Thermal expansion behavior, phase transitions and some physico-mechanical characteristics of fired doped rice husk silica refractory

Benjamin Iyenagbe UGHEOKE^{a,*}, Othman MAMAT^a, B. ARI-WAHJOEDI^b

^a*Department of Mechanical Engineering, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar 31750, Tronoh, Perak, Malaysia*

^b*Department of Fundamental and Applied Sciences, Universiti Teknologi PETRONAS,
Bandar Seri Iskandar 31750, Tronoh, Perak, Malaysia*

Received: November 17, 2012; Revised: February 03, 2013; Accepted: February 06, 2013

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Abstract: This paper presents the findings on thermal expansion behavior of slaked lime doped rice husk silica (RHS) refractory monitored between 25 °C and 1500 °C. It also reports the phase transition analysis within the temperature range of 850–1450 °C. A sudden expansion of 0.7% noticed at 220 °C is due to the transformation of α -cristobalite to β -cristobalite. The highest expansion (0.85%) reached within the temperature range of 650–850 °C, remains almost constant for the investigated temperature range, and is not high enough to cause macro cracks in the refractory. The phase transition order is similar to those reported for quartzite refractory after 600 °C, though the crystallization temperature is lowered due to the presence of the dopant. Modulus of rupture, apparent porosity, bulk density, refractoriness and reheat change are reported and their results meet with the standards qualifying them for use in coke ovens.

Keywords: rice husk silica refractory; thermal expansion; phase transitions; physico-mechanical characteristics

1 Introduction

Silica refractory exhibits complex phase transformations due to the presence of a combination of low tridymite, α -cristobalite and residual α -quartz. If these three phases are present in the refractory body with significant quantities, they would result in after-expansion phenomenon. The magnitude of after-expansion phenomenon could be so high as to result in crack formation at temperatures of 117–163 °C, 200–270 °C or 573 °C, which correspond

respectively to the inversions of low tridymite to high tridymite, α -cristobalite to β -cristobalite, and α -quartz to β -quartz. For this reason, silica refractory has been adjudged to have poor thermal shock resistance at low temperature (below 600 °C).

Research has long established the fact that rice husk is a rich source of amorphous (biogenic) silica [1,2], which has, amongst other applications, been used in the production of insulating refractory [3,4]. Rice husk silica (RHS) is different in both structure and chemistry from the silica obtained from quartzite, the main source of the raw material used in silica refractory manufacture. RHS is amorphous and hydrated, while quartzite is crystalline and

* Corresponding author.
E-mail: ugheokeb@gmail.com

non-hydrated. Based on the structure and chemistry of RHS, it is hypothesized that RHS could be used as raw material for the production of silica refractory with improved low-temperature thermal shock resistance [5].

Nayak and Bera [6] have done some studies on the phase transitions that occur in sintered RHS ceramics. They give an overview of the inversions that occur amongst various polymorphs of silica as RHS is sintered between 700 °C and 1400 °C. However, when silica refractories are manufactured, there is a necessity of doping the silica with some mineralizer (which is usually an alkali metal oxide), that would aid in the early tridymitization of the refractory, since the presence of tridymite is thought to improve the physico-mechanical properties of the sintered refractory [7]. The addition of mineralizer during manufacture affects the phase transition temperature, as it changes the temperature range over which any silica polymorphs is stable. This assertion was confirmed by the work of Nayak and Bera [6], when they reported different inversion temperatures amongst RHS of varying degrees of alkali impurities. The second effect that the mineralizer has is the formation of alkali silicates, which are known to present dimensional stability to the refractory during use. Liquid phase sintered at lower temperature is thought to result from the formation of some visco-elastic phases, which inhibit crack propagation through the refractory body when in service [8]. Thus, it is necessary to study the expansion behavior of a formulated refractory in order to predict its behavior during service. The thermal expansion behavior of RHS refractory doped with slaked lime ($\text{Ca}(\text{OH})_2$) and the effect of the dopant on phase transitions have not been studied or reported in the extant literature.

This paper reports the thermal expansion behavior studies of RHS refractory doped with slaked lime using a dilatometer within the temperature range between 25 °C and 1500 °C. It also reports the results of phase transformation analysis which takes place in the silica refractory body after firing in the temperature range of 850–1450 °C, using X-ray diffraction (XRD). The implications of these expansion and phase transitions on the formed refractories are presented. The paper also discusses some physico-mechanical properties of the developed RHS refractory, so as to give insight on its service performance.

2 Materials and methods

2.1 Materials

RHS was obtained from Malaysian rice husk through a hydro thermo-baric process reported elsewhere [9]. The mean composition of the RHS determined by X-ray fluorescence (XRF) is shown in Table 1. Its average particle size was determined as shown in Section 2.2.1. Analytical reagent grade slaked lime ($\text{Ca}(\text{OH})_2$, R&H Chemicals) with average particle size of 50 µm was used as mineralizer in compounding the refractory, and pellets of polyethylene glycol 8000 (PEG, Merck) was as supplied. A solution of 5 wt% concentration prepared from the pellets of PEG using standard measure of distilled water was used as binder.

Table 1 Chemical composition of hydro thermo-baric treated RHS used in the investigation

Compound	Percentage (wt%)
SiO_2	99.040
K_2O	0.111
P_2O_5	0.376
CaO	0.180
Al_2O_3	0.210
Fe_2O_3	0.083

2.2 Methods

2.2.1 Particle size analysis of RHS

RHS obtained from the hydro thermo-baric process [9] was analyzed using a Zetasizer Nano ZS (ZEN 3600). 2 g of the RHS particles were homogeneously mixed with deionized water to make a dilute solution for the measurement of nanoparticles' size. Homogeneous mixing was achieved through a combination of manual or mechanical and magnetic stirring. Several readings were taken, all at room temperature to establish consistency.

2.2.2 Refractory composition and compounding

Each batch of sample composition weighed 15 g. Of this 15 g, the mineralizer ($\text{Ca}(\text{OH})_2$) accounted for 1.4 wt%. All weight measurements were accomplished using analytical balance (Mettler Toledo) with an accuracy of 0.001 g. An appropriate amount of the prepared PEG solution was added carefully to the powder mix to form slurry. The slurry was stirred for 1 h to ensure homogeneous mixing of the powders and binder by using a magnetic stirrer. The excess water was evaporated from the slurry in an oven at a

temperature of 105 °C and the dry powder mix was pulverized in ceramic mortar to minimize agglomeration. Calculated amounts of the homogeneously mixed powders were measured into mould and compacted under a pre-determined pressure of 105 MPa using an auto palletizing machine, to form refractory green bars of 35 mm×9 mm×6 mm, which were later fired in line with the firing regimes stated in Section 2.2.3.

2.2.3 Firing of the refractories

Samples of the green test bars were fired in the temperature range of 850–1450 °C, at an interval of 100 °C. The holding time at each temperature was 6 h. The samples used for the dilatometric investigations were fired at 1350 °C.

2.2.4 Characterization

X-ray diffractometer (XRD, Bruker D8 Advance, Germany) was used to determine the mineralogical composition and phase transitions in the sintered refractory. Each specimen was scanned in a range of $2^\circ \leq 2\theta \leq 80^\circ$ at a scanning speed of 4 (°)/min. For the thermal expansion studies, a Shinku-Riko LIX Laser Interferometric Dilatometer was used and it gave plots of the thermal expansion and coefficients of thermal expansion of the samples at different temperatures, ranging from 25 °C to 1500 °C. The modulus of rupture (MOR) tests were performed in line with the prescription of ASTM 133 [10], using a 5 kN universal testing machine (UTM, Lloyd LR-5K). The cross head speed was set to 0.5 mm/min. The boiling water method described in ASTM C20 [11] was used to perform apparent porosity and bulk density tests. Tests on refractoriness were done in line with a modified ASTM C24 [12]. The test cones used were trigonal pyramids with base dimensions of 7 mm×7 mm×7 mm, having a height of 35 mm. The objective was to check if the samples could withstand the thermal stresses at 1650 °C (the equivalence of cone number is 28), without distortions or melting. The samples were fired at 1650 °C for about 80 min. Linear shrinkage was determined by measuring the dimensional changes occurring between the green and fired samples using a digital vernier caliper. The dried linear dimensions of the green refractories were measured after air drying overnight. The green samples were fired at 1350 °C for 6 h, after which the cool length was recorded. The percentage of linear shrinkage L_s was determined using Eq. (1), in which L and ΔL are the original (dried green length) and change in length as a result of the firing,

respectively:

$$L_s = -\frac{\Delta L}{L} \times 100\% \quad (1)$$

The furnace used for performing the linear shrinkage as well as the reheat change tests was Carbolite 1450. All other firing/sintering processes were accomplished in a Carbolite 1800 Furnace under air atmosphere.

3 Results and discussion

3.1 RHS particle size analysis

Figure 1 shows a narrow and unimodal particle size distribution pattern for the tested hydro thermo-baric process purified RHS. It is a representative presentation of the 50 replica tests carried out. From the results, the average particle size of the RHS was determined to be 117 nm. This is the assumed particle size of the RHS used in all other experiments reported in this paper.

Fig. 1 Particle size distribution for the RHS obtained from the hydro thermo-baric process.

3.2 Phase transitions and thermal expansion studies

Figure 2 shows the X-ray diffractograms of the sintered silica refractory. At 850 °C, the refractory remains largely amorphous dominated by opal-CT form of silica, referred to as silica glass by many authors [6].

As the sintering temperature increases to 950 °C, crystallization begins in the refractory body with the formation of tridymite. This is the shoulder at $2\theta = 26.5^\circ$. However, the amorphous phase still remains the major phase in the entire refractory. At 1050 °C, the entire refractory is now largely crystalline, with tridymite peaks at $2\theta = 22.5^\circ$ coexisting with a cristobalite phase growing strongly at $2\theta = 27^\circ$. Meanwhile, some of this cristobalite has inverted back to a hexagonal β -quartz and then forming a peak of

Fig. 2 Stacked XRD patterns (a)–(g) of RHS refractory sintered at 850–1450 °C.

cristobalite mixed with tridymite at $2\theta = 22.5^\circ$, 45° and 67.5° . At 1250 °C, much of the tridymite had transformed to high-temperature form of cristobalite with traces of quartz. Also at this temperature, a wollastonite phase manifested at $2\theta = 36.5^\circ$ and continued its growth progressively, becoming greatly pronounced at 1350 °C. The quartz formed in addition to the tridymite still remaining has inverted completely to cristobalite between 1250 °C and 1350 °C and so remained till 1450 °C, which is the maximum temperature monitored for the transformation. At this temperature, the cristobalite coexisted with traces of wollastonite.

The early crystallization of the refractory at the temperature range between 850 °C and 1050 °C is as a result of the dopant (mineralizer)—slaked lime and the OH group in opal, the presence of which lowers the inversion temperature of silica polymorphs [6–9,13,14]. In fact, Nayak and Bera [6] have reported that complete crystallization of RHS with 99.87% purity only takes place at about 1300 °C. The implications of these phase transitions for silica refractory performance are enormous.

Badly transformed silica bricks manifest considerable after-expansion effects during service temperatures, usually in excess of 1200 °C. This is mostly as a result of the presence of high percentage of quartz, which exhibits high volumetric increase as it inverts to cristobalite beyond 1250 °C. Thus, it is usually recommended that depending on the grain size, residual quartz in silica refractory should range between 3% and 6% for fine and coarse grains [15]. As

is evident from Fig. 2, the after-expansion effect in the temperature range of 1250–1350 °C is not pronounced when considered in relation to the maximum witnessed at the temperature range of 650–850 °C. It is actually a negative expansion perceived to be a consequence of lattice contraction of tridymite.

There are some salient inferences that could be deduced from the thermal expansion behavior of the doped silica refractory (Fig. 3). In the temperature range of 25 °C to about 220 °C, there is a gradual rise in the expansion of the silica refractory. The peak expansion in this temperature range is about 80 μm , or 0.24% of the original 33.1 mm length of the fired silica refractory. At about 220 °C, there is a sharp amount of expansion of 230 μm or about 0.7% (Table 2) of the total sintered length of 33.1 mm. This sharp expansion witnessed at 220 °C is no doubt, a phase transition of a silica polymorph. From the reports of Kikuchi *et al.* [16], it represents the inversion of α -cristobalite to β -cristobalite. This observation in the thermal expansion of RHS refractory is totally different from that of sintered silica refractory made from quartzite. In the quartzite manufactured silica refractory, there is a lack of this sharp rise at 220 °C; instead, points of inflexion are noticed at temperature range of 117–163 °C or 570–580 °C, corresponding to the inversions of low tridymite to high tridymite and α -quartz to β -quartz [16]. In the same vein, the magnitudes of the attendant expansion are different for RHS and quartzite refractories. While the normally reported linear expansion that accompanies α -cristobalite to β -cristobalite is between 4% and 5%

for quartzite refractories on raw material basis [15,17], it is lower for RHS refractory (0.7%). The preliminary reason that could be adduced for this low expansion is the presence of the wollastonite phase in the sintered refractory, which acts as expansion stabilizer, inhibiting much of the expansion that would have occurred. One other effect the mineralizer exhibits is that it is able to undergo liquid phase sintering with many of the impurities in the RHS to form some visco-elastic phases. For instance, anorthite was detected in the sintered refractory. One of the positive effects of these visco-elastic phases is that they are capable of forming shields around crack-tips, thus leading to better thermal shock resistance [8].

From the curve of Fig. 3, the maximum expansion witnessed (about 0.85%) is found at the temperature range of 650–850 °C, and could be attributed to a combination of the volume expansions which characterize the transformation of α -quartz to β -quartz and α -cristobalite to β -cristobalite. After this expansion peak, the curve of the dilatogram shows a smooth and very low contraction in dimensions up to 1500 °C. In terms of thermal shock resistance, these observations hold good promise for low and high temperature thermal shock resistance. Apart from the sudden expansion at about 220 °C, which is not high enough to cause cracks in the refractory body, the expanded volume is almost constant thereafter. This means the refractories would be able to cope with rapid changes in temperatures, whether at low or high temperature ranges. To prove this point, samples of silica refractory

were made, pre-fired at 1350 °C. The pre-fired samples were subjected to three thermal cycles within 25 °C and 650 °C using high heating rates: 15 °C/min, 20 °C/min and 25 °C/min. X-ray radiographs were taken of the samples before and after the thermal cycles. Thereafter, the samples were observed for macro cracks formation. These were absent as evidenced in Fig. 4. The traditional method for thermal shock resistance determination for silica refractory as prescribed by BS 1902-1A [19] was employed. The samples were heated up to 450 °C and quenched in water and removed. At each point they were removed, the samples were observed for macro cracks and if none was observed, they were pulled laterally by hand. They were placed right back in the furnace to be heated up again after observation. Five samples were tested and all of the samples withstood over 30 cycles before they could be pulled apart by hand. It is noteworthy that the recommended heating rate for silica refractory made from quartz sources in order to forestall the occurrence of macro crack formation is 10 °C/min [18].

It is interesting to note that these observed transitions from one polymorph to the other are reversible and this is clearly demonstrated in the lower of the cooling curves plotted in the dilatogram (Fig. 3). The curves for the coefficients of thermal expansion, which gave peak values at 220 °C are essentially for design purposes, which is not the focus of the present paper.

Fig. 3 Graphs showing the curves of thermal expansion and coefficients of thermal expansion of the sintered refractory.

Fig. 4 X-ray radiographs of RHS refractory samples (a) before and (b) after being subjected to high heating rates of (1) 15 °C/min, (2) 20 °C/min and (3) 25 °C/min.

3.3 Physico-mechanical properties

Table 2 shows the test results for the modulus of rupture (MOR), bulk density (BD), apparent porosity (AP), linear shrinkage (LS), permanent linear (reheat) change (PLC), linear thermal expansion (TE) and maximum linear thermal expansion (TE_{max}).

In the MOR test, five samples were investigated using a 5 kN UTM (Lloyd Instruments). The ASTM C133 [10] prescribed the equation for calculating MOR for a three-point bend test:

$$\text{MOR} = \frac{3PL}{2bd^2} \quad (2)$$

where P , L , b and d are the applied load, the span (distance between mid-pivot crests), the width and the thickness of the fired specimen, respectively. From Fig. 4, the values of these parameters are clearly shown, obtained and used in the prescribed Eq. (2) to calculate the MOR. The results and the accompanying statistics (standard deviation) are presented in Table 2. The result shows a mean MOR of about 14 MPa compared to the prescription of 3.45 MPa for silica refractory in ASTM C133 [10], so it could be concluded that this MOR result is a positive indicator.

BD and AP share an inverse proportional relationship and they are useful in refractory for the

Table 2 Physico-mechanical properties of RHS, each quantity had sample size of five

Quantity	Mean value	Standard deviation	Recommended or reported values
MOR (MPa)	13.9335	0.017654	3.45 [20]
TE (%)	0.6980	0.0148	4–5 [15,17]
TE _{max} (%)	0.8462	0.0091	Up to 7 [17]
BD (g/cm ³)	1.3438	0.0044	0.72–0.76 [3]
AP (%)	41.9238	0.0083	66–68 [3]
LS (%)	5.4012	0.0052	Not available
PLC (%)	0	0	Not available

purpose of control of mechanical properties and thermal conductivity. Usually, the higher AP is, the lower BD, thermal conductivity and MOR are. Although there are no standard values prescribed for the bulk density or apparent porosity of silica refractory, Reference [3] has reported that rice husk silica insulating refractory employing lime as dopant ranged from 0.72 g/cm³ to 0.76 g/cm³ for BD and 66% to 68% for AP. The comparison of these values with the results of the current research is shown in Table 2, and it is clear that this work reports superior values. The reason that could be adduced for these improved properties is that the process parameters (compaction pressure, firing temperature, and percentage of the dopant) for the production of silica refractory had been optimized (though not reported along this paper due to the page limit). Thus, the use of compaction pressure of 105 MPa, firing temperature of 1350 °C and 1.4 wt% of the mineralizer are not just arbitrary.

Using the optimized production parameters stated above, the RHS refractory recorded a zero-percent reheat change, which was performed in accordance with ASTM C113 [21]. This is due to the stabilization effect of wollastonite and the very low, but reversible thermal expansion of the refractory. The linear shrinkage is about 5.4%, which may be due to a combination of loss on ignition, liquid phase sintering and lattice contraction.

3.4 Refractoriness

In this test, the effect of the dopant on the refractoriness of the RHS refractory was in focus. Samples A, B, C, D and E contained 0, 1 wt%, 1.4 wt%, 1.8 wt% and 3.4 wt% of slaked lime, respectively. As evident from Fig. 5(b), the mix containing between 1 wt% and 1.8 wt% of the slaked lime witnessed the negligible distortions. All the samples withstood a firing temperature of 1650 °C (which corresponds to standard cone number 28) without melting, but the distortions in Samples A and E

suggest that their mix (0 and 3.4 wt% of the slaked lime, respectively) may be not suitable for RHS refractory manufacture. This is because such distortions could result in refractory brick warpage while in use.

Fig. 5 Pyrometric cone equivalents of RHS refractories: (a) before and (b) after firing at 1650 °C.

4 Conclusions

The phase transitions in RHS refractories doped with slaked lime have been studied. From the work, it is evident that RHS refractories only have a sharp but low thermal expansion (0.7%) at a temperature about 220 °C, which is considered not high enough to cause micro or macro cracks in the refractory body. Thus, it is inferred that RHS refractory has better low-temperature thermal shock resistance than silica refractory made from quartzite. Moreover, the

contraction witnessed at high temperatures is low, which may be due to the stabilization effect created in the refractory body as a result of the formation and presence of wollastonite. The phase transitions witnessed in the temperature range between 850 °C and 1450 °C are similar to those of quartzite silica refractories. The MOR observed for these refractories is about 14 MPa, which is about four-fold of the recommended value for silica refractory. The moderate values of apparent porosity and bulk density of the investigated RHS refractory coupled with the high refractoriness (in excess of 1650 °C) and MOR make them suitable for the application in coke ovens, without the risk of low-temperature thermal shock resistance that is associated with quartzite-manufactured silica refractory.

Acknowledgements

This work was supported in part by the Malaysian Ministry of Science, Technology & Innovation (MOSTI) E-Science Fund (Project Code 03-02-02-SF0089) and UTP graduate assistantship scheme. The authors appreciate these kind gestures.

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