A possibility for utilization of biowaste through synthesis of garnet pigments of CaO-Fe₂O₃-SiO₂ system

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Rice husk (RH) is widely spread agricultural waste product in the world. They can not be fully utilized as food for livestock, fertilizer or fuel, so the methods of their utilization are under extensive investigation. Rice husk are known to contain about 20 % chemically active SiO_2 which can be used for production for a number of silicon containing compounds, including ceramic pigments.

The present study was carried out with rice husk obtained from treatment of Krasnodarski 424 brand of rice grown in Bulgaria. The rice of this brand has 17.8 % husk. They are arc-shaped and the following dimensions: length – about 8 mm, width from 2 to 3 mm and thickness from 0.10 to 0.15 mm. The husk contains 74.5% organic matter (cellulose, hemicellulose and lignine) and water; the rest is inorganic matter consisting of 20% SiO₂ and 5.5% mixture of the following oxides: CaO, Fe₂O₃, MgO, Al₂O₃, Na₂O, K₂O, MnO₂, as well as traces of Cu and Pb. The husk oxidation was carried out at the following temperatures: 500°C, 600°C, 650°C, 700°C, 850°C, 1000°C and 1200°C. The color of the oxidized residue depends strongly on the burning temperature. Up to 500°C, the ash was almost black since the organic matter had not been burnt totally yet. At temperatures about 600-700°C, the initial rice husk sample turned into grey-white ash of varying intensity due to the presence of non-oxidized carbon in it while at higher temperature the product obtained was microcrystalline white ash with high content of SiO₂ due to full release of carbon.

The analyses of the composition of rice husk ash (RHA) showed that, due to the full oxidation of the carbon organic matter at temperatures above 800°C, the solid residue was almost pure SiO_2 with small amounts of other inorganic oxides. Table 1 shows the composition of the oxidized powder.

Component	Quantity, mass. %
SiO ₂	94,47
Fe ₂ O ₃	1,32
K ₂ O	1,08
MgO	1,03
Al_2O_3	0,98
CaO	0,62
MnO_2	0,49
Na ₂ O	0,01
Cu	traces
Pb	traces

Table 1. Composition of oxidized ash obtained at 1000°C

Fig. 1 presents photos of the used rice husk - raw and oxidized.



Fig. 1 Photos of rice husk: a) raw and b) oxidized

Two firing temperatures: 1000° C and 1100° C with isothermal soaking of 2 hour have been chosen for the production of garnet ceramic pigments, type 3CaO.Fe₂O₃.3SiO₂ (andradite). As a raw materials were used CaCO₃ and Fe₂O₃, as a sources of CaO and Fe₂O₃ of respectively, and as a source of silica rice husks oxidized at 650 0C were added.

The figure below shows the technological scheme for the synthesis of pigments of the garnet pigments of the CaO- Fe_2O_3 -SiO₂ system, and radite type.

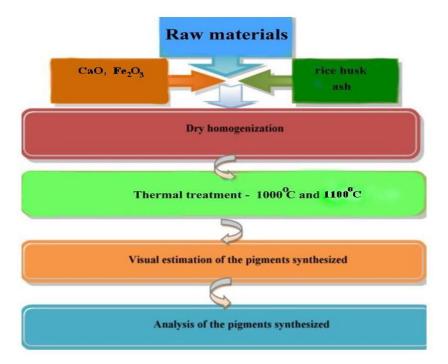


Fig. 2 Technological scheme for the synthesis of garnet pigments of the CaO-Fe₂O₃-SiO₂ system

sample	colour	L	a *	b *
RH 1 / 1000°C		46,99	5,87	10,81
RH 1 / 1100°C		43,15	4,92	9,96

The color of the pigments was determined by using a Lovibond Tintometer RT 100 Color spectrometer.

Conclusions

The synthesis of andradite garnet pigments of CaO-Fe₂O₃-SiO₂ system by utilization of biowaste (rice husk) was demonstrated. The rice husk ash obtained by burning rice husk in air at 1000°C was found to contain predominantly SiO₂ (94.47 mass.%). The pigments were synthesized at a final firing temperatures of 1000 °C and 1100 °C. It was demonstrated that the best results were obtained with the pigments synthesized at $1000^{\circ}C - a^* = 5.87$, $b^* = 10.81$. It was established that the garnet pigments synthesized can be used in glazes for faience tiles.

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