

A structural investigation relating to the pozzolanic activity of rice husk ashes

Deepa G Nair^{a,*}, Alex Fraaij^a, Adri A.K. Klaassen^b, Arno P.M. Kentgens^b

^a *Civil Engineering and Geosciences, Materials Science and Sustainable Construction, Delft University of Technology, The Netherlands*

^b *Physical Chemistry/solid-state NMR, Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands*

Received 4 August 2006; accepted 31 October 2007

Abstract

Various factors determine the applicability of rice husk ash (RHA) as a pozzolanic material. The amount and accessibility of reactive sites is thought to be a key factor. A structural study of RHA samples in relation to their reactivity has been performed; Silica in RHA formed by burning rice husk in a laboratory furnace under continuous supply of air have been characterized as a function of incineration temperature, time and cooling regime. The characterization methods included chemical analyses, conductivity measurements, microscopic analysis, X-ray diffraction (XRD) and ²⁹Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR). In line with earlier observations, the analyses show that the highest amounts of amorphous silica occur in samples burnt in the range of 500 °C–700 °C. The ²⁹Si NMR data allow direct identification of the reactive silanol sites in the RHA samples. De-convolution of the NMR spectra clearly shows that the quickly cooled RHA resulting from burning rice husk for 12 h at 500 °C has the highest amount of silanol groups. This sample also induced the largest drop in conductivity when added to a saturated calcium hydroxide solution giving an indication of its reactivity towards lime. Therefore, this RHA is the favorable sample to be used as pozzolanic cement additive.

© 2007 Elsevier Ltd. All rights reserved.

Keywords: Rice husk ash; Silica; Pozzolanas; Cement; ²⁹Si MAS NMR; XRD

1. Introduction

Cementitious binders are vital for all types of construction activities. The use of pozzolanas as alternatives for the commonly used Portland cement have been (re)introduced in the last few decades either for cost reduction, performance, durability or environmental reasons. According to Malhotra and Metha [1] pozzolanas are defined as siliceous or siliceous and aluminous materials which in themselves possess little or no cementing property, but will in a finely dispersed form in the presence of water chemically react with calcium hydroxide at ordinary temperature to form compounds possessing cementitious properties. Already in the antiquities volcanic soils were used to produce hydraulic mortar. These days, fly ash or pulverized

fuel ash (PFA), furnace clinker, and agricultural wastes (plant ashes) are commonly used pozzolanas.

Of all the plant residues, the ash of rice husks contains the highest proportion of silica. Rice plants ingest orthosilicic acid from ground water, where upon it is polymerised to form amorphous silica in the husks [2]. Rice husk is a by-product in the process of obtaining rice grain. It contains nearly 20% silica in hydrated amorphous form. Under controlled combustion conditions, amorphous silica with high reactivity is produced [3]. It has been demonstrated that RHA can be added to concrete mixtures to substitute the more expensive Portland cement to lower the construction cost and to make a significant contribution towards the provision of low cost building materials and consequently to affordable shelter. RHA is not just a cheap alternative, however, as it has been used to improve the durability of concrete [4] and to produce high-performance cement [5].

Until the early seventies researchers utilized rice husk ash derived from uncontrolled combustion in their investigations. Mehta [3] established that a highly reactive ash can be produced by maintaining the combustion temperature below 500 °C under

* Corresponding author. Faculty of Civil Engineering, School of Engineering, Cochin University of Science and Technology, Cochin, India. Tel.: +91 9846249839.

E-mail addresses: deepalavanya1@rediffmail.com, deepagnair@cusat.ac.in (D.G. Nair).

oxidising conditions for relatively prolonged period or up to 680 °C provided the high temperature exposure was less than one minute. Prolonged heating above this temperature may cause the material to convert (at least in part) to crystalline silica; first to cristobalite and then tridymite. Chopra et al. have reported that for incineration temperatures up to 700 °C the silica was predominantly in amorphous form and that the crystals present in the ashes grew with time of burning [6]. Other investigators also concluded that the combustion environment affects specific surface area, so that time, temperature and environment must be considered in the pyroprocessing of rice husks to produce ash of maximum reactivity [7,8]. According to Hamad et al [9] ash prepared at a temperature of about 500 to 600 °C consists of amorphous silica. Cristobalite was detected at 800 °C and after burning at 1150 °C both cristobalite and tridymite were present. However, some reports cited by Nehdi et al [8] state that silica in RHA can remain in amorphous form at combustion temperatures of up to 900 °C if the combustion time is less than one hour, whereas crystalline silica is produced at 1000 °C with combustion time greater than 5 min. Other reports claim that crystallisation of silica can take place at temperatures as low as 600 °C, 500 °C, or even at 350 °C with 15 h of exposure [10].

James and Rao preformed a systematic study of RHA processing and its reactivity. They indicated that isothermal heating at a minimum of 402 °C (675 K) is required for complete destruction of organic matter from rice husk and to liberate silica [11]. On combustion, the cellulose-lignin matrix burns away, leaving a porous silica skeleton; this can be ground to a fine powder with high surface area. In a separate paper James and Rao [12] studied the ability of RHA to combine with lime as a function of the temperature, ranging from 400 °C to 900 °C, at which the rice husk was burnt. They showed that silica and lime react to form a calcium-silicate hydrate (C–S–H) gel and defined a so-called reactivity index by comparing the reactivity of RHA to that of a reference silica aerogel. It was found that combustion at 500 °C produced the most reactive silica. James and Rao conclude that the reaction to form C–S–H gel is “surface assisted” so that the specific surface area is an important parameter. In a more recent study by Yu et al.[13] it was concluded that C–S–H gel is formed by a dissolution-precipitation process where the silica in RHA is quickly dissolved in the high pH Ca(OH)₂ solution and subsequently Ca_{1.5}SiO_{3.5}·xH₂O precipitates. The dissolution of silica is strongly influenced by their surface structure where the charge of the surface plays an important role depending on the binding or release of protons at Si–OH surface groups [14].

So to produce a highly pozzolanic RHA it has to contain the maximum amount of amorphous silica with a high surface area and the presence of many silanol groups. A decrease in surface area can be attributed to crystalline growth and pore opening. While X-ray diffraction can be used to study the crystalline fractions of the material it is not well suited to study the amorphous phase. ²⁹Si solid-state NMR probes the local structure of a silicon atom and does not rely on long-range order in the samples and is therefore a powerful technique to characterize amorphous silica. In silica, ²⁹Si chemical shifts depend on the degree of condensation of the SiO₄ tetrahedra in the material. Assignment of the spectra of silicates is done on the basis of the second coordination sphere of silicon [15] using the Qⁿ nomenclature. Here ‘n’ designates the

number of siloxane bonds a certain silicon atom is participating in. Through these siloxane bonds a silicon atom can be bonded to a maximum of four other silicon nuclei. As each of the Qⁿ species have a distinctive chemical shift, ²⁹Si NMR can give information about the degree of condensation of a silica network. Within each Q species the exact chemical shift value depends on the Si–O–Si bond angles. This also allows one to get insight in the crystallinity of the materials. Crystalline samples are characterized by well-defined bond angles which are reflected in narrow NMR resonances, whereas amorphous samples are characterized by distributions in bond angles in general leading to broad Gaussian line shapes [16,17]. Although the use of ²⁹Si solid-state NMR in the study of silicates and zeolites is widespread, its use in the study of pozzolanas and specifically RHA has been rather limited. Hamdan et al. [18] used NMR to study rice husk silica as base material for the synthesis of zeolites. Their results show that samples burnt above 700 °C are mostly crystalline showing Q⁴ resonances of cristobalite and tridymite. On burning rice husk at 700 °C the ashes consist of highly condensed amorphous silica showing a broad Q⁴ resonance, without any observable silanol groups. Abreu et al. [19] investigated the structure and hydration kinetics of an ash obtained by burning rice husk in a fluidized bed furnace at temperatures up to 890 °C. The NMR spectrum showed the presence of Q³ and Q² sites in the amorphous fraction of the sample as well as a small amount of crystalline material assigned to cristobalite.

With the long term goal to formulate criteria for burning rice husks in the field to generate cheap but high-grade building materials, this paper focuses on the structure of rice husk ashes resulting from a variation in combustion conditions. The factors investigated are combustion temperature, duration of combustion and the cooling regime. These parameters are discussed in view of the formation of amorphous silica for getting the most reactive pozzolana from rice husk under controlled conditions in the laboratory. RHAs are characterized by X-ray diffraction (XRD), ²⁹Si magic-angle spinning (MAS) nuclear magnetic resonance (NMR), chemical analyses, conductivity measurements and microscopic analysis.

2. Experimental methods

2.1. Rice husk ash sample preparation

Rice husk samples were collected from Alleppey district of Kerala (India). Ash samples were prepared by burning 50 g of rice husk in a laboratory oven under the continued supply of air for different durations of burning (15 min to 24 h). An initial duration of two hours pre-heating was maintained in all the cases to attain the desired temperature. Two ash samples were collected in each case. One sample was taken out of the oven immediately after completion of the burning process [so called “quick cooling” (Q)]. The second sample was collected after allowing the sample to cool naturally inside the oven [so called “Slow cooling” (S)]. Testing conditions were:

1. temperature variation (500 °C, 700 °C, 900 °C)
2. duration of burning (15 min, 6 h, 12 h, 24 h)
3. nature of cooling (Quick cooling, Slow cooling)

The RHA samples produced from the laboratory under different testing conditions are represented with a unique designation throughout this paper for convenience. For example, RHA500-6Q and RHA500-6S designate the rice husk ash samples produced at a temperature of 500 °C and a burning duration of six hours. Q and S indicate the nature of cooling. In order to find the parameters influencing the formation of reactive silica the samples collected from different regimes are subjected to chemical analyses, conductivity measurements, XRD, ^{29}Si NMR and microscopic analysis. In addition to this systematic burning temperature and time variations two samples were combusted for 24 h at 300 °C as shorter combustion times are very likely to be too short to expel all carbon from the sample. Finally, an incidental sample was heated to 1100 °C overnight in an attempt to produce purely crystalline material.

2.2. Loss on ignition and total silica

The duration of incineration was varied from 15 min to 24 h to study its influence on the formation of reactive silica. ASTM C 311-00 standards [20] were used for the determination of the loss on ignition (LOI) and total silica content of RHA samples. The pre-weighed RHA sample is kept in an oven (800 °C) and weighed again. The difference in weights is the weight of organic content that released as CO_2 . The same sample (carbon removed) is taken and boiled in Nitric acid. It is then filtered through a weighed glass fibre filter and subsequently washed with demineralised water. The filter is dried (overnight) in an oven at 105 °C and weighed again. The weight change gives the total amount of SiO_2 (Total silica, both crystalline and amorphous).

2.3. Soluble fraction of silica

Rice husk ash samples are weighed in an analytical balance and boiled in 100 ml of 2.5 N (10%) NaOH. The solution is then filtered through a filter paper and washed with demineralised water. This filter is dried in an oven at 800 °C (2 h), cooled and weighed to get the weight of insoluble silica. Depolymerised silica remains dissolved in the solution and are expressed as the percentage of soluble silica.

2.4. Pozzolanic activity

The drop in electrical conductivity of a saturated solution of calcium hydroxide when a RHA sample is added can be taken as a measure of the pozzolanic activity of the samples [21]. Initially the conductivity of a saturated calcium hydroxide solution (200 ml, 40 °C) is measured. To this 5 g of RHA sample is added. The electrical conductivity is measured after two minutes of continuous stirring. The difference between the initial and final conductivities is calculated as a measure of pozzolanicity. This is identified as a rapid method to evaluate the pozzolanic activity of rice husk ash [10,12,22,23].

2.5. X-ray diffraction analysis

The XRD analyses were performed on a Bruker D8 Avance X-ray diffraction system operating with a 50 kV, 50 mA Cu

radiation source and a Philips PW1820 diffractometer. This diffractometer uses a 40 kV, 50 mA Cu radiation source.

2.6. Microscopic analysis

A Jeol FESEM 6330F was used to obtain scanning electron micrographs (SEM) of a selection of the RHA samples.

2.7. ^{29}Si magic-angle spinning nuclear magnetic resonance

^{29}Si solid-state magic-angle spinning (MAS) NMR experiments were performed on a Chemagnetics Infinity 300 MHz (7.1 T) and a Chemagnetics Infinity 600 MHz (14.1 T) NMR spectrometer. On the 7.1 T spectrometer a Bruker 10 mm MAS HX probe head was employed, whereas a Chemagnetics 6 mm MAS HX Apex probe was used on the 14.1T spectrometer. Spectra were obtained using single pulse excitation using a $\pi/2$ excitation pulse (5 μs , $\nu_1 = 50$ kHz) and a relaxation delay of 600 s. For a few selected samples, spin-lattice relaxation times T_1 were determined using a saturation-recovery experiment. In all cases the relaxation curves were strongly multi-exponential and in some cases full relaxation had not been reached after 600 s. This means that some caution has to be taken into account with the quantitative interpretation of the spectra. The relaxation curves were fitted using the Kohlrausch–Williams–Watts type stretched exponential function. These described the data well and were used to determine the average spin-lattice relaxation time $\langle T_1 \rangle$ [24] in order to estimate the possible errors in quantification due to the partial saturation of part of the spin system. Spinning speeds ranging from 3 kHz to 6 kHz were used in all cases fast enough to avoid spinning sidebands. Spectra are referenced with respect to tetramethylsilane (TMS) using the ^{29}Si resonance in Zeolite A (−89.7 ppm) as a secondary standard. Spectra were processed using the MatNMR [25] processing software. Deconvolution of the ^{29}Si MAS NMR spectra was done by a least-squares fitting procedure as implemented in MatNMR. The deconvolution procedure was initiated by manually choosing the number of lines and starting values for chemical shift and line width. All parameters were allowed to vary freely in the fit procedure except for the line shape, which was fixed to a Gaussian line shape for the resonances of the various Q-species in the amorphous phase of the material.

3. Results and discussion

3.1. Loss on ignition and total silica

Fig. 1 shows the variation of the loss on ignition, which is a measure for the residual carbon content, and the percentage soluble silica, which is considered as a measure of the reactivity for the various RHA samples. The influence of different incineration times, temperatures and cooling regimes can be discussed based on the results of the chemical analyses.

It is noticed that short burning durations (15 to 360 min) are insufficient at all temperatures to achieve complete removal of the carbon content of rice husk. At a burning temperature of

300 °C even after incineration for 24 h the ashes contain more than 50% organic material. Therefore samples incinerated for shorter times at 300 °C were not further considered in this study. Burning temperatures of 500 °C, 700 °C and 900 °C resulted in ash samples with low carbon content at longer durations (12 h to 24 h) of incineration. At 500 °C and 700 °C the ashes show a high percentage of soluble silica. A further interesting observation is that in for combustion at 300 °C, 500 °C and 700 °C a small fraction of the silica is insoluble. This fraction varied slightly in an unsystematic way. Apparently in all samples a small fraction of very condensed silica is present that does not dissolve the treatment used here. The RHA900 samples show a strong decrease in the percentage of soluble silica as a function of incineration time as the loss on ignition was almost nil at this temperature indicating that with increasing temperature a larger amount of the silica has crystallized and therefore does not dissolve under the conditions used in this study.

From these observations we conclude that temperatures of 500 °C and 700 °C and burning times of more than 12 h are favored to produce reactive rice husk ashes. They show similar results for the percentage of soluble silica at the different cooling regimes. The percentage of carbon in these samples is somewhat lower in the slow cooling regime as compared to the

quick cooling regime. Although various studies show different results for a diverse variation in RHA production these results are in line with observations made in studies such as that James and Rao [12]. This chemical analysis cannot discriminate between RHA500 and RHA700 samples in terms of optimal incineration conditions in relation to pozzolanicity, however. Therefore further characterization of the samples is necessary.

3.2. Pozzolanic activity

The pozzolanic activity test, using the decrease in electrical conductivity when adding a defined amount of RHA to a saturated calcium hydroxide solution, can provide further insight. This test is a quick measure of the reactivity of the ash based on the presence of amorphous silica [21]. As discussed by Q.Yu et al. [13] the electrical conductivity mainly depends on the concentration of Ca^{2+} and OH^- , so the decrease in conductivity is attributed to the interaction between them and the RHA that was added. Table 1 shows that both RHA500 and RHA700 samples gave large conductivity changes which can be interpreted as good values for pozzolanicity. RHA500 samples consistently showed higher values than the RHA700 samples however, demonstrating their overall higher reactivity.

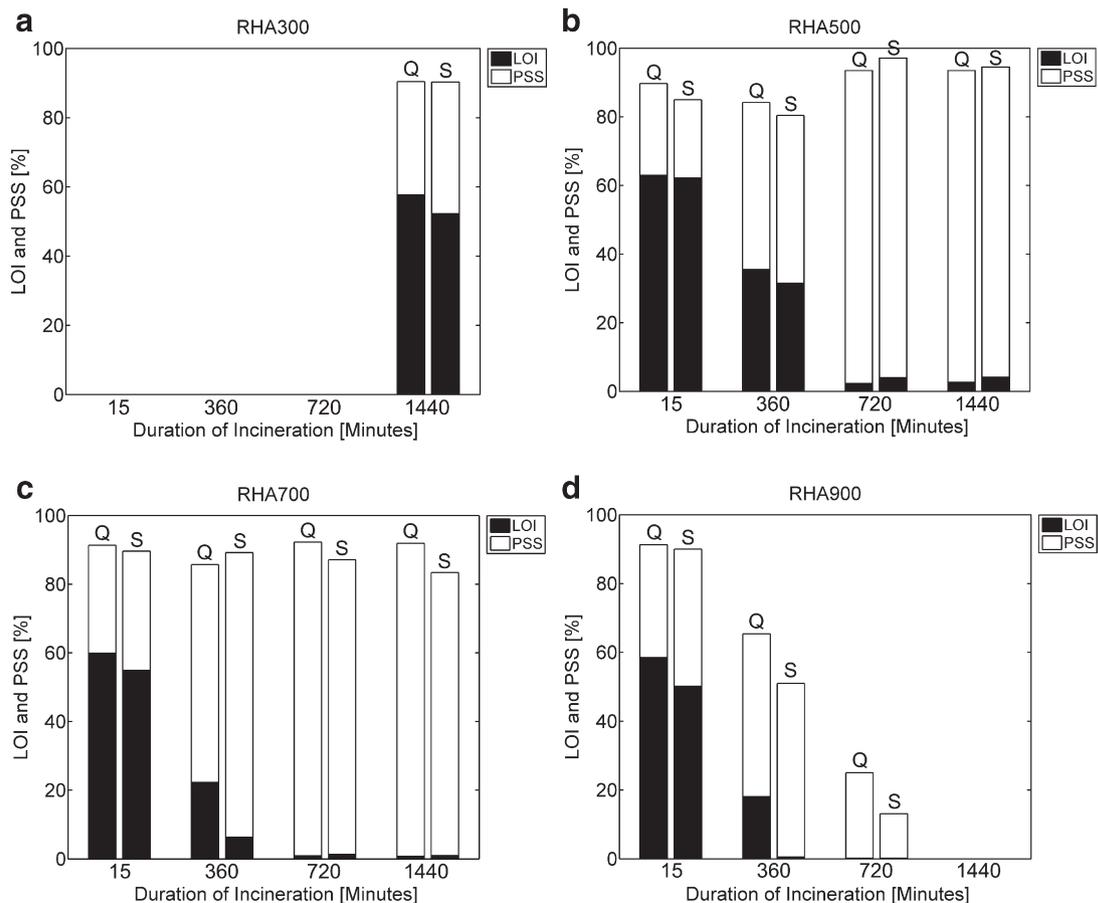


Fig. 1. Percentage of soluble silica (PSS) and loss on ignition (LOI) in quick (Q) and slowly (S) cooled RHA samples prepared using incineration temperatures of a) 300 °C, b) 500 °C, c) 700 °C and d) 900 °C for durations varying from of 15 to 1440 min (0.25 to 24 h).

Table 1

Difference in the electrical conductivity of a saturated solution of calcium hydroxide on adding a defined amount of the respective RHA sample

Sample	Conductivity variation (Δ mS/cm)
RHA700-12S	3.2
RHA700-12Q	3.6
RHA700-24S	3.0
RHA700-24Q	3.5
RHA500-12S	5.3
RHA500-12Q	5.4
RHA500-24S	5.2
RHA500-24Q	5.2

A large change in conductivity is interpreted as a high pozzolanic activity [9]. On the basis of these experiments, all samples qualify as good pozzolanas. RHA500-12Q clearly shows the highest activity.

3.3. X-ray diffraction (XRD) analysis

XRD analyses were performed for selected samples to identify differences in the formation of amorphous or crystalline silica for different combustion times, temperatures and cooling regime. A qualitative assessment of the crystallinity of the samples can be obtained from the intensity of the narrow reflections as compared to the broad band around 22° (2θ).

The intense broad peak observed for the RHA500 samples (Fig. 2) indicates the amorphous nature of silica at different testing conditions at this temperature. Similar results were obtained for the RHA700 samples (not shown) again showing hardly any crystalline reflections. For the RHA900-6Q some reasonably sharp and intense reflections start to show up on top of the broad amorphous background, evidencing that at these temperatures crystalline cristobalite starts to form. Only after incineration at 1100°C the material becomes highly crystalline as is evident from Fig. 3 displaying the XRD pattern of a RHA1100 sample consisting of sharp reflections which can be assigned to cristobalite and tridymite.

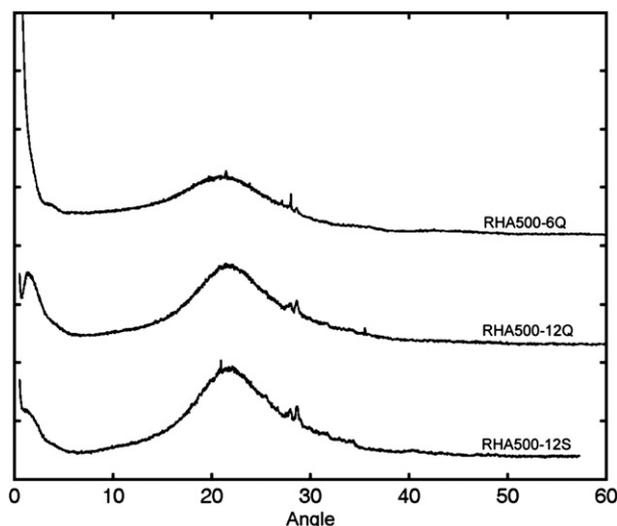


Fig. 2. XRD patterns of RHA500-6Q, RHA500-12Q and RHA-12S samples. The broad line centred at $2\theta=22^\circ$ is typical for amorphous silica.

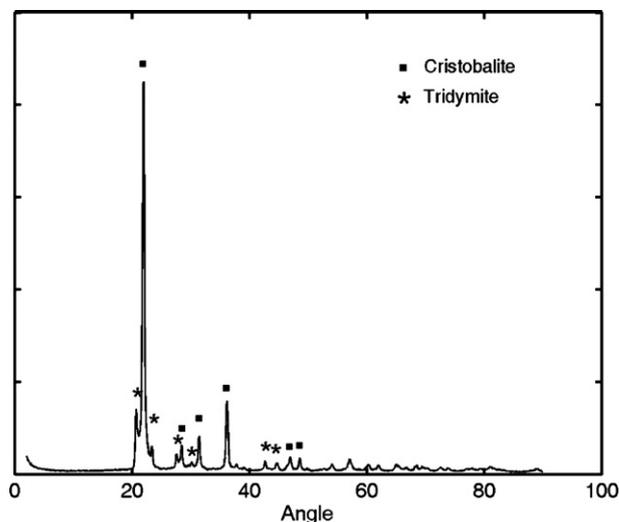


Fig. 3. XRD pattern of RHA1100 showing sharp lines indicating the crystallinity of the sample. The typical reflections of cristobalite and tridymite are indicated.

3.4. Microscopic analysis

Fig. 4 shows the morphology of different RHA500 samples produced under similar controlled conditions in the lab but with different cooling regime. The difference in the morphology between RHA500-12Q and RHA500-12S shows that particle size increases significantly in the slow cooling regime as compared to quick cooling. This is remarkable in view of the pozzolanic activity test discussed in Section 3.2. As can be concluded from Table 1 the reactivity of the RHA500 samples toward lime is similar. This indicates that the dissolution of the silica in the very basic lime solution does not differ strongly for the different samples. Intuitively one might think that small particles dissolve faster than large ones. However, particle size cannot be interpreted in terms of crystallinity or surface area as the particles can have a high meso- and microporosity. Furthermore, we do not observe particles with a specific morphology that could be related to certain crystalline fractions. The same was true for the RHA700 samples.

3.5. ^{29}Si MAS NMR

Although XRD and SEM give some insight in to the crystallinity of the samples, they could not provide information about the composition and reactivity of the amorphous fraction of the RHAs. Therefore we resort to ^{29}Si MAS NMR to get more insight concerning the presence of reactive silanol groups in the samples. The spectra of the samples prepared at 500°C and 700°C are dominated by a broad peak at approximately -111 ppm with a small shoulder at -102 ppm (Fig. 5). From this we conclude that in these ashes a very dense silicate network has formed mostly consisting of Q^4 branches with a small amount of Q^3 sites from terminating silanol groups resonating at -102 ppm. These silanol groups are the only reactive sites in the silica and can thus be regarded as being responsible for the pozzolanicity of the materials if they are accessible. Deconvolution of the spectra into Gaussian lines, by least-squares fitting of

the spectra as described in the experimental section, results in very wide Gaussian curves with a width of approximately 10 ppm for the Q^4 sites and about 6 ppm for the Q^3 sites. This suggests that the network is mostly amorphous with a large variation in Si–O–Si bond angles [16,17]. None of the spectra of the samples burnt at 500 °C or 700 °C show the presence of any significant amount of crystalline material in line with the XRD observations and an early study of rice husk ashes by Hamdan et al [18]. The situation changes at a temperature of 900 °C, for these samples a relatively narrow line (FWHH \sim 3 ppm) appears at -111 ppm, on top the broad amorphous resonances, which is assigned, to the formation of cristobalite on the basis of the XRD data. Treatment at an even higher temperature of 1100 °C significantly changes the spectrum (Fig. 6) with narrow lines at -110 ppm (FWHH 1 ppm) and -112 ppm (FWHH 3.5 ppm) indicating that the sample mostly consists of a mixture of cristobalite and tridymite [15], in line with the XRD observations.

For a possible quantification of the results the spin-lattice relaxation is an important parameter. Fyfe et al. [26] studied the relaxation of silicon in high surface area silica gels. They observed marked differences in the T_1 of Q^2 , Q^3 and Q^4 species, with the latter having the longest T_1 's with values up to 45 s.

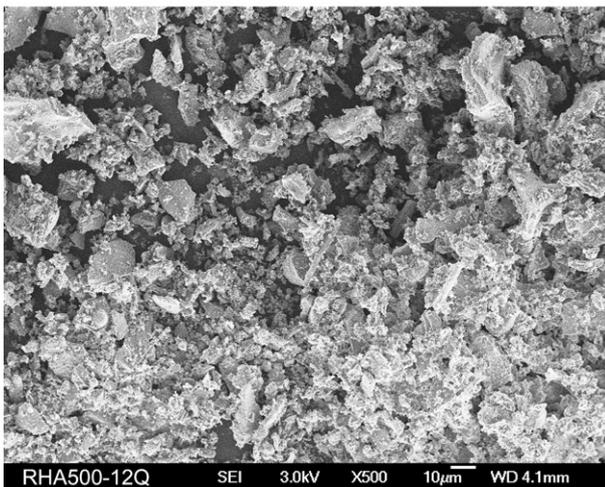
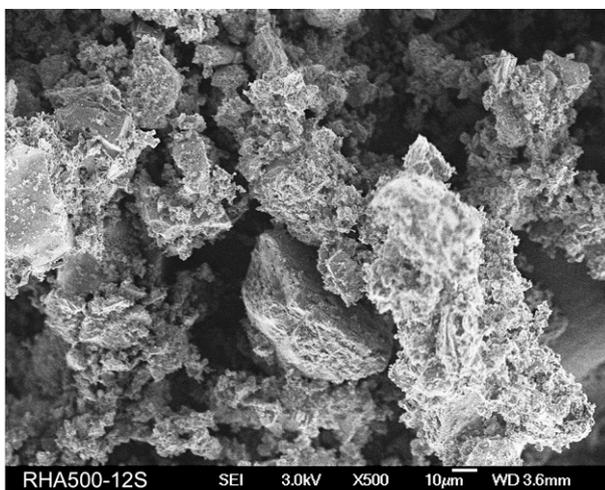


Fig. 4. SEM images for RHA samples burnt at 500 °C but differing in cooling procedure. Larger particles are observed for slowly cooled particles.

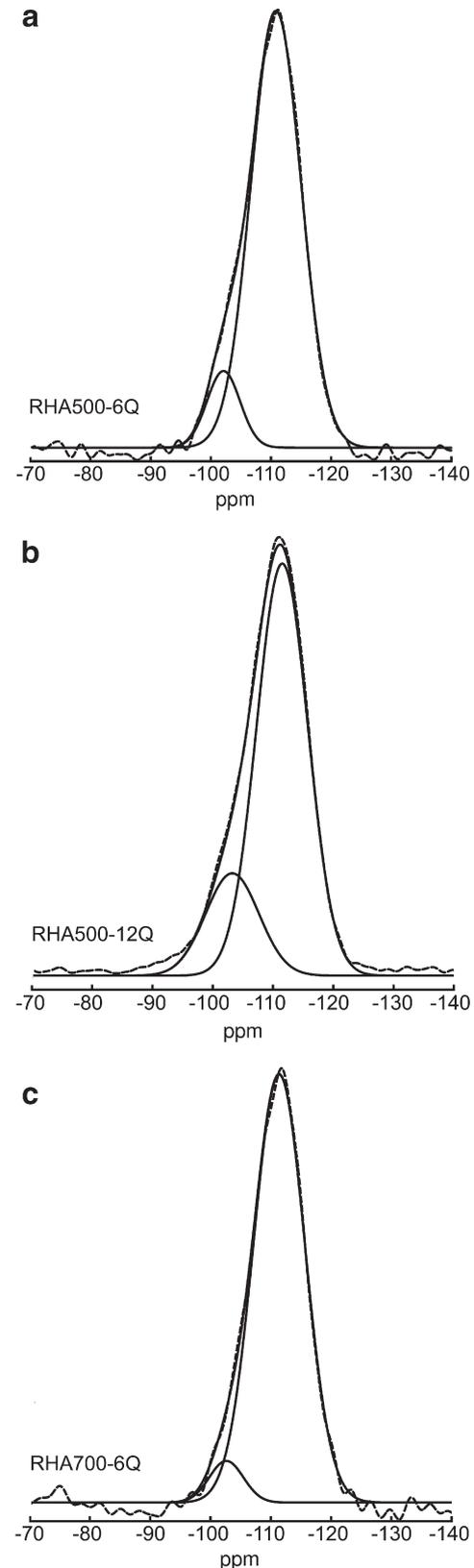


Fig. 5. ^{29}Si MAS NMR spectra for RHA samples burnt at different temperatures for varying time. a) RHA sample burnt at 500 °C for 6 h and cooled quickly (RHA500-6Q). b) RHA500-12Q and c) RHA700-6Q. The broad resonance at -111 ppm is assigned to Q^4 branches in condensed amorphous silica. The shoulder at -102 ppm indicates the presence of silanol (Q^3) sites.

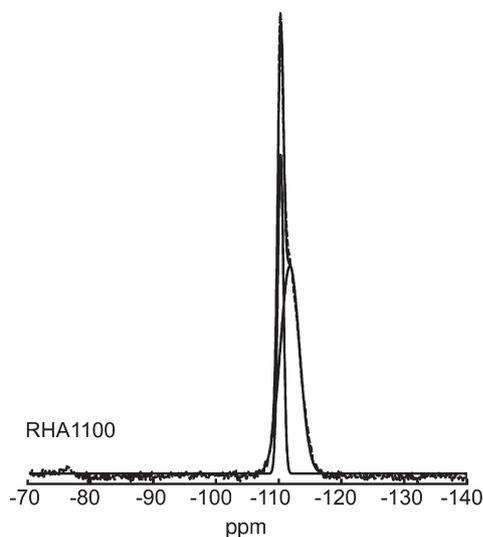


Fig. 6. ^{29}Si MAS NMR spectrum of RHA1100. The narrow lines at -110 and -112 ppm are assigned to crystalline cristobalite and tridymite [15].

Pfleiderer et al. [27] obtained somewhat longer T_1 values and found the relaxation curves to be multi-exponential. In the present study the spin-lattice relaxation for a few selected samples was determined using saturation-recovery experiments. In all cases the recovery of ^{29}Si magnetization appears to be strongly multiexponential with short relaxation contributions of less than a second to contributions of hundreds of seconds. This is a typical behavior expected for highly condensed silica. Due to their low natural abundance and small chemical shift anisotropy silicon spins in the core of a silica particle relax very slowly, whereas ^{29}Si spins at the surface of a particle have more efficient relaxation mechanisms by their coupling to protons from the surface silanol groups and/or to paramagnetic oxygen present at the surface of the particles [28]. The bulk silicon is thought to relax by spin-diffusion of magnetization to the surface, which is very inefficient in silica considering the low gyromagnetic ratio and the relatively large distances between neighboring ^{29}Si spins. The spin-lattice relaxation

time could therefore in principle be a measure for the surface area. This is very difficult to quantify, however, as this relaxation time also depends on particle morphology and the possible presence of paramagnetic impurities such as iron in the samples. Considering the fact that a distribution in particle size and porosity/morphology occurs in the samples a strong distribution of spin-lattice relaxation is to be expected in the samples as is confirmed experimentally. For the RHA samples burnt at 500°C an average spin-lattice relaxation time [24] $\langle T_1 \rangle = 147$ s has been determined showing that with a recycle delay of 600 s a quantitative analysis of the spectra is possible with good accuracy as the intensities of the sites with the longest T_1 's are underestimated by a maximum of 5%. For the samples processed at 700°C the average $\langle T_1 \rangle$ more than doubled to 337 s. By extrapolating the KWW stretched exponential function it was estimated that for these samples a prohibitively long relaxation delay of ~ 2000 s would be needed to get fully quantifiable results. As the relaxation delay of the Q^3 sites is expected to be shorter than that of the Q^4 sites the amount of the Q^4 sites may be underestimated. This could amount to a relative error of 20%. For the samples with crystalline content, the average spin-lattice relaxation time dramatically increased to ~ 1000 s which could lead to intensity misjudgements of a factor of 2 for the slowest relaxing (crystalline) Q^4 sites.

Table 2 summarizes the results of the spectral deconvolution of the various ^{29}Si MAS NMR spectra of the RHA samples. Q^4 sites assigned to be present in the amorphous respectively crystalline parts of the samples are listed as separate rows in the table. The line shape was assumed to be purely gaussian for all resonances in the amorphous phase. Of particular interest is the amount of silanol species (Q^3) present in the amorphous material as this is thought to be related to the reactivity of the samples and their pozzolanic properties. Table 3 lists the relative amount of Q^3 sites present in the amorphous part of the samples taking the earlier stated uncertainties in the quantification into account. The amount of Q^3 sites in the RHA500-6Q and RHA500-6S samples is 10% and 6% respectively. This indicates that the condensation reactions in the ashes are

Table 2
Results of the spectral deconvolution of the ^{29}Si MAS NMR data for various RHA samples

Sample	RHA500-6Q	RHA500-6S	RHA500-12Q	RHA500-12S	RHA700-6Q	RHA700-6S	RHA900-6Q	RHA900-6S
Q^3								
Peak positions (ppm)	-102.1	-101	-103.2	-102.4	-102.6	-101.7	-103.5	-103.1
Peak area (a.u.)	7.6	4.7	40.4	21.0	3.0	2.4	2.5	0.3
FWHH (ppm)	6.5	6	10.4	7.5	6.7	5.6	6.6	7.4
Q^4								
Peak positions (ppm)	-110.9	-110.2	-111.5	-111.1	-111.4	-111.2	-111.8	-112.2
Peak area (a.u.)	65.4	75.0	156.1	156.4	45.5	76.3	32.8	28.5
FWHH (ppm)	9.8	10.6	10	10	10	11.7	8.3	8.9
Crystalline Q^4								
Peak positions (ppm)							-111.1	-111.3
Peak area (a.u.)							6.4	12.7
FWHH (ppm)							2.5	3.1

Peak positions are quoted in ppm relative to tetramethylsilane (TMS). For each line the integrated peak area (in arbitrary units) corresponds to the relative amount of ^{29}Si spins. The full width at half height (FWHH) in ppm reflects the variation in Si–O–Si bond angles that is experienced for the various Q^3 and Q^4 sites. For the RHA900 samples a second narrower Q^4 resonance is observed assigned to the appearance of crystalline material.

Table 3
Lower and upper estimate of the percentage of silanol sites in the amorphous fraction of rice husk ashes produced under different conditions based on spectral deconvolution of their ^{29}Si MAS NMR spectra

Sample	RHA500-6Q	RHA500-6S	RHA500-12Q	RHA500-12S	RHA700-6Q	RHA700-6S	RHA900-6Q	RHA900-6S
Q^3 (%)	9–10	5–6	19–21	10–12	5–6	2–3	3–7	<1

At incineration temperatures above 500 °C ^{29}Si spin-lattice relaxation times become prohibitively long to obtain fully quantitative data (see text).

progressing during the cooling process leading to a more condensed network with less surface sites for the slowly cooling samples.

An intriguing observation is that the amount of silanol groups increases by increasing the incineration time to 12 h to 21% and 12% for the samples RHA500-12Q and RHA500-12S respectively. This is in line with an earlier investigation of Ibrahim and Hemaly [16] who reported a continuous increase in the specific surface area and pore volume in RHA samples produced at 500 °C with increasing burning duration up to 12 h. Almost constant values of BET surface area and pore volume were reported when the duration was increased from 12 h to 24 h. Most likely the presence of organic material plays a key role here. During incineration expelling the carbon fraction and silica condensation are interacting processes. As long as organic material is present in the material it can act as a template around which the silica condenses. As soon as this material is expelled it will leave voids in the silica leading to the formation of porous particles which can have very high internal surfaces. Indeed our LOI data (Fig. 1) show that at incineration temperatures of 500 °C not all of the carbon has been expelled after 6 h. At burning times of 12 h all carbon is removed which explains that no further changes in pore volume were observed by increasing the incineration temperature from 12 to 24 h.

Moving to a higher burning temperature of 700 °C the amount of silanol groups is 6% and 3% for the RHA700-6Q and RHA700-6S samples respectively which is a marked decrease when compared to the samples burnt at 500 °C. This is in line with the expectation that a higher burning temperature leads to faster oxidation of the organic content which, in combination with the efficient condensation of the silica, leads to a denser network with less surface sites. This higher degree of condensation is further confirmed by the observed increase in average spin-lattice relaxation time. Again a slow cooling process leads to a further reduction of the silanol sites. It should furthermore be noted that the quoted Q^3 content is an upper limit as the increase in the spin-lattice relaxation time for these samples may lead to an overestimation of the amount of (faster relaxing) Q^3 species. Going to even higher burning temperature of 900 °C we observe the first formation of crystalline material, although the majority of the material is still amorphous. In the RHA900-6Q sample there is still a reasonable amount (7%) of Q^3 species present in the amorphous fraction of the sample. Again it should be noted that this amount is an estimated upper limit as the spin-lattice relaxation times of this condensed material becomes prohibitively long to obtain fully quantitative data.

In summary, the ^{29}Si NMR data give direct access to identification of the reactive sites in the RHA samples. First of

all it can be used to observe the onset of the formation of crystalline material complementary to XRD experiments. Furthermore it is possible to directly observe the surface silanol sites. Spectral deconvolution of the spectra clearly identifies the RHA500-12Q sample as having the highest amount of silanol groups making samples processed under these conditions favorable for pozzolanic cement additives.

4. Conclusion

An in-depth characterization of rice husk ashes has been conducted to identify the optimum conditions for producing a reactive ash from rice husk. The amount of soluble silica and loss on ignition in the different RHA samples showed that incineration at 300 °C is unsuitable, as not all carbon is expelled from the samples. These analyses furthermore indicate the reactivity of samples burnt at 500 °C or 700 °C. This agrees with the earlier investigations of Mehta [2] and Hamad et al [8] who have identified the temperature range of 500 to 700 °C as optimum for reactive ash formation, although very different processing times have been suggested.

Electrical conductivity tests verify the good pozzolanic activity of the RHA500 and RHA700 samples, with uniformly higher values for the samples incinerated at 500 °C. XRD and microscopic analysis confirmed the amorphous character of both the RHA500 and RHA700 samples with the first crystalline material appearing at processing temperatures of 900 °C and higher.

^{29}Si MAS NMR proved to be a very effective tool to get insight in the formation of reactive material on a local structural level. First of all it can accurately determine at which temperature significant amounts of crystalline material starts to be formed. At lower incineration temperatures the broad Gaussian line shapes in the spectra of the different RHA samples supports the amorphous nature of the silica in samples burnt at temperatures of 500 °C and 700 °C. At higher temperatures a gradual conversion to crystalline material is observed, in agreement with the XRD results. Optimal incineration temperatures are those where all carbon content is expelled at the end of the processing. NMR also allows one to directly observe the surface silanol sites in the amorphous phase, which are thought to relate to the activity of the sample in the pozzolanic reaction with lime. The amount of Q^3 sites in the amorphous phase of the RHAs varied with a clear maximum for RHA500-12Q with a $Q^4:Q^3$ ratio of 4:1. This sample also showed the highest conductivity drop in the pozzolanic activity test. So we come to the conclusion that the most reactive rice husk ashes are produced after incineration for 12 h at 500 °C and subsequently quickly cooling the sample down by directly removing it from the oven.

Acknowledgement

The authors thank Dr. R. de Gelder (Institute for Molecules and Materials, Radboud University) for acquisition of the XRD spectra and their interpretation. Mr. G.J.A. Janssen (Radboud University) is acknowledged for the SEM pictures. The first author would also like to express her sincere thanks to Prof. Klaas van Breugel and Dr. Hans Pietersen, Faculty of civil Engineering and Geosciences for their valuable discussion and suggestions.

References

- [1] V.M. Malhotra, P.K. Mehta, *Pozzolanic and Cementitious Materials*, Gordon & Breach Publishers, Amsterdam, 1996.
- [2] K. Kamiya, A. Oka, H. Nasu, T. Hashimoto, Comparative study of structure of silica gels from different sources, *Journal of Sol-Gel Science and Technology* 19 (2000) 495–499.
- [3] P.K. Mehta, Siliceous ashes and hydraulic cements prepared there from, U.S. Patent, 1978.
- [4] J.S. Coutinho, The combined benefits of CPF and RHA in improving the durability of concrete structures, *Cement & Concrete Composites* 25 (2003) 51–59.
- [5] M.H. Zhang, V.M. Malhotra, High-performance concrete incorporating rice husk ash as a supplementary cementing material, *Aci Materials Journal* 93 (1996) 629–636.
- [6] S.K. Chopra, S.C. Ahluwalia, S. Laxmi, Technology and manufacture of rice husk masonry cement, ESCAP/RCTT Third Workshop on Rice Husk Ash Cements, New Delhi, 1981.
- [7] K. Ankra, Studies of black silica produced under varying conditions, Ph.D. Thesis, University of California, Berkeley, 1976.
- [8] M. Nehdi, J. Duquette, A. El Damatty, Performance of rice husk ash produced using a new technology as a mineral admixture in concrete, *Cement and Concrete Research* 33 (2003) 1203–1210.
- [9] M.A. Hamad, I.A. Khattab, Effect of the combustion process on the structure of rice hull silica, *Thermochemica Acta* 48 (1981) 343–349.
- [10] D.D. Bui, Rice husk ash a mineral admixture for high performance concrete, Civil Engineering and Geosciences, Ph.D. Thesis, Delft University of Technology, Delft, 2001.
- [11] J. James, M.S. Rao, Silica from rice husk through thermal-decomposition, *Thermochemica Acta* 97 (1986) 329–336.
- [12] J. James, M.S. Rao, Reactivity of rice husk ash, *Cement and Concrete Research* 16 (1986) 296–302.
- [13] Q.J. Yu, K. Sawayama, S. Sugita, M. Shoya, Y. Isojima, The reaction between rice husk ash and Ca(OH)₂ solution and the nature of its product, *Cement and Concrete Research* 29 (1999) 37–43.
- [14] T. Hiemstra, W.H. van Riemsdijk, Multiple activated complex dissolution of metal (hydr)oxides: a thermodynamic approach applied to quartz, *Journal of Colloid and Interface Science* 136 (1990) 132–150.
- [15] G. Engelhardt, D. Michel, *High-Resolution Solid-State NMR of Silicates and Zeolites*, J. Wiley and Sons Ltd., Chichester, 1987.
- [16] R. Dupree, *Nuclear Magnetic Resonance as a Structural Probe for SiO₂*, J. Wiley and Sons Ltd, Chichester, 2000.
- [17] R.F. Pettifer, R. Dupree, I. Farnan, U. Sternberg, NMR determinations of Si–O–Si bond angle distributions in silica, *Journal of Non-Crystalline Solids* 106 (1988) 408–412.
- [18] H. Hamdan, M.N.M. Muhid, S. Endud, E. Listiorini, Z. Ramli, Si-29 MAS NMR, XRD and FESEM studies of rice husk silica for the synthesis of zeolites, *Journal of Non-Crystalline Solids* 211 (1997) 126–131.
- [19] R.F. Abreu, J. Schneider, M.A. Cincotto, Structure and hydration kinetics of silica particles in rice husk ash studied by Si-29 high-resolution nuclear magnetic resonance, *Journal of the American Ceramic Society* 88 (2005) 1514–1520.
- [20] ASTM, Standard methods of sampling and testing fly ash or natural pozzolanas for use as a mineral admixture in Portland cement concrete, www.astm.org.
- [21] M.P. Luxan, F. Madruga, J. Saavedra, Rapid evaluation of pozzolanic activity of natural-products by conductivity measurement, *Cement and Concrete Research* 19 (1989) 63–68.
- [22] Q.G. Feng, H. Yamamichi, M. Shoya, S. Sugita, Study on the pozzolanic properties of rice husk ash by hydrochloric acid pretreatment, *Cement and Concrete Research* 34 (2004) 521–526.
- [23] S. Goni, A. Guerrero, M.P. Luxan, A. Macias, Activation of the fly ash pozzolanic reaction by hydrothermal conditions, *Cement and Concrete Research* 33 (2003) 1399–1405.
- [24] M. Laviolette, M. Auger, S. Désilets, Monitoring the aging dynamics of glycidyl azide polyurethane by NMR relaxation times, *Macromolecules* 32 (1999) 1602–1610.
- [25] J.D. van Beek, matNMR: a flexible toolbox for processing, analyzing and visualizing magnetic resonance data in Matlab(R), *Journal of Magnetic Resonance* 187 (2007) 19–26.
- [26] C.A. Fyfe, G.C. Gobbi, G.J. Kennedy, Quantitatively reliable Si-29 magic-angle spinning nuclear magnetic-resonance spectra of surfaces and surface-immobilized species at high-field using a conventional high-resolution spectrometer, *Journal of Physical Chemistry* 89 (1985) 277–281.
- [27] B. Pfeleiderer, K. Albert, E. Bayer, L. van de Ven, J. de Haan, C. Cramers, A new approach to the silica-gel surface — characterization of different surface regions by Si-29 magic angle spinning NMR relaxation parameters and consequences for quantification of silica-gels by NMR, *Journal of Physical Chemistry* 94 (1990) 4189–4194.
- [28] J. Klinowski, T.A. Carpenter, J.M. Thomas, The origin of Si-29 spin-lattice relaxation in zeolites — a means of rapid acquisition of NMR-spectra and of probing internal sites in microporous catalysts, *Journal of the Chemical Society-Chemical Communications* (1986) 956–958.