# Use of Rice Husk and Rice Husk Ash for Metallurgical Grade Silicon: The Production, Purification and Upgrade

Innocent O. Oboh<sup>1</sup>\*, Aondona P. Ihom<sup>2</sup> and Idorenyin E. Markson<sup>2</sup> <sup>1</sup>Department of Chemical and Pertoleum Engineering, Faculty of Engineering, University of Uyo, Uyo, PMB 1017 Uyo, Akwa Ibom State-Nigeria. <sup>2</sup>Department of Mechanical Engineering, Faculty of Engineering, University of Uyo, Uyo, PMB 1017 Uyo, Akwa Ibom State-Nigeria. email: innocentoboh@uniuyo.edu.ng, <u>oseribho@gmail.com</u>, <u>innocentoboh@uniuyo.edu.ng</u>

DOI: 10.56201/ijemt.v9.no1.2023.pg83.99

### Abstract

The demand for low-cost silicon which constitutes about 27% of the Earth's crust and is the second most abundant element in mass, after oxygen, has led to a search for unconventional sources of silicon. Rice processing and associated businesses are growing vigorously. Rice husk obtain from rice milling process as by product is attracting as a value added material for domestic and industrial processing such as preparing valuable silicon based materials since the presence of silica in rice husk has been known for so many years now. This paper presents a study on the production of metallurgical grade silicon from rice husk using various methods that had been established previously, by other researchers. The production, purification and upgrade of metallurgical-grade silicon (MG-Si) from agricultural waste materials is important as this metal has a range of diverse industrial applications. The production process involved pretreating the rice husk, leaching and pyrolysis to extract the silica, and then converting the extracted silica to metallurgical grade silicon. This study demonstrates the potential of using rice husk as a source of silicon as the alloying element in the aluminium industry, and provides valuable insights into the various methods of the production of metallurgical grade silicon from the silicon from unconventional sources.

Keywords: Rice husk, silicon, metallurgical grade silicon, rice husk ash, acid leaching, pyrolysis

#### 1. Introduction

Rice covers 1% of the earth's surface and is staple food for more than half of the world's population. Approximately, 741.3 million tonnes of rice paddy were produced between the year 2012 and 2014 (STAT, 2015) of which Nigeria produced 4.8 million tonnes of the rice paddy. About 20% of the rice paddy produced is husk (Beagle, 1978).

Rice Husk is a solid waste product from rice milling industries (Yunusa et al., 2016). The statistics generated worldwide for the production of rice husk annually gave an output of about 80 million tonnes. From that amount, over 97% of the rice husks were generated in the developing countries,

IIARD – International Institute of Academic Research and Development

Page 83

including Malaysia. According to the Malaysian Ministry of Agriculture, 408,000 metric tonnes of rice husk are produced each year (Syuhadah and Rohasliney , 2012). In 2002 Nigeria produced about 3,367,000 tonnes of rice per annual from which 673,400 tonnes of rice husk are separated as byproduct (Frolking, , 2002). In 2014, Nigeria produced 4.8 million tonnes of rice paddy, a 42.6% increment in rice husk in 12 years. With recent developments, new research methods, systematic and potential application of rice husk for manufacturing new products could solve many issues related to its disposal and burning of heaps of rice husks, which are responsible for pollution (Yadav , 2021).

Agro-industrial wastes are abundant in Nigeria among which rice husk occupies very important position. Rice husk is insoluble in water because of its high silica and lignin content, tough, woody and abrasive in nature with low nutritive properties and resistance to weathering with its silica content being the highest among all of them (Genieva, 2008).

Rice husks is one of the major source of value added material towards utilization of waste and is directly responsible for cost reduction in various processing industries as well as domestic applications. In all the rice producing countries rice husk is easily and almost freely available all over. Rice husk composition include around 16-25% of paddy (Giddel and Jivan, 2007; Soltani,et al., 2015). The composition of rice husk is shown in Table 1

S.NO	COMPOSITION	%
1	Hemicelluloses	24.3%,
2	Lignin	19.2%
3	Cellulose	34.4%
4	Ash	18.85%
5	Trace elements.	3.25 %

Table 1: Composition of Rice Husk (Giddel and Jivan, 2007; Soltani, et al., 2015).

Table 1 show that hemicelluloses present in the composition of rice husk is one of the major source of xylose, activated carbon, and silicon dioxide. The percent elemental composition of Rice husk include- Hydrogen 8.80%, Silicon 9.01%, Carbon 37.05%, Nitrogen 11.06%, and Oxygen 35.03 % (Sarang et al., 2009). Silica is 17-25% in husk (Real et al., 1996; Conradt, et al., 1992).

Although, a lot of synthetic silica are produced commercially, the ones produced from plant origins such as rice husks have been seen to have some significant advantages over those from mineral and synthetic origins. In particular, the processing steps are relatively simple and require no elaborate infrastructure or the use of costly reagents as in the case of the synthetic processes (Yunusa et al., 2016).. Presence of more amount of silica content in rice husks as compared to other agricultural waste provide an opportunity to explore direct and indirect applications in different field, which makes it an important market value product and can give a good economic return to the producer (Yadav , 2021).

Rice husk ash is obtained when husk is burnt in ambient temperature and pressure condition. It has been reported that around 20 million tonnes ash is produced per year around the world (Soltani, et al., 2015).. If properly burnt yields about 20% (average) ashes, which exceeds 90-wt percentage  $SiC_2$  (Zhang et al., 2010). The chemical composition of rice husk ash is dependent on a number of factors, such as the type of soil for growing rice plants, the fertilizing practices, environment,

temperature and duration of burning. These factors influence both the percentage of silica and its mineralogical nature.

Handling of this Rice husk is a big problem because of its low density and less commercial interest. Transportation of this husk is also problematic, and its creates various problem related to its disposal and when it is burnt in the field it creates serious environmental issue (Pode, 2016). Rice husk and rice husk ash could be obtained freely or for a nominal price. The heap burning method produces poor quality rice husk ash. It consists of large amount of unburnt carbon, which lowers the silica content (Patel et al., 1978). The original amorphous nature of the silica is destroyed and the resulting ash is largely of crystalline character; as a result, it becomes comparatively less chemically reactive (Mehta ,1977). To obtain high silica content, the combustion process according to the specification of amorphous content available, be performed, as the chemical treatment and combustion process were believed to lead the change of the microstructure silica from amorphous to crystalline state (Burzo, 2013). After combustion, the produced rice husk ash may contain 80% -95% of silica mineral, while others are metallic impurities. It is economically feasible raw material for preparing silica gels as well as powder. Rice husk ash has become a major source for synthesis of silica (Patil et al., 2014; Supakorn et al., 2009; Shelke et al., 2010; Della et al.,2002; Supitcha et al., 2009; Singh et al.,2008). Precipitated silica can be widely utilised in many of the industries today (Rama-Rao et al., 1989). Rice husk has very high value applications, for example, it is used in preparation of silica (silica gel as well as powder), zeolites, silicon nitride and silicon carbide. It is also, used in the preparation of silicon chip and making of lightweight construction materials. It has various other important applications such as synthesis of silicones and it's alloys, synthesis of soluble silicate, synthesis of chemical based silicon (Pode, 2016; Della et al., 2002; Tzong-Horng, 2004; Wang et al., 1998; Conradt et al., 1992; Mohamed et al., 2015).

# 2. Physico-chemical properties of metallurgical grade silicon

Metallurgical grade silicon has elemental composition as: ~2500 ppm – Al, Fe; ~600 ppm – Ca, Cr, Ti, Ni; ~100 ppm – B, Cu, Mg, Mn, Mo, P, V, Zr and others.. To remove the interfering compounds, for example silicon carbide, an excess of the initial silicon dioxide is used. As a result, high purity silicon is obtained (98% and higher) from of the plasma process (Jadhavar et al., 2017; Cai et al., 2014; Su et al., 2012; Bi et al., 2012; Abdi et al., 2008; Niu et al., 2006).

The structural and electrophysical parameters of the Metallurgical grade silicon are also the main criteria for the suitability of metallurgical grade silicon. Electrophysical parameters largely depend on the degree of chemical purity of silicon, on the structure of its crystals, their location and dimensions, as well as on the presence of intergranular boundaries, the accumulation of dislocations and various inclusions of phase formations (Jeong and Kim, (2012).

# 3. Production and purification of silica from Rice Husk and rice husk ash

In nature, the polymorphs of silica are quartz, cristobalite, tridymite, coestite, stishovite, lechatelerite and opal (Velupillai et al, 1997). It is this silica concentrated in the rice husk when it is burnt at a particular temperature over a specific time that makes the ash so valuable unlike every other agricultural waste product.

The production of silica from rice husk can be easy and requires low cost. The silica content found in rice husk is widely used in many industries (Zhang et al., 2010). Yunusa et al (2016) described a method of production of silica from Rice husk where they said it was sieved to eliminate clay particle and this was washed with distilled water and dried in an oven at 100°C for 24hrs. Acid

leaching of the rice husk was carried out to remove soluble elemental impurities such as iron, magnesium, calcium etc. The process of leaching was carried out at 10 wt% solids in 10wt% HCl. The HCl solution was prepared from a standard HCl stock of concentration of 37 wt% and density of 1.19 g/ml. The dried RH was soaked in the prepared solution of 10 wt% HCl for 24hrs. The treated rice husk was washed again thoroughly with distilled water until pH became 7 and then dried at 1000°C for 24hrs. After which pyrolysis followed in an oxygen atmosphere at over 400°C for 6 hours.

Rice husk ash is obtained by burning of rice husk and chlorinating its silica content to silicon tetrachloride, a raw material for silicon. Theoretically, the direct reduction of  $SiC_2$  sand with carbon to yield Si could be possible but temperature must be more than 2000°C. When  $SiO_2$  in rice husk reacts with chlorine gas in the presence of carbon, the  $SiC_2$  can easily and efficiently change to  $SiCl_4$  at a lower temperature (Basu et al, 1973).

 $SiO_2 + 2C + 2CI_2 \rightarrow SiCl_4 + 2CO$  (21)

SiCl<sub>4</sub> is purified by distillation because of its boiling point of 57.6 °C, and this high purity SiCl<sub>4</sub> is converted to high purity Si by reacting with Zn metal (Okutani, 2009).

Many impurities like magnesium silicate or orthosilicate were leached with hydrogen fluoride followed by a combination of hydrogen fluoride and tetraoxosulphate (VI) acid, which were more or less completely removed (Ikram and Akhter, 1988). On the other hand, magnesium compounds (silicate) and untreated silica were leached with a mixture of concentrated tetraoxosulphate (VI) acid and hydrogen fluoride at around 110°C in a Teflon vessel Banerjee et al., 1982). After acid treatment the products were washed and dried. The final products were fine powders of silicon. Therefore, purification of silicon from impurities should be accompanied by the establishment of its structure, preferably with a minimum amount of intergranular boundaries, and also by studying the relationship between the structure and properties of metallurgical silicon (Zhilkashinova, et al., 2018).

Some studies that investigated methods used to obtain and purify silica from rice husk ash can be seen in Table 2 and in addition, also, treatments by some researchers used to further purify silica from rice husk ash are shown in Table 3.

Study	Objective	Summary of method used	Main results
Sankar et al.,	To produce	• Combustion of rice husk in	Spherical,
2016	nanosilicon powder	the open.	completely
	from three kinds of	Acid leaching	amorphous silica
	rice husk.	<ul> <li>Incineration at 700°C under</li> </ul>	particles with large
		atmospheric conditions	specific surface area
			and composed only
			by Si and O from all
			kinds of rice husk.
Bakar, 2016	To investigate the	• Washing of rice husk with	All the silica
	ideal conditions to	water	produced had
	obtain high purity	Acid leaching	amorphous
	silica.		particles, and rice

Table	<b>2.</b> Studies	that inve	estigated	methods	used to	obtain	and	purify	silica	from	rice	husk	ash

		• Incineration at 500, 600, 700, 800, and 900 °C for 2 h under atmospheric conditions	husk leached with HCl produced the highest content of silica (99.58%) at 600 °C.
Ma et al.,2012	To develop a new, recycling-based technique to produce silica from RHA.	<ul> <li>Acid leaching of RHA</li> <li>Extraction in reactor with NH4F</li> <li>Acid precipitation of silica</li> </ul>	Spherical, completely amorphous silica particles measuring 50 to 60 nm in diameter and containing only Si andO, with yield of 94.6%.
Liou, 2011	To investigate the effect of experimental conditions on the characteristics of the nanosilica obtained.	<ul> <li>Leaching of rice husk with water and then HCl</li> <li>Incineration</li> <li>Extraction with NaOH, forming silicate</li> <li>Precipitation</li> </ul>	Best results with pH 3, silicate 0.15M, aging time of 12 h at 50°C, with 99.48% purity silica.
Fernandes,2006	To evaluate the leaching of RHA with NaOH to easily obtain highly reactive colloidal silica.	<ul> <li>Extraction of silica with NaOH 1M</li> <li>Precipitation using H<sub>2</sub>SO<sub>4</sub> drop by drop</li> </ul>	The best Si:Na mass ratio was 4:1, and the highly reactive colloidal silica was obtained at low energy investment.
Yalçin and Sevinç, 2001	To obtain high purity silica with large specific surface area and to evaluate the competitiveness of silica from rice husk.	<ul> <li>Washing of rice husk with water</li> <li>Chemical treatments (acid leaching, alkaline leaching)</li> <li>Incineration at 600°C under different conditions (static oven, argon flow, oxygen flow, air flow)</li> </ul>	Amorphous silica particles with maximum specific surface area of 321 $m^2/g$ 99.66% purity, depending on the treatment. The highest purity silica was obtained with prior acid treatment and incineration in oxygen atmosphere.
Kalapathy, 2000	Investigate the efficacy of acid leaching of RHA before alkaline extraction and washing of silica	<ul> <li>Acid leaching</li> <li>Extraction of silica with NaOH</li> <li>Precipitation with HCl</li> <li>Washing with water</li> </ul>	Initial acid leaching did not improve purity, the washing with water reduced Na and K levels, and silica yield was

IIARD – International Institute of Academic Research and Development

	obtained with water.		excellent when extraction was carried out with NaOH 1 N.
Conradt, 1992	To obtain high purity silica with large specific surface area and to evaluate the competitiveness of silica from rice husk.	<ul> <li>Washing rice husk with water</li> <li>Different chemical treatments (acid leaching, alkaline leaching, and enzymatic digestion)</li> <li>Incineration at 600°C (static oven, air flow, steam)</li> </ul>	Except for leaching with NaOH, all other treatments produced amorphous silica with large specific surface area, and high purity silica was obtained with acid leaching with HCl.
Riveros, 1986	To optimize the production of silica from rice husk.	<ul> <li>Washing rice husk with water</li> <li>Acid leaching</li> <li>washing with distilled water and dried</li> <li>Incineration</li> <li>Leaching of RHA</li> </ul>	Silica with approximate purity of 99.98% with three washing cycles, 6-h acid leaching, 6 leaching cycles with HCl 3% at 90°C, and the main contaminant was Ca (100 ppm).
Maeda et al,2001	To investigate the effect of experimental conditions on the characteristics of the silica polymorphs obtained.	<ul> <li>Decarbonization</li> <li>high temperature in the presence of oxygen</li> </ul>	The relative proportion of the different silica polymorphs in RHA depends not only upon the combustion temperature and atmosphere but also on the time for which the RH has been burnt.
Mehta,1977	To optimize the production of amorphous silica from rice husk.	<ul> <li>Decarbonization</li> <li>keeping the temperature below 500 C for prolonged periods</li> <li>maintaining oxidizing conditions</li> </ul>	Obtained totally amorphous silica

Yeoh, 1979	To obtain the relationship between temperature and duration of burning of rice-husk in the development of amorphous rice- husk ash silica	<ul><li>Decarbonization</li><li>high temperature</li></ul>	Ash remained amorphous at 900C, when this temperature was maintained for a period less than one hour.
Heaney, 1994	Study of the structure and chemistry of the low-pressure silica Polymorphs	<ul> <li>Decarbonization</li> <li>high temperature</li> <li>Heated for more than five minutes</li> </ul>	Ash becomes crystalline silica when heated at 1000 C for more than five minutes. The most common form of crystalline silica found in RHA is quartz, but cristobalite and tridymite are also present as the other forms of crystalline silica, although tridymite and cristobalite are stable at 867-1470 C and 1470-1727 C, respectively, at atmospheric pressure
Chopra et al,1981	The production of rice husk ash and its transformations	<ul> <li>Carbonation</li> <li>burnt RH at 700 C</li> </ul>	Evaluated the ash by X-ray diffraction (XRD) techniques and found that it was amorphous. Further heating of this ash at the same temperature transformed some of it into a quartz crystalline state.
Ankra, 1975	Studied the production of black silica under varying conditions	<ul> <li>Carbonation</li> <li>efficient RH pyroprocessing</li> <li>chemical treatment</li> </ul>	It was proposed that cellulose and other combustibles should be burnt out without

IIARD – International Institute of Academic Research and Development

Ikram and	Preparation of	<ul> <li>grinding of RH before preparing ash.</li> <li>Prepared RHA containing</li> </ul>	damaging the pore structure of the silica-rich skeleton. He showed that if pyroprocesssing occurs in the range 450°C - 500°C, the residual carbon, though amorphous in nature, cannot be removed on later thermal treatment. The result; revealed
Akhter,1988	Polycrystalline Silicon Dioxide from Rice Husk Ash.	<ul> <li>87% of SiC<sub>2</sub> to produce polycrystalline silica from it</li> <li>Acid leached RH was heat treated at 300 C to 1200 C for four hours and subjected to extensive XRD studies.</li> </ul>	that the ash was amorphous below 800 C, with its conversion to crystalline form commenced at 800 C. Tridymite and a quartz co-existed in comparable quantities at this temperature and the proportion of the latter silica phase increased with increasing temperature.

# Table 3. Treatments used to purify silica from rice husk ash

References	Treatment
Dietl,1981; Iler, 1979;	RHA samples were washed with HCl 1M (10 g sample/100 mL
Zemnukhova. et al,2006;	acid) for 1 h. RHA was filtered and washed with deionized water
Bullis, 1990; Goetzberger,	upon neutral pH. Samples were dried at 105°C for 24 h and then
et al, 2003.	treated in a muffle stove in air at 800°C for 1 h at 5 °C/min and
	cooling in the oven down to environment temperature.
Braga, et al,2008;	Extraction based on the solubility of amorphous silica in alkaline
Lee,2010; Ikram and	pH and precipitation in lower pH. All parameters used were based
Akhter, 1988; Bathey and	on a literature review of the articles. Briefly, 200 mL NaOH 1 M
Cretella, 1982	were added to 20 g RHA.
	The material was boiled for 1 h with constant stirring. After
	cooling, samples were filtered and the filtrate obtained was titrated
	with HCl 1 M upon neutral pH. After aging time of 48 h, water

	was added and the mixture was centrifuged and washed serially. The material was dried in a stove at $105^{\circ}$ C for 48 h
Wang at al 1003	Perperted that the adjustic combustion temperature of this
wallg et al,1993	reaction is 1760K and the product Si (molting point 1682K) is
	malted
H : ( 12000	
Hussein et al,2009	Utilized RHA for extracting solar grade silicon, depending upon
	the silica content of prepared RHA. 18:27 (Mg:Si0 <sub>2</sub> ) was found as
	the most suitable ratio for reduction; resulting silicon powder
	leached with different acids and evaluated as 99.85% pure.
Patel et al,1987	Treated rice husk at temperature up to 1000°C, for different time
	durations and attempted to retain the amount of rice husk carbon,
	necessary for carbothermic reduction of accompanying $SiC_2$ .
	Husk was also treated with various acids and bases separately.
	This experimentation resulted is 99% pure silicon.
Barati et al, 2011	A method of obtaining silicon of 6N (99.9999%) purity by
	reducing white rice husk ash with magnesium at a temperature of
	800°C followed by several successive acid leaching treatments
	was reported.
Singh and Dindhaw, 1978	They reported obtaining silicon of 6N (99.9999%) purity by
	reducing white rice husk ash with magnesium at temperature of
	800 °C followed by several successive acid (mixtures of HF,
	$H_2SO_4$ and $HCl$ ) leaching treatments. The reduction was also
	investigated at temperatures of 850 and 900 °C. The silica in their
	rice husk fired beyond 800 °C was observed to have attained some
	degree of crystalinity. They also suggested the possibility of
	obtaining silicon of similar purity by directly smelting the purified
	amorphous silica with carbonaceous reductants in electric furnace
	followed by leaching with acids and repeating the smelting and
	leaching for about nine times. The authors however did not
	disclose the method used to analyze their silicon to the 6N purity
Amick at al 1082	They patented a process for producing rice busk silice with
Alliek et al. 1982	adjusted silica to earbon ratio for direct reduction into high nurity
	adjusted since to carbon ratio for direct reduction into high purity
	sincon with no addition of carbonaceous reductants. The method
	as described by Afflick <i>et al.</i> comprise of feating fice flusk in
	semiconductor grade hydrochloric acid followed by pyrolysis of
	LICIAR and stream for a period of shout one hour. The surplused
	HCI/Ar gas stream for a period of about one nour. The pyrotyzed
	rice nusk which has a carbon -to -slift ratio of 4:1 was further
	processed in a conventional fluid bed combuster with $Ar/CO_2$
	atmosphere at a temperature of 950 °C to obtain stoichiometric
	carbon -to- silica ratio of 2:1. Reduction of the ash so produced at
	a temperature of 1900 °C REPORTEDLY yielded silicon with total
	impurity less than 75 ppm. The boron and phosphorus content
	were reported to be less than 10 ppm each.

Hunt et al, 1984 Bose et al, 1982	Investigated the possibility of producing high purity silicon from rice husk by purifying the rice husk silica according to the method of Amick <i>et al</i> , followed by pelletizing and reduction in a modified electric arc furnace. The pelletizing was carried using carbon black as a reductant and sucrose as a binder. The authors concluded that purified RHA could be a potential silica source for solar grade silicon production.
	rice husk ash at a temperature of 600-650 °C to melting and directional solidification and found that boron was the active impurity in the polycrystalline silicon ingot obtained. They determined the minority carrier life time of their polycrystalline silicon material to be of the order of 1-5 $\mu$ s and concluded that to be promising for photovoltaic applications.
Banerjee <i>et a</i> l, 1982	They reduced acid leached rice husk ash by intimately mixing the ash with magnesium powder and firing the powdered mixture in a sealed graphite crucible in a muffle furnace. The reaction product was successively leached in mineral acids (HCl, H <sub>2</sub> SO4, and HF) in a Teflon beaker. A spectrochemical analysis of the final silicon product showed a high boron content of 20-200ppm as well as high magnesium (50-1000ppm) and aluminum (10-200 ppm). They attributed the contamination of the silicon to the use of laboratory grade magnesium and also from glassware. In comparison with the silica produced by Singh and Dhindaw, Barnerjee <i>et al.</i> reported the silica had attained some degree of crystalinity when produced from roasting of husk at temperatures between 500-600 °C.
Ikram and Akhter, 1988	Reported silicon of 99.95% purity with Boron content of approximately 2ppm. The process steps followed by Ikram and Akhter, comprise boiling rice husk in 1:10 HCl and distilled water for 15 minutes, burning of the acid treated husk in air to obtain black ash, firing of the black ash in a muffle furnace to obtain white ash, leaching of the white RHA in dilute HCl, reduction of the leached white RHA with magnesium of 4N purity followed by sequential leaching with HCl, HF and a mixture of HF and H <sub>2</sub> SO4. Contrary to the report by Banerjee <i>et al</i> and in agreement with Singh and Dhindaw, these authors reported that no crystalinity was observed in the RHA produced at 620 °C. Only the RHA fired to 900 °C had attained significant crystallinity with reflections or sharp peaks of different phases of SiO <sub>2</sub> in their XRD pattern. They concluded that the silicon can be upgraded to solar grade silicon by conventional refining methods.
Mishra et al., 1985	They mixed a stoichiometric composition of granular calcium and purified rice husk silica and subsequently fired the powdered mixture in a sealed sillimanite crucible in a muffle furnace at

IIARD – International Institute of Academic Research and Development

temperature of about 720 °C. The reduction product was milled to
fine powder and successively leached with concentrated nitric acid
(HNO <sub>3</sub> ) and hydrofluoric (HF) acid to obtain silicon of 99.9%
purity with a boron content of 10 ppm. They suggested that the use
of MgO coated crucibles and high purity reagent can lead to
producing solar grade silicon by this method.

# 4. Upgrade of Metallurgical grade silicon

Several methods for purification of metallurgical grade silicon have been reported in literature. One of these methods is to upgrade economical metallurgical grade silicon to higher grade of silicon using plasma purification. Target impurity concentrations are summarized in Table 4 and are compared to typical impurity concentrations that are found in metallurgical grade silicon (Sarti and Einhaus, 2002).

Impurities	MG-Si (ppm)	UMG-Si (ppm)
В	40	<30
Р	20	<15
0	3000	<2000
С	600	<250
Fe	2000	<150
Al	100-200	<50
Ca	500-600	<500
Ti	200	<5
Cr	50	<15

Table 4. Target impurity concentrations in upgraded metallurgical grade (UMG) silicon

# 5. Application of metallurgical grade silicon in alloys

It is known fact that alloys present good corrosion and weldable properties. Typical markets are building and transport industries (Ceccaroli and Lohne, 2003). In the aluminium industry, silicon is added to molten aluminium in which it is dissolved. Silicon is used in order to improve the viscosity, the fluidity of liquid aluminium and the mechanical properties of commercial alloys. The iron, calcium and phosphorus content in silicon are particularly critical for such applications. Two important groups of aluminium alloys in which silicon is one of the main alloying elements are Casting alloys which are produced by adding silicon to the melt, the fluidity is improved. Aluminium alloys near the eutectic composition are therefore, used in thin-walled castings. If a few tenths of a percent of magnesium is added, the alloys may be age-hardened and thus double their yield strength. To counteract the formation of large needle-shaped particles, the alloys are normally modified with sodium, strontium or phosphorus. The alloys present good corrosion properties. The other are the wrought alloys which are widely used as medium-strength structural alloys. Typical silicon content is 0.5 to 1.0%. These alloys have good hot-working properties and are age hardening. These alloys are therefore well suited for extrusion of profiles.

# 6. Further uses of metallurgical grade silicon

Metallurgical-grade silicon (MG-Si) is an important metal, which has a range of diverse industrial applications.

Silicon of high purity is used in semiconductor technology (Cochard et al., 2013; Hassan et al., 2016). While silicon of technical purity is used in ferrous and non-ferrous metallurgy, for obtaining alloys (Ozawa et al., 2016; Fan et al., 2016), doping (Ardeshiri et al., 2017) and deoxidizing steel and alloys (Garibaldi et al., 2016). as well as in the production of silicides (Savelli et al., 2016; Cho et al., 2010; Kittl et al., 2008; Homewood et al., 2001), etc. Metallurgical grade silicon is the main raw material for the production of solar-grade silicon used in the production of photovoltaic energy converters for solar cells (Yu et al., 2016; Eisenlohr et al., 2016). Metallurgical grade silicon is also used in the preparation of organosilanes, and the production of hyperpure 'electronic grade' silicon (>99.99% Si), which is used in the electronics industry as well as solar cells (PV Education. 2013; Ali et al., 2018).

# 7. Conclusion

Silicon and its compounds have broad prospective application in a number of industrial fields but, the sustainable, gainful, and scalable synthesis of them from rice husk and rice husk ash is encouraging. Utilization of rice husk could reduce the cost of waste treatment and solve the disposal problems. For manufacturing and synthesizing new materials, rice husk and its ash are used directly. It is an inexpensive alternative to obtain silicon for the ally industries. The metallurgical grade silicon, depending on its purity, can be prepared by various methods. To produce the silicon to satisfy the requirements of various industries that require silicon as their raw material, it is important to remove the impurities of it at every step; one of the approach may be by acid leaching at high temperature to improve the final product's purity.

# Funding

This project was possible because of the provision of fund by Tertiary Education Trust Fund (TETFUND) Nigeria under the Institutional Based Research Grant number TETFUND/DR&D/CE/UNI/UYO/2020/RP/VOL.1.

#### Acknowledgement

The authors will like to appreciate the managements of TETFUND for providing the fund and University of Uyo for the enabling environment to carry out this research work.

### References

- Abdi Y, Hashemi P, Mohajerzadeh S, Jamei M, Robertson MD, Burns MJ, MacLachlan JM (2008) Silicon nano-crystalline structures fabricated by a sequential plasma hydrogenation and annealing technique. Thin Solid Films 516:3172–3178
- Abu Bakar R, Yahya R, Gan SN. (2016). Production of High Purity Amorphous Silica From Rice Husk. *Procedia Chemistry*. 19:189-195.
- Ali, H.H.M. El-Sadek, M.H. Morsi, M.B. El-Barawy, K.A. and Abou-Shahba, R.M. (2018). Production of metallurgical-grade silicon from Egyptian quartz. *The Southern African Institute of Mining and Metallurgy, Vol. 118, pp. 143-148. ISSN 2225-6253.*
- Amick, J., A. (1982). Purification of rice hulls as a source of solar grade silicon for solar cells. Journal of the electrochemical society. 129 (4), 864-866.
- Ankra, K. (1975). *Studies of black silica produced under varying conditions* (Doctoral dissertation, University of California, Berkeley).
- Ardeshiri A, Sohi MH, Safaei A (2017) Surface alloying of A2618 aluminum with silicon and iron by TIG process. Surf Coat Tech 310:87–92
- Banerjee, H. D, Sen, S. and Acharya, H. N. (1982). Investigations on the production of silicon from rice husks by the magnesium method. Materials science and engineering. 52(2), 173-179.
- Barati, M. et al. (2011). Production of high purity silicon from amorphous silica, WO Patent 2,011,022,817.
- Basu P. K. Judson King C. and Lynn S. (1973). Rice husk as a source of high purity silica. America Institute of Chemical engineers Journal. Vol 19, pp.43a
- Bathey, B. R. and Cretella, M. C. (1982). Review Solar-Grade Silicon, Journal of Materials
- Beagle, E.C. (1978). Rice Husk conversion to energy. Rome, Italy. FAO Agricultural Services Bulletin 37.
- Bi Y, Su X, Zou S, Xin Y, Dai Z, Huang J, Wang X, Zhang L (2012) Plasma-etching fabrication and properties of black silicon by using sputtered silver nanoparticles as micromasks. Thin Solid Films 521:176–180
- Bose, D. N, Govindacharyulu, P. A and Banerjee, H. D. (1982). Large grain polycrystalline silicon from rice husk. Solar energy materials. 7 (3), 319-321.
- Braga, A. F. B., Moreira, S. P., Zampieri, P. R., Bacchin, J. M. G. and Mei, P. R.(2008) New
- Bullis, M. W. Silicon Material Properties, in Handbook of Semiconductor Silicon
- Burzo, M. Komarov, P. and Raad, P. (2013). Thermal transport properties of gold-covered thinfilm silicon dioxide, IEEE Transactions on Components and Packaging Technologies, Vol. 26, no. 1, pp. 80-88.
- Cai L, Ren X, Fan B, Zheng J, Chen C (2014) Effect of temperature on crystalline silicon solar cells processed from chemical and metallurgical route. Optik 125:3918–3921 Calcium Reduction of Rice-husk White Ash, Journal of Materials Science. Vol. 20,
- Ceccaroli, B and Lohne, O. (2003). Solar-grade Silicon Feedstock: in *Handbook of Photovoltaic Science and Engineering*, Edited by A. Luque and S. Hegedus. Hoboken, NJ: Wiley, pp. 154-160.

Characterization of rice husks and the products of its thermal degradation in air or

- Cho IJ, Park KT, Lee SK, Nersisyan HH, Kim YS, Lee JH (2010) Rapid and cost-effective method for synthesizing zirconium silicides. Chem Eng J 165:728–734
- Chopra, S. K, Ahluwalia, S. C and Laxmi, S. (1981). Technology and manufacture of rice-husk ash masonry (RHAM) cement. In: Proceedings of ESCAP/RCTT Workshop on Rice-HuskAsh Cement, New Delhi.
- Cochard J, Yonenaga I, M'Hamdi M, Zhang ZL (2013) A novel constitutive model for semiconductors: the case of silicon. J Mech Phys Solids 61:2402–2432
- Conradt, R., Pimkhaokham, P. and Leela-Adisorn, U. (1992). Nanostructured silica from rice husk. Journal of Non Crystalline Solids. 145:75-79
- Della, V. P., I. Kuhn and Hotza, D. (2002). Rice husk ash as an alternate source for active silica production. Materials Letters. 57(4):818-821.
- Dietl, J. (1981). Current Aspects in Low-cost Silicon Technology, in Proceedings Symposium on
- Eisenlohr J, Tucher N, Hauser H, Graf M, Benick J, Bl<sup>\*</sup>asi B, Goldschmidt JC, Hermle M (2016) Efficiency increase of crystalline silicon solar cells with nanoimprinted rear side gratings for enhanced light trapping. Sol Energy Mater Sol Cells 155:288–293
- Fan Q, Chai C, Wei Q, Yang Y, Yang Q, Chen P, Xing M, Zhang J, Yao R (2016) Prediction of novel phase of silicon and Si-Ge alloys. J Solid State Chem 233:471–483
- Fernandes AA. (2006). *Síntese de Zeólitas e Wolastonita a Partir da Cinza da Casca do Arroz.* [Thesis]. São Paulo: Universidade de São Paulo.
- Frolking, S., Qiu, J., Boles, S., Xiao, X., Liu, J., Zhuang, Y., and Qin, X. (2002). Combining remote sensing and ground census data'to develop new maps of the distribution of rice agriculture in China. Global Biogeochemical Cycles, 16(4).
- Garibaldi M, Ashcroft I, Simonelli M, Hague R (2016) Metallurgy of high-silicon steel parts produced using selective laser melting. Acta Mater 110:207–216
- Genieva, S. D., Turmanova, S. C., Dimitrova, A. S., and Vlaev, L. T. (2008).
- Giddel, M. R.,andJivan, A.P. (2007). Waste to wealth, potential of rice husk in India literature review. International Conference on Cleaner Technologies and Environmental Management PEC. pp586-590
- Goetzberger, A. Hebling, C and Schock, H. (2003). Photovoltaic Materials, History, Status and
- Hassan HARA, Hassan MAM, Agool IR (2016) Construction of semiconductor nanocomposite on porous silicon using chemical method. Optik 127:11411–11417
- Heaney, P. J. (1994). Structure and chemistry of the low-pressure silica polymorphs. Reviews in mineralogy and geochemistry. 29 (1), 1-40.
- Homewood KP, Reeson KJ, Gwilliam RM, Kewell AK, Lourenc o MA, Shao G, Chen YL, Sharpe JS, McKinty CN, Butler T (2001) Ion beam synthesized silicides: growth, characterization and devices. Thin Solid Films 381:188–193

http://composite.about.com/library/glossary/a/bldef-a329.htm.

- Hunt, L. P. Dismukes, J. P. Amick, J. A. Schei, A. and Larsen, K. (1984). Rice Hulls as a Raw
- Hussein, A. M., EL-Saied, Houssni and Yasin, Mohamed H. (2007.).Bioconversion of hemicelluloses of rice hull black liquor into single-cell protein. Journal of chemical technology and biotechnology. 53 (2), 147-152.
- Ikram, N and Akhter, M.91988). X-ray diffraction analysis of silicon prepared from rice husk ash. Journal of materials science. 23 (7), 2379-2381.
- Iler, R.K. (1979). The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface

- Jadhavar A, Pawbake A, Waykar R, Jadkar V, Kulkarni R, Bhorde A, Rondiya S, Funde A, Patil D, Date A, Pathan H, Jadkar S (2017) Growth of hydrogenated nano-crystalline silicon (nc-Si:H) films by plasma enhanced chemical vapor deposition (PE-CVD). Energy Procedia 110:45–52
- Jeong KP, Kim YK (2012) Electrical properties of the multi-crystalline silicon ingots grown with UMG (upgraded metallurgical grade) silicon materials. Sol Energy Mater Sol Cells 107:201–204
- Kalapathy U, Proctor A, Shultz J. A simple method for production of pure silica from rice hull ash. *Bioresource Technology*.; 73(3):257 262.
- Kittl JA, Opsomer K, Torregiani C, Demeurisse C, Mertens S, Brunco DP, Van Dal MJH, Lauwers A (2008) Silicides and germanides for nano-CMOS applications. Mater Sci Eng B 154-155:144–154
- Lee, S. M. Dictionary of Composite Materials Technology. (2010). Accessed online at
- Liou TH, Yang CC. Synthesis and surface characteristics of nanosilica produced from alkaliextracted rice husk ash. *Materials Science and Engineering B*.; 176(7):521-529.
- Ma X, Zhou B, Gao W, Qu Y, Wang L, Wang Z, et al. (2012). A recyclable method for production of pure silica from rice hull ash. *Powder Technology*. 217:497-501.
- Maeda, N., et al. Development of a new furnace for the production of rice husk ash. Aci special publications. 199 (2), 835-852.

Material for Producing Silicon, Journal of the Electrochemical Society. Vol. 131, pp. 1683-1686.

Materials and New Processing Technologies for Photovoltaics., Edited by; Amick, J.A. Kapur, V.K. and Dietl, J. Pennington, NJ 10 S. Main St., Pennington 08534: The Electrochemical Society. Vol. 81-3, pp. 48-61.

- Mehta, P. K. (1977) Properties of blended cements made from rice husk ash. In: A Cl Journal Proceedings, A CL.
- Mehta, P. K. Properties of blended cements made from rice husk ash. In: A Cl Journal Proceedings, ACI..
- Mishra, P. Chakraverty, A. and Banerjee, H. D.(1985) Production and Purification of Silicon by
- Mohamed, R. M., I. A. M khalid and Barakat, M. A. (2015). Rice husk ash as a renewable source for the production of zeolite NaY and its characterization. Arabian Journal of Chemistry. 8(1):48-53.

nitrogen atmosphere. Journal of Thermal Analysis and Calorimetry. 93(2), 387-396.

- Niu Y, Liu X, Ding C (2006) Phase composition and microstructure of silicon coatings deposited by air plasma spraying. Surf Coat Tech 201:1660–1665
- Okutani Takeshi (2009). Utilizaton of silica in Rice hulls as raw materials for silicons semiconuctors. Journal of metals, materials and minerals. Vol 19 No. 2, pp51-59. Outlook. Materials Science and Engineering: R: Reports. Vol. 40, pp. 1-19.
- Ozawa H, Hirose K, Yonemitsu K, Ohishi Y (2016) High-pressure melting experiments on Fe–Si alloys and implications for silicon as a light element in the core. Earth Planet Sci Lett 456:47–54
- Patel M., Karera, A. and Prasanna, P. (1978). Effect of thermal and chemical treatments on carbon and silica contents in rice husk. Journal of materials science, 22 (7), 2457-2464.
- Patel, M., Karera, A. and Prasanna, P. (1978).Effect of thermal and chemical treatments on carbon and silica contents in rice husk. Journal of materials science. 22 (7), 2457-2464

IIARD – International Institute of Academic Research and Development

Page **97** 

Patil, R. Dongre, R. and Meshram, J. (2014). Preparation of silica powder from rice husk. Journal of Applied Chemistry. 27:26-29.

 Pode, R., (2016). Potential applications of rice husk ash waste from rice husk biomass power plant. Renewable and Sustainable Energy Reviews. 53:1468-1485
 pp. 4387-4391. Processes for the Production of Solar-grade Polycrystalline Silicon: A review. Solar

Energy Mater. Solar Cells. Vol. 92, pp. 418-424.

Properties, and Biochemistry," Wiley, New York. pp. 462-463.

PV EDUCATION. (2013). Refining silicon.

http://pvcdrom.pveducation.org/MANUFACT/REFINE.HTM

- Rama-Rao, G. Sastry, A. R. K. and Rohatgi P. K. (1989). Nature and reactivity of silica available in rice huskand its ashes. Bulletin Material Science. Vol 12, pp 469 -479.
- Real, C. M., Alcalaand J.M.Criado. (1996). Preparation of silica from rice husks. Journal of the American Ceramic Society.. 79(8): 2012-2016.
- Riveros H, Garza C. (1986) Rice husks as a source of high purity silica. *Journal of Crystal Growth*.; 75(1):126-131.
- Sankar S, Sharma SK, Kaur N, Lee B, Kim DY, Lee S, et al. (2016). Biogenerated silica nanoparticles synthesized from sticky, red, and brown rice husk ashes by a chemical method. *Ceramics International*. 42(4)4875-4885.

Sarang, M.,S. Bhattacharyya and Behera, R. C. (2009).Rice effect of temperature on morphology and phase transformations of nanocrystalline silica obtained from rice husk. Phase transitions: a multinational journal. 82(5):377-386.

- Sarti D. and Einhaus R.(2002). Silicon feedstock for the multi-crystalline photovoltaic industry. Solar Energy Materials and Solar Cells, 72, 27-40.
- Savelli G, Stein SS, Bernard-Granger G, Faucherand P, Mont'es L (2016) Monocrystalline molybdenum silicide based quantum dot superlattices grown by chemical vapor deposition. Superlattice Microst 97:341–345 science, 28 (14), 3693-3708.

Science. Vol. 17, pp. 3077-3096.

- Shelke, V. R., S. S. Bhagade and Mandavgane, S. A. (2010). Mesoporous silica from rice husk ash. Bulletin of Chemical Reaction Engineering and Catalysis. 5(2):63-67.
- Singh, D., R. Kumar, A. Kumar and Rai, K. N. Synthesis and characterization of rice husk silica, silica carbon composite and H<sub>3</sub>PO<sub>4</sub> activated silica.Ceramica. 54(330):203-212.
- Singh, R. and Dhindaw, B. K. (1978). Production of High Purity Silicon for use in Solar Cells, in Sun, Mankind's Future Source of Energy : Proceedings of the International Solar Energy Congress. pp. 776-781.
- Soltani, N.,Bahrami A,Pech-Canul MI and Gonzalez LA.(2015). Review on the physicochemical treatments of rice husk for production of advanced materials. Chemical EngineeringJournal. 264:899-935.
- STAT, FAO. FAO (Food and agriculture Organisation); Rice market monitor, http://www.fao.org/fileadmin/templates/est/COMM MARKETS MONITORING
- Su H, Zhang J, Liu L, Fu H (2012) Preparation, microstructure and dislocation of solar-grade multicrystalline silicon by directional solidification from metallurgical-grade silicon. T Nonferr Metal Soc 22:2548–2553

- Supakorn, P., C. Pattanasuk S. Supon, K. Pristanuch, N. Kiattisak and Lee, C. (2009). Synthesis and characterization of SiO<sub>2</sub> nanowires prepared from rice husk ash. Journal of Metals, Materials and Minerals. 19(2):33-37.
- Supitcha, R., Wachira, P. and Natthapong, S. (2009) Preparation of silica gel from rice husk ashusing microwave heating. Journal of Metals, Materials and Minerals. 19 (2):45-50.

Syuhadah, S. N. and Rohasliney, H. (2012) Rice husk as biosorbent: A review, Health and the Environment Journal, Vol. 3, no. 1, pp. 89-95.
Technology, Edited by; W. C. O'Mara, R. B. Herring and L. P. Hunt, Park Ridge, N.J., (1990). U.S.A.: Noyes Publications. pp. 349-350.
thermo-chemical conversion of biomass. *Energy conversion and management*, 51

- Tzong-Horng, L. (2004). Evolution of chemistry and morphology during the carbonization and combustion of rice husk. Carbon. 42(4): 785-794. utilization in the synthesis and processing of materials. Journal of materials
- Velupillai, L., Mahin, D. B., Warshaw, J. W., & Wailes, E. J.(1997). A study of the market for rice husk-to-energy systems and equipment. Louisiana State University Agricultural Center, USA.
- Wang, H. P., K. S. Lin, Y.J.Huang, M. C. Li, and Tsaur, L. K. (1998). Synthesis of zeolite ZSM-48 from rice husk ash. Journal of Hazardous Materials. 58(1):147-152.
- Wang, L.L, Munir, Z.A and MAXIMOV, Y.M. (1993). Thermite reactions: Their
- Yadav V. (2021). Rice husk ash: A systematic review of its applications. International Journal of Current Research, Vol. 13, Issue, 06, pp. 17706-17713.
- Yalçin N, Sevinç V. Studies on silica obtained from rice husk. *Ceramics International*. 27(2):219-224.
- Yeoh, A.K, et al. The relationship between temperature and duration of burning of rice-husk in the development of amorphous rice-husk ash silica. In: Proceedings of UNIDO/ESCAP/RCTT, Follow-Up Meeting on Rice-Husk Ash Cement, Alor Setar, Malaysia. 1979.
- Yu P, Wu J, Liu S, Xiong J, Jagadish C, Wang ZM (2016) Design and fabrication of silicon nanowires towards efficient solar cells. Nano Today 11:704–737
- Yunusa, S., Ahmed, A. S. Bawa, S, G., Iyun, J. F. and Dauda, M. (2016). Preparation of High Grade Silica from Rice Husk for Zeolite Synthesis. Nigerian Journal of Basic and Applied Science, 24(1): 41-45 DOI: <u>http://dx.doi.org/10.4314/njbas.v24i1.7</u> ISSN 0794-5698.
- Zemnukhova, L., Egorov, A., Fedorishcheva, G., Barinov, N., Sokolânitskaya, T. and Botsul, A. (2006). Properties of Amorphous Silica Produced from Rice and Oat Processing Waste, *Inorganic Materials*. Vol. 42, pp. 24-29.
- Zhang, H. Zhao, X. Ding, X. Lei, H. Chen, X. An, D. and Wang, Z. (2010). A study on the consecutive preparation of d-xylose and pure superfine silica from rice husk, Bioresource Technology, 2010. Vol. 101, no. 4, pp. 1263-1267.
- Zhang, L, XU, C. C., and Champagne, P. (2010). Overview of recent advances in
- Zhilkashinova, A. M, Kabdrakhmanova, S. K., Troyeglazova, A. V. Abilev, M. B. (2018). Structure and Properties of Metallurgical-grade Silicon. Silicon. https://doi.org/10.1007/s12633-017-9751-6