage of crystalline silica. However, if it is burnt under controlled conditions, amorphous silica is produced which is highly reactive in nature. A low cost method for producing activated RHA for pozzolanic ash suitable for masonry binders was patented in 1980 [14]. Hamad and Khatab studied the thermal decomposition of rice husk in the laboratory [21]. They observed that the ash formed at lower temperatures (773–873 K) consisted of amorphous silica. The crystalline forms cristobalite and trydimite were detected at temperature >1073 K and >1423 K respectively. The ash produced by combustion of rice husk in a fixed bed at different air rates was also evaluated. At lower rates of combustion, amorphous silica was formed whereas at higher rates, silica crystallises. Crystallisation of silica has to be prevented by controlling the temperature and time of burning so that maximum amorphous variety is produced. Milling the ash to get high surface area can increase the reactivity. A horizontal cyclone furnace was designed [22] and developed for combustion in the mill and the energy was used for par boiling and drying paddy. The ash produced did not contain any volatile matter but some traces of unburnt carbon. Another study reported [23] burning of RH (-10 mm) in a fluidised bed of fine sand (0.5 mm diameter) with cross section of 380×406 mm and total height of 4.8 m. The operating conditions were → bed temperature 923–1173 K, fluidising velocity 0.4–2.2 m/s, bed depth 30–60 cm and excess air levels of 30–95%. Complete combustion was reached over a wide range of fluidising conditions. Ash from the bed was used to manufacture pozzolan cement by mixing it with Portland cement (30:70 ratio). This pozzolan cement was found to have higher strength. The fluidised bed combustion of rice husk was found to be highly energy efficient producing ash with good pozzolanic properties [24]. However, detailed study is required for establishing the advantages of fluidised bed combustion of rice husk so that commercialisation of the process can be thought of. In general, energy requirement for the production of RHA is less amongst the admixtures of cement except for fly ash [25] as can be seen from Table III.

A proto type incinerator was designed with special features to burn rice husk and produce amorphous and highly reactive silica [26]. A schematic diagram of the reactor used by one of the researchers for the incineration of RH is shown in Fig. 1 [27] while that of the incinerator used for controlled burning of RH is published elsewhere [28].

Recently, a study concentrating on RHA technology has been reported [29] where RHA is produced without using expensive fuels. The heat generated during the incineration of rice husk has been eventually transformed into mechanical energy for grinding the ash. This fine RHA on blending with Portland cement produces high strength concrete. Studies conducted in our laboratory indicate the possibility of converting RH into amorphous fine silica of high reactivity which can be used in high strength concrete. Chouhan *et al.* have reported [30] that the temperature of ashing of rice husk influences the compressive strength of lime—RHA mortar. Here again, reactivity of the silica plays the most significant role. The quality of the RHA is thus dependent on various factors like ashing temperature, time, rate of heating, type of furnace/kiln, etc. However, the efficiency of combustion, optimum utilisation of the energy etc. are extremely important in determining the economics of the whole process, which require to be looked into through careful studies.

TABLE III Energy requirements for production of various cementitious/pozzolan materials [25]

Materials	Total energy required KJ/kg of material
Cement	372
Lime	173
Hydrated lime	142
Burnt clay pozzolan	68
Rice husk ash	12
Surkhi (burnt brick)	12
Fly ash	0

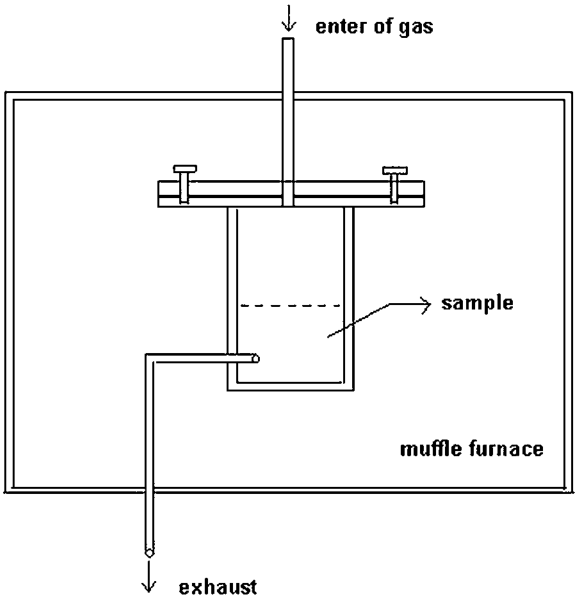

Figure 1 The reactor used for incineration of rice husks.

Amorphous silica is one of the industrial white minerals along with china clay, $CaCO_3$ and talc, which are used as filler in paper, paint, rubber, fertilisers and insecticides. In some of these applications, whiteness of the filler material is important. Table IV shows dependence of whiteness of silica obtained from RH on the temperature of incineration [31].

Amorphous silica of high purity, small particle size and high surface area can be of use as an adsorbent or catalyst support in fine chemical synthesis. In order to prepare amorphous silica with high purity from rice husk, either thermal treatment [8] of the husk or treatment with various chemicals was attempted [27, 31–36] before and after combustion at temperatures ranging from 773 to 1673 K for different intervals of time. The chemicals included HCl, H_2SO_4, HNO_3, NaOH, NH_4OH, etc. Chakraverti *et al.* [32] found that leaching

TABLE IV Dependence of whiteness of silica on the temperature of incineration (period of incineration: 2 hrs) [31]

	% Whiteness reading (reflectance measurements)	
Temperature (K)	Raw husk used	Charred RH used
623	3.4	–
673	4.0	8.9
723	17.8	–
773	29.0	27.5
823	31.3	–
873	36.4	27.2
973	–	30.7
1073	35.0	40.3
1123	57.0	36.9
1223	–	24.8

of rice husk with dilute HCl (1 N) removed most of the metallic ingredients. The ash from complete combustion of acid treated husk was white whereas that from the untreated husk under same conditions gave light brown product. The acid treatment of husk did not affect the amorphousness of the silica. Huang [15] patented a process for producing amorphous superfine silica powder (with >92% silica and average diameter 0.04–0.05 μm from rice husk. Nano structured silica with very high purity, >99% SiO_2 and surface area $\geq$250 m^2/g has been prepared [27, 33]. Chemical treatment before combustion was found to be more advantageous. The formation of black particles in the silica from untreated husk was found higher than that from acid treated husk. Potassium in the husk was shown to cause this phenomenon, which is removed to a great extent by acid treatment [34, 35]. Pre treatment of rice husk with HNO_3 and calcination at 873 K is reported to give white, amorphous and chemically pure silica (98.5%). Sidheswaran attributed this to the formation of nitro derivatives of lignin, which was washed out and prevents the coke formation during calcinations [31]. The effect of treating RH and RHA with organic acids has not been reported so far. Recently, study on the pre and post treatment of RH and RHA using acetic acid has been taken up in our laboratory.

3. Structure and properties

Introduction of more and more sophisticated instruments in the field of material characterization has enabled detailed structural studies of rice husk and its thermally treated products. Various researchers have used advanced techniques like SEM-EDAX, FE SEM, XPS, AFM and solid state MAS NMR. Rice husk is a fibrous material and a combination of silica and organic material with non-uniform composition. The ash contains ~95% silica in a hydrated amorphous form similar to silica gel. The silica is present all over, but is concentrated on protuberances and hairs (trichomes) on the outer epidermis, adjacent to the rice kernel [9]. Fig. 2 is the SEM photographs of RH and Fig. 3 clearly shows the protuberances and silica.

The nature of Si bonding in raw rice husk is complex and it appears to be bonded with the carbohydrates [8]. Structure of the organic content in RH given elsewhere, suggested the concept of bonding of Si with organic molecules, which was confirmed earlier by EDAX studies [3]. The partial burning of rice husk caused decomposition of organic part and breaking of the bonds with Si. Fig. 4 is a SEM photograph of white ash of RH [12]. The fibrous nature and the small grains in RH did not seem to be disturbed by burning [13]. The SiO groups become attached to each other to produce a low form of cristobalite. The resulting amorphous carbon and silica in the white ash show an XRD pattern (Fig. 5) with a broad maximum [13]. Upon complete burning, the single phase amorphous SiO_2 showed a diffused XRD peak with maximum at about $2\theta = 21.8°$.

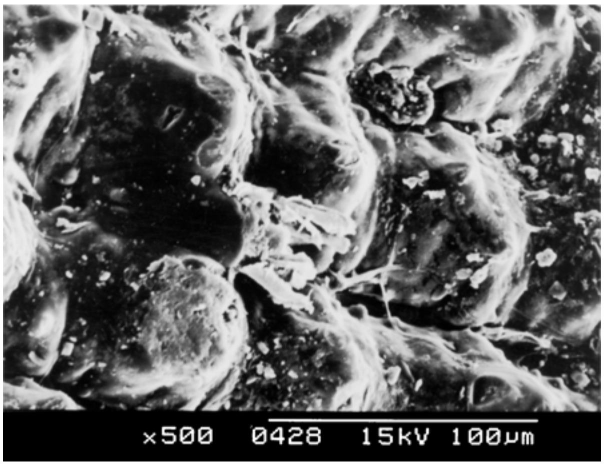

Figure 3 SEM of RH showing protuberance, outer epidermis and silica.

The silica in RHA is X-ray amorphous, ultrafine in size, highly porous and chemically reactive provided the burning of the husk is carried out under controlled conditions. At low temperature, up to 973 K, the silica liberated is amorphous. If higher calcination temperature is employed, crystalline polymorphs like α-cristobalite, α-quartz and α-tridymite are formed. Quantification of the different forms of silica produced under various burning conditions is essential for optimising the process conditions. The pozzolanic activity of the product is directly related to the quantity of amorphous silica. Recently, a rapid analytical method has been developed for determining amorphous silica in

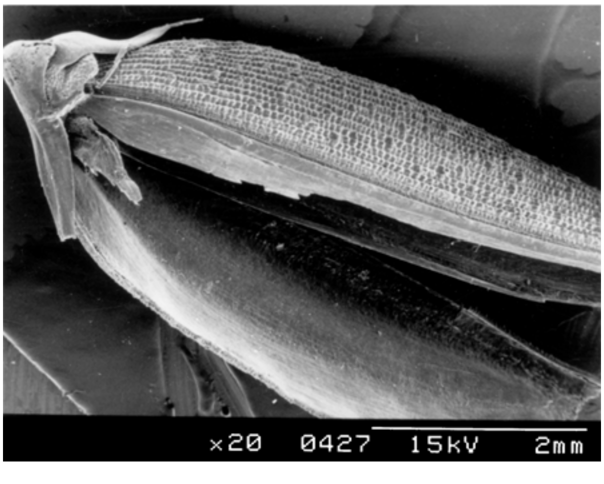

Figure 2 SEM of RH showing fibrous nature.

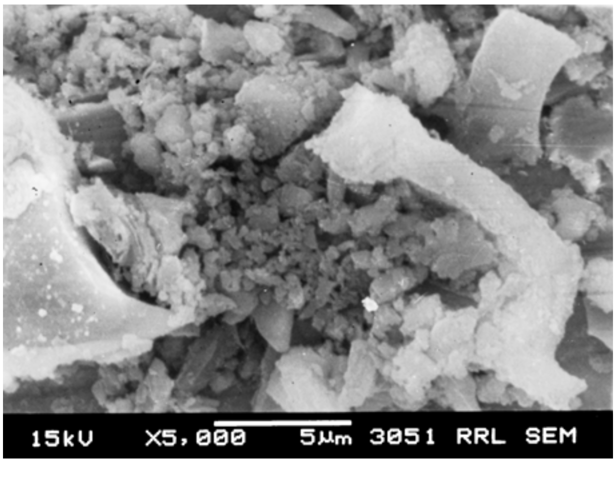

Figure 4 SEM of white ash of RH.

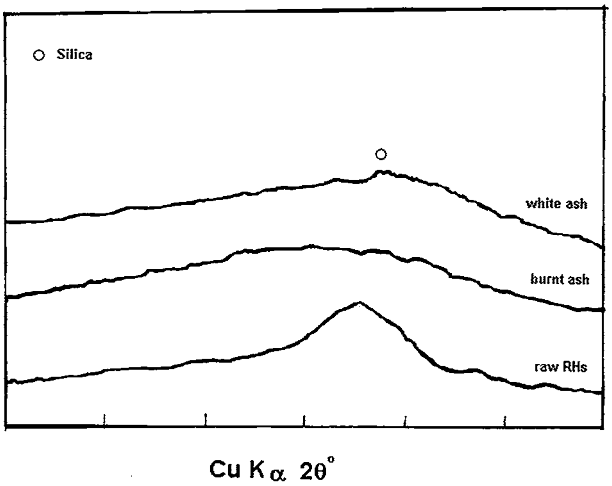

Figure 5 XRD patterns of the raw rice husks, burnt rice husks and rice husk white ash.

RHA and therefore assessing its potential pozzolanic activity [36]. The reactivity of rice husk silica was found maximum for ashing temperatures 673–873 K and soaking time 6–12 hrs by studying the various products using SEM, lime reactivity and surface area measurements [5, 10]. SEM studies of converted RH also revealed that part of RH rich in organic matter (forming CO) tended to form a SiC skeleton structure on interacting with that part which is rich in SiO_2. Morphological studies of the untreated rice husk ash showed particles of size ranging from 0.03 to 100 μm with average size of 75 μm and they had irregular geometry and spherical morphology [27]. The silica obtained from acid treated husk had homogeneous particle distribution with irregular geometry (APS 0.03 μm) as well as some spherical ones (0.06 μm) with a tendency to agglomerate as confirmed from the TEM studies. A comparative study of XPS analysis of amorphous silica from different sources was reported [37], which indicated that rice husk could be a cheap source for high-grade silica. Scanning or atomic force microscopy (SFM/AFM) was used for the surface characterisation of untreated and pyrolysed rice husk samples [38]. The XAFS analysis confirmed that the strong interaction between silica and the potassium ions in the rice husk leading to a dramatic decrease in the surface area of the product ash [39]. This phenomenon may be attributed to the coarsening of particles due to the alkali-silica fusion. It is interesting to note that all X-ray amorphous silicas are not similar in their reactivity. Hence, other techniques probing into the structural properties of silica are necessary to evaluate the reactivity of amorphous silica. The structure of silica has been recently studied [40] by ^{29}Si NMR and Field Emission Scanning Electron Microscopy (FESEM). The results showed that amorphous silica prepared by physical combustion with controlled temperature contained only Si(OSi)(4) tetrahedral units and was the most reactive silica source compared to other silica samples prepared by chemical extraction or uncontrolled burning. Thus amorphous silica with specific properties like high purity, good reactivity and large surface area can be produced form rice husk and the process can be economically viable if the fuel value of the material is also made use of.

4. Applications

4.1. RHA as a possible substitute for condensed silica fume in concrete

Pozzolanic materials are used to prevent or minimise cracking in concrete due to the expansive gel formed by the alkali—silica reaction. Silica fume and RHA have been classified as "highly active pozzolans." Many articles have been published [25, 41–47] on the synthesis, properties and applications of silica fume particularly for its pozzolanic activity. Table V gives the general classification of mineral admixtures with their chemical and mineralogical composition and particle characteristics [25].

TABLE V Classification of mineral of admixtures [25]

Classification	Chemical and mineralogical composition	Particle characteristics
II. Highly active pozzolans		
a. Condensed silica fume	Consists essentially of pure silica in non crystalline form.	Extremely fine powder consisting of solid spheres of 0.1 μm average diameter (about 20 m^2/g surface area by nitrogen adsorption).
b. Rice husk ash; (Mehta-Pitt process)	Consists essentially of pure silica in non crystalline form.	Particles are generally less than 45 μm but they are highly cellular (about 60 $m^2 \cdot g$ surface area by nitrogen adsorption).
III. Normal pozzolans		
a. Low calcium fly ash	Mostly silicate glass containing aluminium, iron, and alkalies. The small quantity of crystalline matter present consists generally of quartz, mullite, sillimanite, hematite, magnetite.	Powder corresponding to 15–30% particles larger than 45 μm (usually 200–300 m^2/kg Blaine). Most particles are solid spheres of average 20 μm diameter. Cenospheres and plerospheres may be present.
b. Natural materials	Besides aluminosilicates glass, natural pozzolans contain quartz, feldspar, mica.	Particles are ground to mostly under 45 μm and have rough texture.
IV. Weak pozzolans		
Slowly-cooled blast furnace slag, bottom ash, boiler slag, field- burnt rice husk ash.	Consists essentially of crystalline silicate minerals and only a small amount of noncrystalline matter.	The materials must be pulverised to very fine particle size in order to develop some pozzolanic activity. Ground particles are rough in texture.

TABLE VI Properties of typical condensed silica fume [45]

Sl. no.	Properties	Condensed silica fume
1	Color	Light to dark gray
2	Specific gravity	∼2.2
3	Bulk density	0.25–0.30 g/cc
4	Silica content	>90%
5	Surface area	20 m^2/g (BET nitrogen adsorption)

Silica fume is produced by the hydrolysis of silicon tetrachloride vapour in a flame of oxygen. It has been used as a constituent in cement concrete to get improved properties in view of this being more effective of various mineral admixtures in reducing the linear expansion of mortars up to 30% at 30% mixing and in some cases up to 83% in mortars containing argillite and 54% in dolomitic limestones [25]. Silica fume in western countries and Japan (1 million metric tonne per annum) is in good demand since it produces ultrahigh strength, conserves the cement, controls the alkali silica reaction, reduces chloride associated corrosion and sulphate attack and increases the early age strength of concrete. Accordingly, its cost is nearly 2–3 times that of cement and hence the use has been for special mixes for repairing and durability. Microsilica especially in the form of condensed silica fume (CSF) is formed as a by-product in ferrosilicon industry. Typical properties of this are listed in Table VI [45].

The micro silica in RHA produced by controlled burning of rice husk has been recently used instead of silica fume for achieving high strength lightweight concrete [48]. The results indicate that the use of rice husk ash leads to enhanced resistance to segregation of fresh concrete and to increased strength compared to a control mixture with Portland cement alone. Effect of cement replacement by silica fume or rice husk ash on the expansion of mortar bar has been studied recently. The results indicate that it is possible to significantly reduce the mortar-bar expansion using silica fume or RHA [49]. When RHA is used as filler in concrete blocks, the strength is enhanced due to its pozzolanic property [50]. An enhancement of cement hydration was observed when 25% substitution of Portland cement was done using a silica waste from a geothermal power plant [51].

4.2. Cement

The chemical reactivity of RHA with lime imparts the pozzolanic property and a number of publications/patents are available [52–68]. In all these studies, RHA has been reported as a source for silica in cement manufacture. Cement produced by grinding a mixture of rice husk ash and hydrated lime was studied for its production conditions and important properties [69]. Influence of mineralisers in the formation of high C_3S cement from RHA and $CaCO_3$ was studied and CuO added as $Cu(NO_3)_2 \cdot 6H_2O$ was found to be the most efficient one [70]. However, RHA can achieve higher value addition (rather than its use as a mere source for silica in cement) when reactive silica is produced under controlled burning of the RH.

4.3. Polymers

Many inorganic powders like clay, $CaCO_3$, dolomite, silica are used as fillers in paper, paint, rubber, plastics, adhesives, pesticides and fertilisers. By the addition of fillers, the mechanical, thermal, chemical and other properties of the material are improved. Extensive studies have been carried out during the last decade on the use of RHA as a filler material in polymers. Burning of rice husk ash yields two grades of fillers, namely white rice husk ash (WRHA) and black rice husk ash (BRHA). Both these RHA have been used as filler in polypropylene, rubber, polystyrene etc. Fuad *et al.* [71] investigated their use as filler in polypropylene and the properties of the composite samples were measured. Flexural modulus and density showed an increase whereas tensile strength, elongation at break and impact strength decreased with increasing filler content. Poor adhesion between polymer and filler was indicated by SEM studies. They have also described a simple and accurate method for determination of filler material density [72]. The mechanical properties of the composites were of comparable values with the prepared polypropylene composites filled with commercial Neuburg silica [73]. Transformation of the crystalline RHA to amorphous RHA resulted in composites with improved tensile strength. The effects of applying titanate, zirconate and silane coupling agents to RHA in polypropylene composites and the change in mechanical properties were also studied [74]. Ishak conducted an investigation on the potential of RHA as filler in epoxidised natural rubber (ENR). Cure studies were carried out on a Monsanto rheometer and the mechanical properties were evaluated. The effect of coupling agents was also tested and the behaviour was compared with two commercial fillers, precipitated silica (grade Vulcasil-S) and carbon black (grade N330). WRHA was better than the BRHA even though inferior to commercial fillers [75]. The tensile, tear and abrasion resistances and hardness of the composites were determined. The RH was chemically treated and FTIR analysis was done to verify the presence of characteristic functional group of precipitated silica in milled RHA and treated RHA. The effect of a coupling agent was also studied. Although the silane-coupling agent did not improve the properties as expected, treated RHA showed exceptional performance in terms of tensile strength and abrasion resistance of the filled vulcanizates. Incorporation of RHA fillers into polypropylene affected some of the thermal properties of the composites [76]. Addition of the BRHA filler raised the thermal degradation temperature while maintaining the oxidative stability. The degradation temperature of the WRHA composites was found to be independent of filler loading but the oxidative stability deteriorated with increasing filler content. DSC studies indicated that both WRHA and BRHA fillers act as weak nucleating agents and increase the degree of crystallinity of polypropylene by a small margin. Incorporation of RHA fillers was found to influence the thermal expansion coefficient and some of the mechanical properties of the composite. A new analytical technique by TGA has been described for computation of filler content in polypropylene—rice hush ash composites [77]. Ishak *et al.* have conducted more detailed studies on the various physical properties of RHA—epoxidised natural rubber composites [78, 79]. Studies on the effect of bonding agents on partial replacement of silica by WRHA in natural rubber compounds showed that the optimum weight ratio of WRHA/silica to obtain maximum enhancement of tensile and tear strength was 20/30 (phr/phr) [80]. It has been reported that the incorporation of multifunctional additive (MFA) improves the curing characteristics and physical properties of WRHA filled natural rubber compounds [81]. A combination of MFA and silane coupling agent Si^{69} still improves the curing rate and improves the mechanical properties [82]. The effects of coupling agent and chemical treatment on rice husk ash—filled natural rubber composites have been investigated recently [83]. Tremendous scope exists in more exhaustive research on the RHA-polymer composites which can lead to the futuristic "organic-inorganic hybrid materials" with specific properties.

4.4. Others

The high reactivity and purity of RHA makes it an ideal starting material/silica source for preparing advanced materials like SiC, SiN, Sialons, elemental silicon, Mg_2Si etc. [9]. The minor constituents in RHA drastically vary from sample to sample depending upon the origin and other factors. For example, the RH samples from different parts of India have CaO in the percentage range 0.17–2.55; MgO 0.23–1.30; Al 0.21–3.8; Fe 0.5–1.95 and Mn 0.03–1.1 as given in Table II. Hence, suitable pre treatments based on detailed analysis of the RH sample from each region is essential for getting amorphous silica of very high purity. There have been several attempts to produce silicon carbide (particles/whiskers) through the pyrolysis of RH at 1173 K and analyze the process and product using X-rays, SEM, EDAX, TEM, Auger and XPS. It was found by Auger that the inner epidermis consisted of C and O_2 with traces of Si. EDAX analysis confirmed the localization of Si mostly in the outer epidermis with small amounts in the inner epidermis and also its possible bonding with polysaccharides as reported earlier [3]. Further, addition of Si_3N_4 (20–60%) to RH black ash (SiC: 55.80%) during the pyrolysis at 1473–1673 K increased the yield of SiC whiskers (76–94%) without any residual SiO_2 [12]. Preparation of solar grade silicon at low cost and with low energy consumption has been published and patented by Banerjee *et al.* [84]. High purity amorphous silica was formed by calcining acid treated rice husk and the silica was reduced to poly crystalline silicon by magnesium [16]. Preparation of SiC from carbonised rice hulls and its detailed characterisation has been recently reported [85]. A highly pure mixture of C and SiO_2 was obtained on pyrolysis of RH leached with acid at high temperature in a non-oxidising atmosphere (N). This product was found suitable for the preparation of Si_3N_4 [86].

Various researchers have studied the use of RHA as a silica source for the synthesis of zeolites like mordenite, faujasite type X and Y etc. [87, 88]. Since all X-ray amorphous silica are not equally reactive, Hamdan *et al.* have investigated the structure of silica by ^{29}Si MAS NMR and FESEM to optimise the synthesis of zeolite Y [40]. Nizami has recently discussed economical preparation of wollastonite using RHA as a source of silica instead of quartz [89]. Reaction was carried out under solid-state conditions at 1173–1573 K for 1 h. The activation energy required for the performed reaction was found to be almost one third of that reported for synthesising $CaSiO_3$ by using quartz.

TABLE VII Plastic and dry properties of body mixes [93]

	Properties	CSR-1	CSR-3	CSR-5	CSR-6
1	Water of plasticity (%)	21.4	23.4	24.0	24.4
2	Dry linear shrinkage (%)	3.62	3.82	3.84	3.88
3	Dry M.O.R (Kg/cm^2)	10.06	10.79	9.90	9.90
4	Bulk density of dry test pieces, g/cc (by mercury balance)	1.617	1.722	1.615	1.572

RHA is used as one of the raw materials with commercial magnesite to produce Forsterite ($2MgOSiO_2$). This has low dielectric loss and is used as high frequency insulator mostly at elevated temperatures [11]. Addition of RHA lowered the firing temperature by about 423–473 K from the conventional raw material. The final product exhibited a density of 2900 kg/m^3 with a porosity of 1%, dielectric loss of 1×10^{-4} and dielectric constant of 8.9 comparable with the best of insulators.

Recently, RHA has been used as a support for Ni catalyst for various organic reactions and was found to be preferable over silica gel [90]. A novel application of RHA is for the pre concentration of gold [91]. It is observed that RHA heated at 573 K can be used as a better adsorbent for gold thio urea complex in comparison to activated carbon. In 1978, Samandani *et al.* reported the use of RHA in the area of ceramics [92]. Recently, Prasad *et al.* has investigated the effect of RHA in white ware composition [93]. Progressive substitution of quartz with RHA in a conventional white ware composition resulted in an early vitrification of the mixes. Table VII shows some plastic and dry properties of white ware body mixes with substitution of quartz by RHA obtained this study. A decrease in melting temperature and thermal expansion of the body mix was observed and the fired strength also increased. This may contribute to the economic production of white wares.

5. Work carried out at RRL-T

Initial studies were carried out [5] in the laboratory in 1986–88 on samples collected from two different regions in south India to investigate into the nature and reactivity of silica available in them and their ashes. Table II shows chemical analysis of RHA samples prepared from these RH and compared with those of other parts of the country and USA. RHA samples were prepared by burning at various temperatures (573–1223 K) with different soaking times from 1–12 hrs. Ash yield,

TABLE VIII Properties of the rice husk ash and imported microsilica samples [94]

Sl. no.	Properties	RHA	MS 1	MS 2
1	Color	Light pink	Gray	White
2	SiO_2 %	95	91	81
3	Loss on ignition	4.0	2.2	1.1
4	Lime reactivity, mg CaO/g ash	95.8	49.3	36.1
5	True density (g/cc)	1.73	2.08	2.83
6	Bulk density (g/cc)	0.30	0.52	0.75
7	SEM	Irregular particles <5 μm	Spherical particles of almost uniform size <0.3 μm	Irregular particles <8 μm
8	Surface area (m^2/g)	139	15.5	2.6
9	Particle size distribution (μm)			
	$+45$	27.0	Nil	Nil
	$-45, +20$	24.0	1.0	7.0
	$-20, +10$	16.0	5.0	15.0
	$-10, +5$	9.5	10.0	20.0
	$-5, +2$	9.0	6.0	26.0
	-2	14.5	78.0	32.0
	Average particle size, d_{50}	12	0.38	4.0
10	XRD	Amorphous	Amorphous	Crystalline

its colour, reactivity and surface area measurements were studied for all these conditions. Micro structural studies using SEM were also made on both RH and RHA samples produced. It was observed that RHA produced at and below 673 K contained unburnt cellulose material while sintering started in RHA only at and above 873 K. The surface area of RHA was found to decrease with increasing sintering temperature as also the reactivity of silica in these RHA samples. Maximum reactivity was observed in RHA produced at 673 K for 6–12 hr and at 773 K for 8–12 hr while those produced at 873 K showed maxima followed by a decrease suggesting the criticality of holding temperature for maximum reactivity.

Recently, preliminary studies were conducted aiming at the development of a process for the production of reactive silica from indigenous rice husk. A few rice husk samples were collected from rice mills of different regions in South India, analysed for their ash content and the one with the highest value was selected for detail study. The sample was cleaned and heated in a programmable furnace at different temperatures. The ash samples were characterised for the chemical and physical properties. The time and temperature of ashing were optimised to get an X-ray amorphous product with high silica content, high lime reactivity, large surface area, white colour and low loss on ignition.

The RHA thus produced in the laboratory and the imported commercial silica fume samples obtained from suppliers (M/S Elkem Pvt. Ltd., Mumbai and Asian Laboratories, New Delhi) were characterised for their SiO_2 content, lime reactivity, XRD, surface area, particle size distribution, density and microstructure. Table VIII gives the details of the properties.

The RHA was found to be superior in most of the properties except for particle size and shape. However, the size of RHA can be reduced by pulverisation. The ideal spherical shape and uniform size are observed only for the Elkem sample. The actual concrete mix tests are to be conducted with the samples for comparison. Details of the work have been published elsewhere [94].

6. Conclusions

Rice husk, which is an agro waste, can be a source for many silicon-based materials if burnt under controlled conditions. The silica thus produced is slightly coloured, X-ray amorphous, ultrafine in size and has high surface area and reactivity. White amorphous silica of high chemical purity can be produced from rice husk by acid treatment followed by controlled burning. Some of the novel applications of the rice husk silica are as filler in polymeric materials, as a possible substitute for condensed silica fume in high strength concrete, starting material for high performance silicon compounds etc. Most of these studies have been carried out at the laboratory level. Development of economically viable processes for getting rice husk silica with specific properties assumes importance at this juncture. Economy of the manufacturing process improves if the fuel value of the material is also utilised. Hence, production of value added materials from rice husk not only facilitates utilisation of an abundantly available agro waste but also reduces the environmental pollution. Tremendous scope exists for further research and development activities to convert all the laboratory findings into commercial production with appropriate technologies. This is particularly relevant to an agro-based country like India, which is still importing micro silica for the preparation of high strength concrete.

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