Rice Husk Ash and Its Reactivity in the Formation of β -2 CaO.SiO₂

H. El-Didamony¹, M.G. Abd El Wahed^{*}, Kh. M. Elewa² and A.A. Amer¹

¹Faculty of Science, Zagazig University, Zagazig; and ²Ain-Shams University, Cairo, Egypt.

ABSTRACT. Disposal or Utilization of rice husk creates a problem for rice-growing countries. Its ash is whitish and fluffy that consists mainly of amorphous silica. This form is inert and not useful for agricultural and industrial purposes.

The results of this study presents the nature of fired rice husk ash. IR-spectroscopy and X-ray diffractometry technique were utilized. The reactivity of rice husk ash toward formation of β -C₂S was also investigated. The results showed that rice husk ash fired up to 700°C is amorphous, whereas cristobalite is formed in increasing quantities at higher temperatures. The rate of formation of β -C₂S from rice husk ash is faster than from silica quartz. It may be concluded that rice husk ash is more reactive than natural quartz.

Rice husk has, for a long time, constituted a hazardous by-product. Convenient method to dispose rice husk is by burning; either in open fields or in steam generators. The burning operation produces an ash that constitutes about 20%. Amorphous silica is the predominant component of this ash (El-Bouseily and El-Shamy 1975).

Silicon occurs as a hydrated amorphous silica. It is not known whether this material is opal or silica gel, however, the evidence for the opaline form is rather strong (Cobel and Burke 1963, and Lanning 1963). It was pointed out that a portion of the silica might be complexed with organic molecules (Harders and Kienow 1966).

Due to the light silica content and the porous texture of the ash produced by the incineration of rice husk, it is recommended for use in the production of silica

 β -C₂S = β -2 CaO.SiO₂

H. El-Didamony et al.

insulators. Furthermore, the SiO_2 in rice husk ash is present in an amorphous state, which increases its reactivity during the firing process used in the manufacture of refractory materials (Reinhardt 1972).

Rice husk ash in highly reactive form is found to be excellent ingredient for making either lime-rice husk ash or Portland-rice husk ash cements (Mehta 1977). Portland-rice husk ash cement containing up to 50% ash displays higher compressive strength than does Portland cement.

The nature of white rice husk ash silica is still under active investigation (Ibrahim and Helmy 1981). The results showed that nuclei disordered cristobalite is present and its growth is governed by two factors, namely nucleation and temperature. The nucleation process manifests itself in the low temperature range 800-900°C, while growth is more pronounced in the temperature range 1000-1100°C.

The aim of the present study is to elucidate the nature of the rice husk ash formed at different firing temperatures from 500° up to 1000°C. The reactivity of such ash is studied in the formation of β -C₂S which is a major phase in Portland cement by the reaction with CaCO₃ in comparison with natural quartz.

Experimental

10 kg of green rice husk were ground in a disc mill and then sieved through 0.5 mm mesh. The thermal behaviour as well as the ash content of the rice husk were studied (El-Bouseily and El-Shamy 1975). DTA showed an endothermic peak at about 130°C that corresponds to heat absorbed during the loss of mechanically held water. This process is accompanied by ca. 4.4% weight loss. The thermal decomposition of the husk is characterized by two exothermic peaks at 340-400°C. These may be due to the presence of cellulose and hemicellulose which are the major constituents of the organic part of the husk. The corresponding weight loss is ca. 36.6%. The remaining part of the husk was decomposed gradually; decomposition completed at 940°C. The weight of the resulting ash was ca. 18% of the rice husk. Chemical analysis of the rice husk ash is as follows: SiO₂ = 94.47; Al₂O₃ = 2.03; Fe₂O₃ = 0.40; CaO = 1.14; Mg = 0.89; Na₂O = 0.67 and K₂O = 0.85%.

Rice husk was heated in a muffle furnace in an atmosphere of air at a constant rate of 20°C min up to required temperature. Heating was initiated at 500°, 600°, 700°, etc. up to 1000°C for 2 hr, then cooled slowly in the furnace. The nature of the silica in the rice husk ash was studied by IR as well as X-ray diffraction (XRD) analyses.

The β -dicalcium silicate, β -C₂S, was synthesized from silica rice husk ash as well as from natural quartz for comparison. The rice husk was ignited at 400°C for 2

46

hr, and the carbon content was determined by ignition at 1000°C for one hour. The particle size of rice husk ash fired at 400°C as well as natural quartz was $-73 \,\mu\text{m}$. The two materials were ground separately in an agate mortar to pass completely through a 200 mesh sieve ($-73 \,\mu\text{m}$). The calculated amount of SiO₂ in the ash was mixed with a stoichiometric amount of CaCO₃, and the resulting mixture was ignited at 1100, 1200, 1300, and 1400°C for 1, 2, 3 and 4 hr, respectively, and then suddenly cooled in the air. The phase constitution was identified with the aid of X-ray diffractometry. Ni-filtered CuK α radiation at 40 kV, 20 mA was used throughout in Philips Pw 1390 diffractometer. The kinetics of formation of β -C₂S were followed by determining the free lime content of the fired samples (Kondo *et al.* 1975).

Results and Discussion

Ibrahim *et al.* (1980) examined the IR-absorption patterns for white rice husk ash silica that was obtained by firing rice husk ash in an atmosphere of air at different temperatures ranging between 500 and 1400°C. The observed ratio of the two main absorption bands occurring at 470 and 800 cm⁻¹ provided insight into the sequence of transformations among different forms of silica. These transformations occurred in three steps: (i) the destruction of Si-OH groups at 700°C, (ii) the formation of disordered cristobalite at 900°C, and (iii) the crystallization of cristobalite and tridymite.

IR-spectra of rice husk ash fired at 500, 600, 700, 800, 900 and 1000°C for 2 hr are shown in Fig. 1. Samples fired between 500° and 700°C showed absorption bands at 470, 795, 1090, 1635 cm⁻¹ and a broad band at 3460 cm⁻¹. Samples fired between 800 and 1000°C displayed more complicated spectral features. An absorbance band at 615 cm⁻¹ started to appear at 800°C, increased in intensity at 900°C, and then decreased in intensity as the temperatures was increased further.

Crystalline form of silica such as quartz and cristobalite display intense sharp IR absorption bands at about 1200, 1100 and 800 cm⁻¹ which presumably arise from the Si-O fundamental (Flörke 1959 and Nakamoto 1978). Silica gel contains two types of siliconoxygen bonds: Si-O or siloxane groups and Si-OH or silonal groups (Ibrahim *et al.* 1980). The Si-O bond displays characteristic IR bands at 400-500 cm⁻¹ that are due to bending vibrations. If the silica tetrahedra are connected to form chains, rings or more complicated structures, they give rise to IR absorption bands at 600-800 cm⁻¹; *i.e.* the Si-O group absorptions occur primarily at: 470, 600, 810 and 1100 cm⁻¹. The absorption bands at 1635 and 3460 cm⁻¹ result from adsorbed water.

IR-spectra of rice husk ash treated at different temperatures closely resemble that of opal. This is due to the absence of stretching frequency at 950 cm^{-1} of silica

H. El-Didamony ct al.

gel. All samples fired up to 700°C display similar absorption patterns that denote the amorphous nature of the ash. The broadening of the band at 795 cm⁻¹ is probably due to overlapping of Si-O and Si-OH vibrations. The increase in sharpness of the Si-O band that occurs with increasing temperature is probably due to the destruction of the Si-OH group. The band at 795 cm⁻¹ due to the Si-O vibration is shifted to 780 cm⁻¹ as the firing temperature is increased from 800 to 1000° C.



Fig. 1. IR-Spectra of rice husk ash fired at different temperatures

Rice husk ash fired at 800°C displayed an IR band at 615 cm⁻¹ thereby denoting initiation of a crystalline phase. The intensity of this band increases as the firing temperature increases to 900 and 1000°C. The appearance of a band at 435 cm⁻¹ indicates the presence of tridymite.

Figure 2 illustrates the XRD patterns of rice husk ash fired from 500 up to 1000°C in comparison with natural quartz. It is clear that the silica of rice husk ash is amorphous at lower temperatures, *i.e.* up to 700°C. At this temperature, crystallinity of the silica is initiated, and a small amount of crystalline phase is formed. This phase may be disordered cristobalite which increases with increasing firing temperature. When the firing temperature increases from 800 to 1000°C, the characteristic pattern of cristobalite increases. In earlier work (Ibrahim *et al.* 1980), the appearance of cristobalite was reported to occur at higher temperature (900°C) than in the present study. This result may be attributed to the firing conditions. In the present work, the ash was allowed to cool slowly, thereby affording conditions that are conductive to crystallization. Sudden cooling delays crystallization of the silica. The crystallinity of quartz is greater than that of ash silica fired at 1000°C. It should be noted that the predominant crystalline phase present in rice husk ash fired up to 1000°C was cristobalite, which is different from that of natural quartz.

Organosilicon compounds are assimilated into the rice plant and form part of the plant tissue. Silicon atoms are first transformed by the combustion process into amorphous silica. Silicon atoms in amorphous silica are bonded to oxygen atoms in two ways: either to two oxygen atoms, thereby forming a siloxane group (Si-O) or to a hydroxyl group, thereby forming a silanol group (Si-O-H). Both groups exist at temperatures up to 700°C but in varying proportions depending on the firing temperature. The siloxane groups unite by the corners to produce low-form cristobalite. Any impurities that are present enter the crystal lattice, thereby forming a kind of solid solution.

Effect of Mode of Silica on the Formation of β -2 CaO.SiO₂

Silica quartz as well as rice husk ash fired at 400°C for 2 hr were used for the preparation of β -C₂S. They were mixed separately with an equimolar amount of CaCO₃ in an agate mortar. The resulting mixtures were then placed in platinum crucible and fired in an electric furnace at 1100, 1200, 1300 and 1400°C, respectively.

Effect of Firing Temperature

The XRD patterns of mixes, prepared from quartz as well as rice husk ash, fired at 1100, 1200 and 1300°C for 4 hr, are shown in Figs. 3 and 4. As the firing temperature is increased, the patterns show a corresponding increase in the intensity of the β -C₂S lines and a decrease in intensity of the patterns that

H. El-Didamony et al.

correspond to quartz, cristobalite and free lime. The results indicate that β -C₂S is formed exclusively when rice husk ash is fired at 1300°C. However the sample, that is obtained when quartz is fired, contains free quartz as well as free lime with the lines of β -C₂S. A very small amount of γ -C₂S is also present as intermediate phase.



Fig. 2. XRD Patterns of rice husk ash fired at different temperatures compared with quartz

There is no chance for formation of CS_2 and CS. This is due to the high concentration of lime which prevents the formation of low lime calcium silicates. Hence, we conclude that rice husk ash is more active than is natural quartz. The free $Ca(OH)_2$ is due to the hydration of free lime and also the presence of $CaCO_3$ is mainly due to re-combination from the atmospheric CO_2 .



Fig. 3. XRD Patterns of B-C₂S prepared from natural quartz as a function of firing temperature

H. El-Didamony et al.



Fig. 4. XRD Patterns of B-C₂S prepared from rice husk ash at different firing temperatures

Effect of Soaking Time

The effect of soaking time on the formation of β -C₂S from quartz as well as from rice husk ash is shown in Figs. 5 and 6. The samples were fired at 1300C for 1, 2, 3 and 4 hr, respectively. The degree of reaction increases with firing time. Only the β -C₂S pattern is observed from soaked rice husk ash, whereas the lines of silica quartz are still present after soaked quartz has been fired for 4 hr at 1300°C. Also, soaking enhances the formation of β -C₂S in the case of natural quartz.

The kinetics of formation of β -C₂S can be seen *via* inspection of Fig. 7. This Figure illustrates the free lime contents of β -C₂S prepared from quartz as well as from rice husk ash as a function of firing conditions. The results revealed that at

any firing temperature, the amount of free CaO decreases as the soaking time increases. As the firing temperature increases, the amount of free lime resulting from incomplete reaction with quartz or rice husk ash decreases. This results reflects the fact that lime is consumed during the formation of β -B₂S. Generally, the content of free lime is lower in rice husk ash than in the ash produced *via* firing



Fig. 5. Effect of soaking time of samples fired at 1300°C prepared from quartz

of natural quartz. This result is mainly due to the increased reactivity of rice husk ash *vis-a-vis* natural quartz. A sample prepared from rice husk ash fired at 1400°C for 3 hr was found to contain 0.7% free CaO in comparison with 20.14% CaO in a sample prepared similarly by silica quartz.



Fig. 6. Effect of soaking time of samples fired at 1300°C prepared from rice husk ash



Fig. 7. Free lime content of samples fired at different tempeatures

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H. El-Didamony et al.

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(Received 06/04/1986: in revised form 21/12/1986) رماد قشرة الأرز ونشاطها في تكوين سلكات الكالسيوم

حمدي الديداموني` و محمد جمال عبدالواحد` خالد محمد عليوه` و أحمد عبدالمنعم عامر`

اكلية العلوم _ جامعة الزقازيق _ الزقازيق _ أكلية العلوم _ جامعة عين شمس _ القاهرة _ مصر

تمثل قشرة الأرز مشكلة في استخدامه في البلاد التي تـزرع نبات الأرز، حيث تـترك رماداً أبيضاً غير متبلور عند حرقها في جـو من الأكسجين. وتعـد قشرة الأرز من المواد القليلة الاستعمال في الأغراض الصناعية والزراعية.

وتهدف هذه الدراسة إلى دراسة طبيعة رماد قشرة الأرز وذلك باستخدام جهاز الأشعة تحت الحمراء وجهاز حيود الأشعة السينية . حيث درست فعالية هذا التراب في تكوين سلكات الكالسيوم بالمقارنة مع الكولوتز الطبيعي . أظهرت النتائج أن حرق قشرة الأرز في درجة ٢٠٠ م يعطي تراباً من السلكا غير المتبلورة ، وعند حرقها عند درجة حرارة أعلى يتكون معدن الكرستوبلايت . وجد أيضاً أن سرعة تكوين سلكات بيتا ثنائية الكالسيوم في حالة استخدام رماد قشرة الأرز أعلى منها في حالة استخدام الكوارتز كمصدر للسلكا .

ويمكن القول أن السلكا المتخلفة عن حرق قشرة الأرز أكثر فعاليةً من الكوارتـز الطبيعي .