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PRODUCTION OF TECHNICAL SILICON AND SILICON CARBIDE FROM RICE-HUSK

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In the article there are studied physical and chemical properties of silicon-carbonic raw material – rice-husk, thermophysical characteristics of the process of rice-husk pyrolysis in nonreactive and oxidizing environment; structure and phase composition of products of the rice-husk pyrolysis in interval of temperatures 150 – 850 °C and high temperature pyrolysis in interval of temperatures 900 – 1 500 °C. There are defined the silicon-carbon production conditions, which meet the requirements applicable to charging materials at production of technical silicon and silicon carbide.

Key words: silicon-carbon, rice-husk, pyrolysis, amorphous silica, properties

INTRODUCTION

Rice-husk is heavytonnage waste product of rice production. Only at rice processing plants of Kazakhstan there annually appear to 50 - 60 thousand tons of rice-husk which is generally sent to waste piles, making significant ecological problems in these regions. Special value of rice-husk, as chemical raw material, is its natural renewability. Due to this, problems of rice-husk utilization are too actual for today in all the countries producing rice: Japan, China, India, USA, Russia [1].

It is known that rice-husk belongs to number of rare materials of vegetable origin containing in its composition significant quantity of silica in amorphous form. Representatives of silicon-rich plants are met among several bloodkinds of tropical and field plants: in the field and needles of some trees. Content of silica in the ash of rice-husk reaches 90 – 97 %. Organic part of rice-husk is presented mainly by lignin 20 – 25 %, hemicellulose to 15 % and cellulose 40 – 45 %.

The first publication on research of properties and composition of rice-husk appeared in Germany in 1871, the next – in two years in the USA. Investigations on rice-husk processing are carried out in all the countries still growing the rice. Investigation results showed that rice-husk exposed to thermal processing may serve as valuable raw material for production of various silicon compounds possessing unique properties [1, 2].

Analysis of existing data on processing of rice-husk with production of amorphous silica showed that the more prospective are:

1. Technological scheme including: leaching of rice-husk by mineral acid solution: water flushing, drying, burning the husk at 450 – 500 °C, and then at 700 °C, packing of the product. Received amorphous silicon dioxide by its physical and chemical indicators exceeds produced in Russia and other countries similar product resulting of sodium silicate and crystal silicon dioxide (Institute of Chemistry FEB RAS) [2].
2. Technological scheme consisting of two consecutive operations: charring of husk in products of combustion of technical propane-butane with air excess with an aim to receive silicon containing product and discharge of final amorphous or crystal silicon dioxide with specified physical and chemical properties according to treatment regime (Engineering and technology center of Institute of Chemistry FEB RAS) [3].
3. Technological scheme including: water washing of rice-husk, thermal treatment – dry pyrolysis without access of oxygen at 500 – 900 °C with production of solid silicon-carbon (homogeneous mixture of amorphous silicon dioxide and carbon C > SiO_2) and liquid organic product (water-soluble mixture of phenols, acids, alcohols and neutral fraction). Silicon-carbon is proposed to be used as filling agent in rubber-technological and special carbonic products, as sorbent and feed additive; organic product – as antiseptic in medicine and agriculture, and also as flotation (RSE NCCPMRM RK) [1].

However, proposed technological schemes allow receive final product having limited application and inapplicable for further usage as a raw material for producing technical silicon.

Due to that, there was carried out work on studying physical and chemical properties of rice-husk as starting material for producing technical silicon and silicon carbide in Chemical Metallurgical Institute named after Zh. Abishev. In the result of carried out investigations there was established that after appropriate oxidation and thermal treatment of rice-husk it is possible to re-

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ceive solid product – silicon-carbon ($C < SiO_2$), in which interrelation of carbon and silicon is close to stoichiometric, that is necessary for reproduction of silicon from silica. In other words, at appropriate oxidation and thermal treatment of rice-husk, there are created conditions for improvement of efficiency of the process of production of new sorts of technical silicon, and silicon carbide, as well.

EXPERIMENTAL STUDIES

As the raw material for the research there was used rice-husk produced after treatment of rice grown in Bakbakty settlement of Almaty region, Balkhash district – region of Ili river's mouth.

By spectral (atomical-emissive) method of analysis there was established presence of rice-husk ash: Mn(0,04 %), Cu(0,03 %), P(0,3 %), Zn(0,015 %), Ti(0,01 %), As(<0,01 %), B(<0,03 %), Li(0,002 %). Also found out: Sc, Sb, Pb, Zr, Ga, W, Cr, Ni, Ba, Be, Nb, Mo, Sn, V, Cd, Yb, Ag, Co, Sr, cumulative quantity of which made 0,030 %. Elements Au, Hf, Hg, In, Ta, Te, Th, TI, U are not found out.

By chemical methods of analysis there was defined content in the rice-husk ash: $Fe_{com.}$ (0,13 %), CaO(3,75 - 5,44 %), Al_2O_3(0,36 %).

Ultimate composition of the rice-husk: C - 39,8 - 41,1 %; H – 5,7 - 6,1 %; O – 0,5 - 0,6 %; N – 37,4 - 36,6 %.

According to literature date, in the rice-husk connection of amorphous dioxide of silicon with carbon is realized molecularly. It provides maximal homogeneity of product appearing at following thermal oxidative treatment – silicon-carbon.

Source raw material for silicon-carbon – rice-husk (RH) is presented by immature kernels and directly, by husk (peeling). Sample of the source raw material in quantity of 3 kg was washed off of dockage and dried up at temperature of 20 – 25 °C to constant mass. Prepared in such a way source raw material for conduction of chemical, technical analyses and studying of phase composition was divided into three samples:

1 – composited sample of initial husk;
2 – husk (peeling);
3 – rice immature kernels.

Results of technical and chemical analyses of these samples are given in the tables 1 and 2.

Table 1 **Technical analysis of the rice-husk**

Sample	Technical analysis / %		
	Water, W^a	Volatile yield, V^d	Ash, A^d
1 - average sample of RH	4,35	49,48	18,65
2 - husk (peeling)	4,25	49,09	18,51
3 - rice immature kernels	4,91	61,95	12,86

From given data of technical and chemical analyses of the rice-husk it follows that silicon oxide in immature kernels is more on 1,38 % than in the husk.

Table 2 **Chemical analysis of the rice-husk**

Sample	Chemical analysis of ash / %				
	SiO_2	Al_2O_3	$Fe_{общ.}$	CaO	P
1 - average sample of RH	89,09	0,36	0,09	5,44	0,3
2 - husk (peeling)	91,31	0,57	0,13	3,75	0,3
3 - rice immature kernels	89,93	0,17	0,15	3,77	0,3

Research of phase composition of selected samples of initial rice-husk was carried out by X-ray phase analysis at installation XRDM-2 with Fe-K_α – radiation. According to X-ray phase analysis, silica (silicon dioxide) in all three selected samples of initial husk has slightly crystallize form as a variety of amorphous state of a material where basic mass is presented by amorphous structure. Thus, at diffractograms it is observed forming peak with interplanar distance of 4,05 Å, related to basic characteristic diffraction maxima of christobalite. It should be noted that diffraction pattern with diffuse peak in this area (angular locations 2Θ = 25 - 32°) is characteristic for amorphous structure of material [4].

There was carried out differential thermal analysis of initial rice-husk at derivatograph Q-1500 in air atmosphere in interval of temperature 20 – 750 °C. Heating rate made 10 °C/min. In studied temperature interval on curve DTA it is observed well expressed endothermal effect with maximum 135 °C, caused by water evaporation, and exothermic effect at the temperature 250 – 270 °C, indicating on beginning of volatile organic emissions lasting to temperature 600 – 650 °C. Mass loss at elimination of moisture and volatiles made correspondingly 7,5 – 10 % and 50 – 60 %.

Investigations on thermal oxidative treatment (pyrolysis) of the rice-husk defined mass loss (water and volatile organic materials) at firing within the limits of temperatures 150 – 700 °C, firing time 10 - 60 min and atmosphere pressure. It is established that mass loss makes: at 150 °C 7,02 and 11,88 %; at 200 °C 7,07 and 10,53 %; at 300 °C 23,92 and 43,46 %; at 400 °C 52,32 and 52,74 %; at 500 °C 57,32 and 61,20 %; at 600 °C 62,38 and 62,34 %; at 700 °C 62,2 and 61,84 % correspondingly at firing during 10 and 60 minutes. That is, for maximal elimination of volatiles from the rice-husk, it is necessary to conduct thermal oxidative treatment in interval of temperatures 600 – 700 °C during 10 - 20 minutes [5].

Thus, with usage of physical and chemical methods of analysis there are studied properties of the rice-husk – heavytonnage waste product of rice production. Ultimate composition is defined, chemical, technical and X-ray phase analyses, DTA are carried out.

It is shown that for further investigations it is appropriate to use the husk without content of immature kernels of rice. Content of silica in its ash is the largest – 91,31 %.

RESULTS AND DISCUSSION

Spectral analysis established presence of Mn, Cu, P, Zn, Ti,As, B, Li, Sc, Sb, Pb, Zr, Ga, W, Cr, Ni, Ba, Be, Nb, Mo, Sn, V, Cd, Yb, Ag, Co, Sr, P. Oxides of ferrum, aluminum, calcium predominate. Results of X-ray phase analysis showed that silica in the rice-husk is present in slightly crystallize form – a variety of amorphous state where basic mass is presented by amorphous structure. According to data of DTA and investigations on oxidative thermal treatment (pyrolysis) of the rice-husk – temperature of maximal elimination of volatiles – 600 – 700 °C, duration – 10 - 20 min.

For smelting of technical silicon, optimal solution as a furnace burden is joint clotting of silicon-carbon and quartzite with production of single-component burden in the form of granule or briquettes. Clotting by the way of briquetting has a range of important advantages by comparison with granulation: firstly, possibility of utilization of raw material of wide grading, and secondly, consistency of the briquets' chemical composition that is provided due to intimate mixing of materials before filling into compression mold. Moreover, wetting ability of the material at that does not have big significance and does not influence on resistance of completed briquette.

For the purpose of metallurgical grading of silicon-carbon and defining of efficiency of its using as a raw material for smelting of technical silicon, there were conducted large-scale laboratory experiments in ore-smelting furnace 0,2 MBA. For conduction of test run there was prepared lot of briquettes in mixture with quartz. By the results of melting operations, degree of silicon extraction made 92 %, what significantly exceeds known practical data.

By the results of tests, there is established principal possibility of smelting high-strength sorts of technical silicon from the rice-husk. Analysis of the results of the test lot on the ore-smelting furnace 0,2 MBA showed that briquettes from silicon-carbon are applicable for production of metal of brightness over 99 %, what corresponds to the best brand of silicon Si00. Also this measure will give an opportunity not only to decrease self-cost of output products, but also will improve technological indicators of production process [6].

Jointly with A.V. Lykov Heat and Mass Transfer Institute (Belarus, Minsk) there are executed investigations at large laboratory facility with electro-thermal boiling bed ETBB and received test samples of silicon carbide. For today test samples pass certification in the same institute. Peculiarity of ETBB reactor is creation of high-reactive environment in boiling bed of carbonic particles through which electric current goes. Released energy is able to provide development of different endothermal reactions. Electrical discharges between particles make microplasma space and are able to destroy chemical bonds in molecules of reacting substances. At that, there are reached high temperatures in ETBB reactors (1 200 °C and higher). Internal diameter of the reactor is 180 mm. Electrode voltage DS 0-200 B, electric current to 150 A [7].

Thus, on the basis of conducted researches there are established parameters of the rice-husk pyrolysis process, at which it is possible to receive silicon-carbon with rational relation of silicon and carbon (with additional correction by composition) necessary for production of technical silicon, and silicon-carbon from which one may produce silicon carbide.

CONCLUSIONS

1. It is established that after corresponding thermal treatment of the rice-husk one may receive solid product – amorphous silica (silicon-carbon), in which interrelation of silica and carbon is close to stoichiometric, necessary for reproduction of silicon from amorphous silica.
2. It is shown that the rice-husk ash mainly consists of amorphous silica, content of which is 91,31 %.
3. Maximal elimination of volatiles arises in interval of temperatures 600 – 700 °C and duration of firing 10 - 20 min.
4. For production of silicon-carbon with optimal interrelation of carbon and silicon necessary for receiving technical silicon or silicon carbide, it is necessary: oxidizing atmosphere (air), intermixing bed (rotating furnace), temperature 800 – 850 °C, duration of pyrolysis 3 - 5 minutes.
5. There is established fundamental possibility of smelting high-strength sorts of technical silicon and silicon carbide from the rice-husk.
6. For smelting of technical silicon, optimal solution as a furnace burden is joint clotting of silicon-carbon and quartzite with production of single-component burden in the form of briquettes.
7. It is shown that briquettes from silicon-carbon are applicable for production of metal of brightness over 99 %, what corresponds to the best brand of silicon Si00.

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Note: The translation of the N. M. Drag, Karaganda, Kazakhstan