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# Effect of rice husk ash in whiteware compositions

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**Abstract**

Quartz was progressively replaced by ground active silica obtained from rice husk ash (RHA) in a traditional whiteware composition and the effect of this replacement on the vitrification behaviour and mechanical and thermal properties in relation to the microstructure of specimens has been investigated. It has been found that the complete replacement of quartz by RHA drastically reduced both the maturing temperature and the percentage of thermal expansion, and increased the strength marginally. The improvement in the properties is attributed to sharp changes in the microstructural features as a result of significant reduction in the content of quartz phase and the simultaneous increase in glassy phase. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

*Keywords:* Rice husk ash; Whitewares

## 1. Introduction

Rice husk ash (RHA) contains an active form of silica ($SiO_2$) and is available in large quantities in India. It has been estimated by the Department of Agriculture, Government of India that the production of paddy will be about 150 million tonnes [1] by the year 2001. Paddy consists of 72% of rice, 5–8% of bran and 20–22% husk on average. Thus, 150 million tonnes of paddy will give us about 33 million tonnes of husk. Presently about 30 million tonnes of rice husk is produced in India per annum. Rice husk contains ash from 13 to 29% by weight depending on the variety, climate and geographic location [2]. About 6.0 million tonnes of rice husk ash is produced in India, which is mostly thrown away as waste. The ash is largely composed of silica (87–97%) with small amount of alkalies and other trace elements. The presence of silica as $SiO_2$ in rice husk ash has been known [3] since 1938. The silica in rice husk is in hydrated amorphous form, either opal or silica gel [4,5]. The use of rice husk ash in the form of silica in the ceramic field was also reported by Samandani et al. [6]. Borthakur et al. [7] also investigated physico-chemical properties of RHA for its application or utilisation.

Quartz is used in almost all whiteware bodies as a major crystalline phase. Quartz grains embedded in the porcelain glassy matrix have a deleterious effect on the mechanical strength mainly because of its transformation during cooling [8–10] which results in the development of stresses which initiate fracture [11]. The thermomechanical properties of whiteware bodies change greatly during the reconstructive and the displacive transformation of free silica due to change in volume, which was reviewed in detail by White [12].

Several investigators [13–22] tried to improve the mechanical properties of whiteware bodies by replacing quartz with other materials viz; sericitic pyrophyllite, kyanite, bauxite, sillimanite sand and alumina. Although the alumina in different forms has a favourable influence on the mechanical properties of whiteware due to the formation of primary mullite, it lowers the recystallization of secondary mullite due to an increase in the viscosity of the glassy phase. On the other hand, Schuller [23] showed that silica-rich glass favours recrystallization of mullite at low temperature and its dissolution at high temperature.

Some improvement in the mechanical properties was observed by several authors [24–27] through the reduction of the particle size of quartz and non-plastic materials. Tomizaki et al. [28] reported that dissolved quartz in the glassy phase and cristobalite phase precipitation

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are dependent on the silica particle size. The low quantity of quartz phase, the high content of cristobalite and the low internal porosity have detrimental effects on mechanical strength.

Rice husk ash (RHA), which contains active silica in large amounts also contains a high proportion of carbon in the composition and hence is presently disposed off by the rice mill industry as waste. Due to the substantial carbon content it has so far not been used in whiteware manufacture. Rice husk ash with minor or negligible amounts of carbon, if incorporated in the whiteware composition, could be expected to make an improvement in the properties and might be beneficial in many ways for the development of technical ceramics.

Keeping this in mind, quartz was progressively replaced by RHA in the present investigation and its effects on the properties of whiteware compositions were studied in detail.

## 2. Experimental procedure

The raw materials selected were Amrapali china clay (Supra grade), potash feldspar and calcined quartz. All the raw materials are abundant in India and are being used for the production of whiteware ceramics in the country. RHA incorporated in the whiteware body was prepared by controlled burning of raw rice husk in air so as to avoid the presence of carbon ($<5$ wt.%) as far as practicable. Calcined quartz and potash feldspar were wet ground separately in a ball mill using porcelain balls as grinding media around 300 mesh. The slurry was sieved, passed through a magnetic channel and dried. Rice husk ash was wet ground in a ball mill using porcelain balls as grinding media for 35 h. The particle size distribution of ground material as well as that of the Amrapali china clay, and the chemical and mineralogical analyses of the raw materials were carried out according to standard procedures. A standard whiteware body mix (CSR-1) was selected as the starting composition and rice husk ash was gradually incorporated into the body by replacing calcined quartz (Table 1).

The test specimens were extruded in a vacuum extruder in the form of cylindrical bars 1.5 cm diameter and 15 cm length. All the test specimens were dried and then fired between 1100 and 1300°C at temperature intervals of 50°C in an electric furnace. The heating rate in the furnace was 3.5°C $\text{min}^{-1}$. The specimens were soaked for 1 h at the respective peak firing temperatures.

Plastic and dry properties such as water of plasticity, dry linear shrinkage, dry strength, and bulk density of dried test specimens were determined by using standard procedures, as well as fired properties such as fired linear shrinkage, fired strength (M.O.R.), water absorption and bulk density. Per cent thermal expansion of matured specimens of different bodies was also measured [thermomechanical analyser (TMA), Shimadzu, Japan, DT-30 Model] under a heating rate of 10°C $\text{min}^{-1}$.

The major crystalline phases were identified by XRD and the microstructural features were studied by SEM on fracture-etched surfaces. The fracture-etched specimens, etched in 10% HF for 3 min were studied for the existence of various phases in the fired specimens.

## 3. Results and discussion

The chemical and rational analyses of Amrapali china clay (Supra grade), potash feldspar, quartz and rice husk ash are presented in Table 2.

The results of wet sieve analyses and particle size distribution of ground and processed raw materials are presented in Table 3. The results showed that the non-plastic materials, viz; feldspar, quartz and rice husk ash had coarser particles of about 1.5–2 wt.% on 53 μm and that the distribution of particles was almost identical.

Plastic and dry properties of body mixes (Table 4) altered marginally when quartz was progressively substituted by RHA in the traditional whiteware composition.

Changes in the fired properties — firing shrinkage, water absorption, fired strength, and per cent thermal expansion — with the gradual replacement of quartz by RHA in the conventional whiteware composition are shown in Figs. 1–4. The firing shrinkage (Fig. 1) of mixes gradually increased with an increase in the addition of RHA in the compositions. The increase in the firing shrinkage of specimens of CSR-6 at maturity (1150°C) on complete replacement of quartz by RHA in comparison with that of specimens of standard mix (CSR-1) was around 48.7%. However, this increase was

Table 1
Body composition with progressive replacement of quartz by rice husk ash in a standard whiteware composition (mass%)

| Mix no. | Amrapali china clay (supra grade) | Ground potash feldspar | Ground calcined quartz | Ground rice husk ash |
|---|---|---|---|---|
| CSR-1 | 50 | 25 | 25 | 0 |
| CSR-2 | 50 | 25 | 20 | 5 |
| CSR-3 | 50 | 25 | 15 | 10 |
| CSR-4 | 50 | 25 | 10 | 15 |
| CSR-5 | 50 | 25 | 5 | 20 |
| CSR-6 | 50 | 25 | 0 | 25 |

only 21.4% for CSR-3 at maturity (1200°C) on partial replacement of quartz by RHA (10 wt.%). This substantial increase in the firing shrinkage of mixes is attributed to the flabby nature of RHA particles and would unfavourably influence the output of body preparation and possibly increase the loss caused by cracking and deformation.

The conventional whiteware composition (CSR-1) attained vitrification and reached zero water absorption (Fig. 3) at a temperature of 1250°C with bulk density (Table 5) of 2.38 g $cm^{-3}$. With progressive incorporation of RHA, the maturing temperature decreased by about 50°C in CSR-3, CSR-4 and CSR-5 containing RHA, 10, 15 and 20 wt.%, respectively. These mixes

Table 2
Chemical analyses and mineralogical composition (rational analysis) of raw materials (mass%)

| Constituents | Amrapali china clay (supra grade) | Potash feldspar | Calcined quartz | Rice husk ash |
|---|---|---|---|---|
| *Chemical analysis* | | | | |
| $SiO_2$ | 46.24 | 65.65 | 96.80 | 88.44 |
| $Al_2O_3$ | 35.46 | 17.84 | 1.90 | 1.21 |
| $Fe_2O_3$ | 1.16 | 0.16 | 0.10 | 0.40 |
| $TiO_2$ | 0.76 | Trace | Trace | Trace |
| CaO | 1.58 | 0.20 | 0.15 | 1.20 |
| MgO | 0.08 | 0.24 | 0.02 | 1.82 |
| $Na_2O$ | 0.10 | 2.75 | 0.46 | 0.50 |
| $K_2O$ | 0.42 | 12.29 | 0.14 | 1.81 |
| L.O.I. | 14.10 | 0.84 | 0.40 | 4.62 |
| *Mineralogical composition (rational analysis)* | | | | |
| Kaolinite | 88.63 | – | 1.43 | – |
| Quartz | 3.10 | 2.70 | 93.47 | – |
| Feldspar | 3.33 | 93.47 | 5.00 | – |
| Calcite | 2.84 | 0.30 | – | – |
| Magnesite | 0.17 | 0.51 | – | – |
| Heamatite | 1.16 | 0.16 | 0.10 | – |
| Rutile | 0.76 | – | – | – |

Table 3
Particle size distribution of materials used for body formulation (mass%)

| Particle size (µm) | Amrapali china clay (supra grade) | Potash feldspar | Calcined quartz | RHA (ground) |
|---|---|---|---|---|
| *By sieve* | | | | |
| >150 | 0.10 | 0.06 | 0.14 | 0.40 |
| −150+106 | 0.30 | 0.55 | 0.32 | 0.52 |
| −106+75 | 0.35 | 0.20 | 0.50 | 0.40 |
| −75+53 | 2.15 | 0.70 | 0.45 | 0.62 |
| <53 | 97.10 | 98.49 | 98.69 | 98.06 |
| *By sedimentation* | | | | |
| >25 pm | 7.0 | 2.5 | 5.0 | 9.5 |
| Between 25 and 15 µm | 6.0 | 10.0 | 8.0 | 11.5 |
| Between 15 and 10 µm | 4.0 | 5.5 | 14.0 | 8.0 |
| Between 10 and 5 µm | 10.0 | 11.5 | 9.0 | 16.0 |
| Between 5 and 3 µm | 11.0 | 22.5 | 12.0 | 13.0 |
| Between 3 and 2 µm | 8.0 | 11.0 | 14.0 | 8.0 |
| Between 2 and 1 µm | 8.0 | 15.0 | 18.0 | 11.0 |
| Below 1 µm | 46.0 | 22.0 | 20.0 | 23.0 |
| Below 10 µm | 83.0 | 82.0 | 82.0 | 71.0 |
| Below 15 µm | 87.0 | 87.5 | 87.0 | 79.0 |

Table 4
Plastic and dry properties of body mixes

| Properties | CSR-1 | CSR-2 | CSR-3 | CSR-4 | CSR-5 | CSR-6 |
|---|---|---|---|---|---|---|
| 1. Water of plasticity, % | 21.4 | 22.8 | 23.4 | 23.8 | 24.0 | 24.4 |
| 2. Dry linear shrinkage, % | 3.62 | 3.62 | 3.82 | 3.82 | 3.84 | 3.88 |
| 3. Dry M.O.R. ($kg/cm^2$) | 10.06 | 10.06 | 10.79 | 10.39 | 9.90 | 9.90 |
| 4. Bulk density of dry test pieces, g/cc (by mercury balance) | 1.617 | 1.80 | 1.722 | 1.686 | 1.615 | 1.572 |

also showed a wide vitrification range (~50°C). However, the body mix CSR-6, on complete replacement of quartz by RHA attained early vitrification (Fig. 3) at a comparatively low temperature of 1150°C only with bulk density of 2.37 g $cm^{-3}$ (Table 5). This body also showed a very wide vitrification range of about 100°C. The reduction in the vitrification temperature of the mixes is attributed to the finer particle size [25] of the starting materials coupled with intimate mixing as well as the active silica present in RHA. Thus, the incorporation of RHA in the range of 10–25 wt.% in the whiteware composition would be a favourable feature in bulk production in view of the enhancement of the densification process as well as the wide vitrification range of body mixes.

Fig. 3 shows that the fired strength of matured specimens of all the body mixes except CSR-6 (25 wt.% RHA) increased with increasing substitution of quartz by RHA. However, the body mix CSR-3 (10 wt.% RHA) showed the highest strength of 91.8 MPa. The increase in strength in CSR-3 was around 7.2% over the standard composition (CSR-1). With the complete replacement of quartz by RHA, the fired strength in CSR-6 (25 wt.% RHA) was 79.2 Mpa, which was about 7.5% lower than that of the standard composition. The decrease in strength in CSR-6 (25 wt.% RHA) evidently lies in the increase in the content of glassy phase in the microstructure due to higher amount of RHA. It is thus, evident that, although the fired strengths of body mixes containing RHA beyond 10 wt.% in the batch, decreased marginally, the higher amounts of RHA are responsible for the formation of additional liquid phase and the enhancement of the densification process.

Hence, the substitution of quartz by RHA in the body mixes did not only lead to the reduction in the maturing temperature compared to the reference body but also increased marginally the fired strength of the body mixes at the respective maturing temperatures, except the body mix (CSR-6), with complete replacement of quartz by RHA.

The thermal expansion of matured specimens (Fig. 4) decreased with the gradual substitution of quartz by RHA in the mixes. The removal of quartz from the mixes leads to the disappearance of boundary stresses and hysteresis [26] at the quartz transformation temperature of 573°C. The decrease in the expansion in the

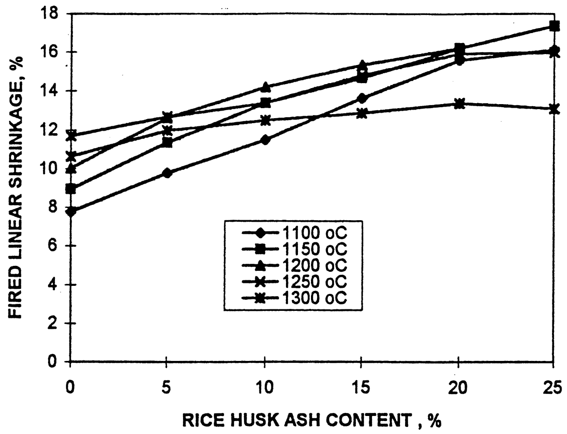

Fig. 1. Effect of RHA on the fired shrinkage of body mixes fired at different test temperatures.

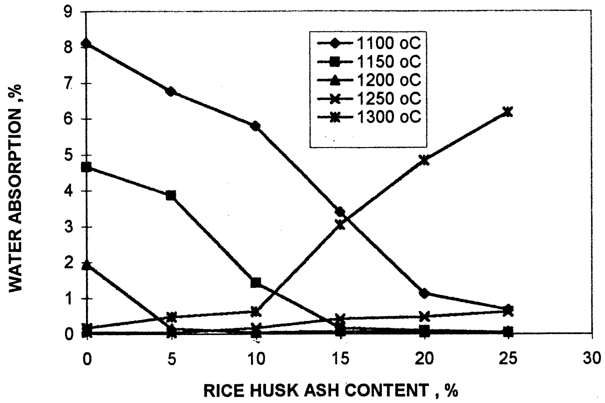

Fig. 2. Effect of RHA on the percentage of water absorption of fired specimens fired at different temperatures.

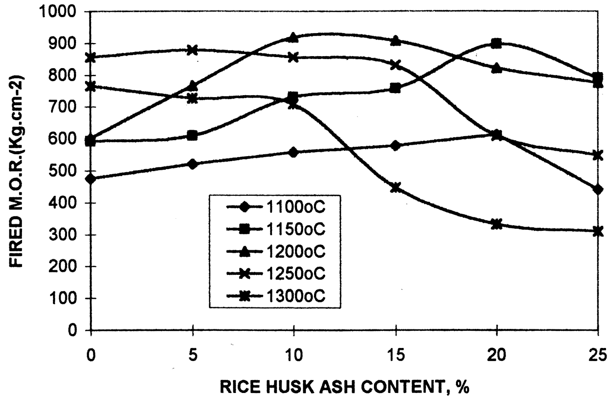

Fig. 3. Effect of RHA on the fired M.O.R. of body mixes fired at different test temperatures.

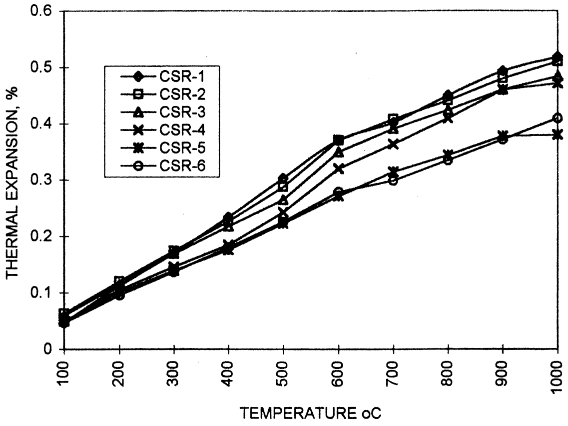

Fig. 4. Percentage of linear thermal expansion of matured test specimens as a function of temperatures.

matured specimens of CSR-6 was 24.6% at 600°C in comparison to the reference body (CSR-1).

XRD patterns of the specimens (Fig. 5) show the presence of two major crystalline phases namely, mullite and quartz in all the body mixes. When RHA completely replaced quartz (CSR-6) the peak intensity of quartz decreased significantly and the peaks heights for mullite remained almost constant. This indicated that the addition of RHA although substantially decreased the content of free quartz in the composition, also confirmed from the decrease in the per cent thermal expansion, but it did not enhance mullite formation.

Scanning electron micrographs of fracture — etched surfaces of specimens of standard body (CSR-1) and

Table. 5
Bulk density of different body mixes fired at different test temperatures

| Mix no. | Bulk density, g/cc | | | | |
|---|---|---|---|---|---|
| | 1100°C | 1150°C | 1200°C | 1250°C | 1300°C |
| CSR-1 | 2.03 | 2.18 | 2.28 | 2.38 | 2.36 |
| CSR-2 | 2.09 | 2.19 | 2.33 | 2.39 | 2.32 |
| CSR-3 | 2.11 | 2.24 | 2.40 | 2.37 | 2.22 |
| CSR-4 | 2.21 | 2.28 | 2.40 | 2.35 | 1.99 |
| CSR-5 | 2.22 | 2.29 | 2.36 | 2.27 | 1.90 |
| CSR-6 | 2.23 | 2.37 | 2.34 | 2.15 | 1.81 |

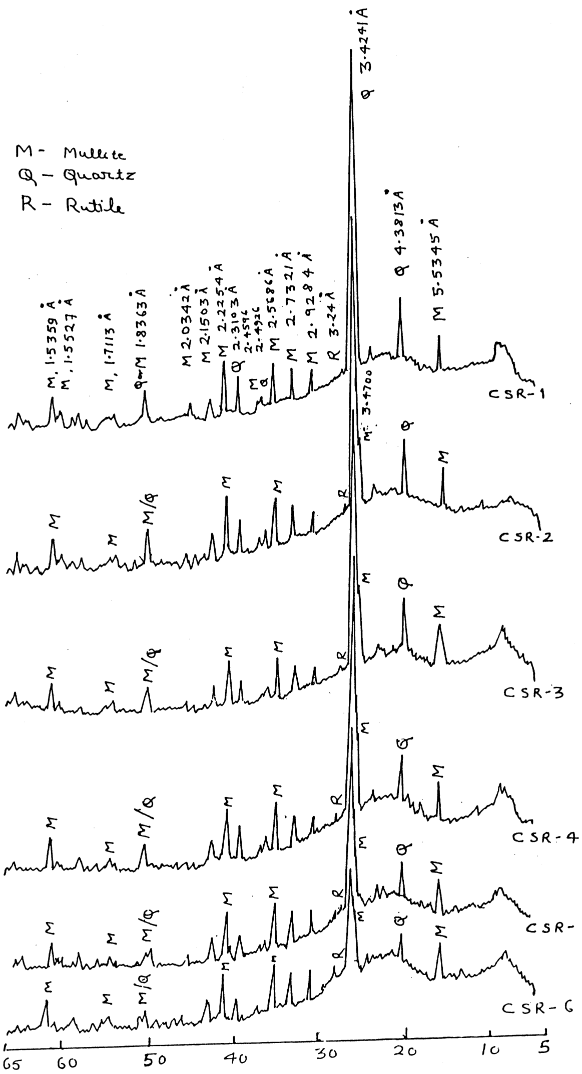

Fig. 5. XRD curves of fired body mixes.

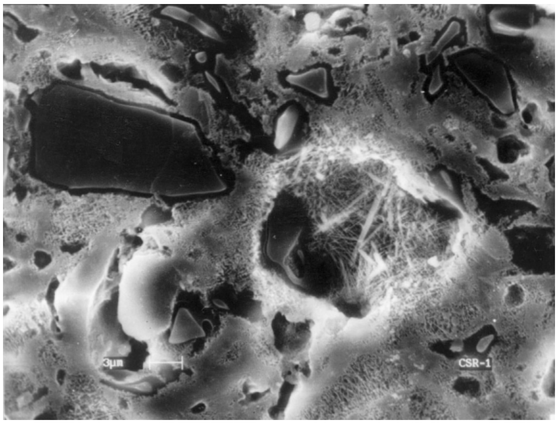

Fig. 6. Short and elongated mullite needles surrounded by other crystalline phases in the matrix of standard body (CSR-1) fired at 1250°C for 1 h.

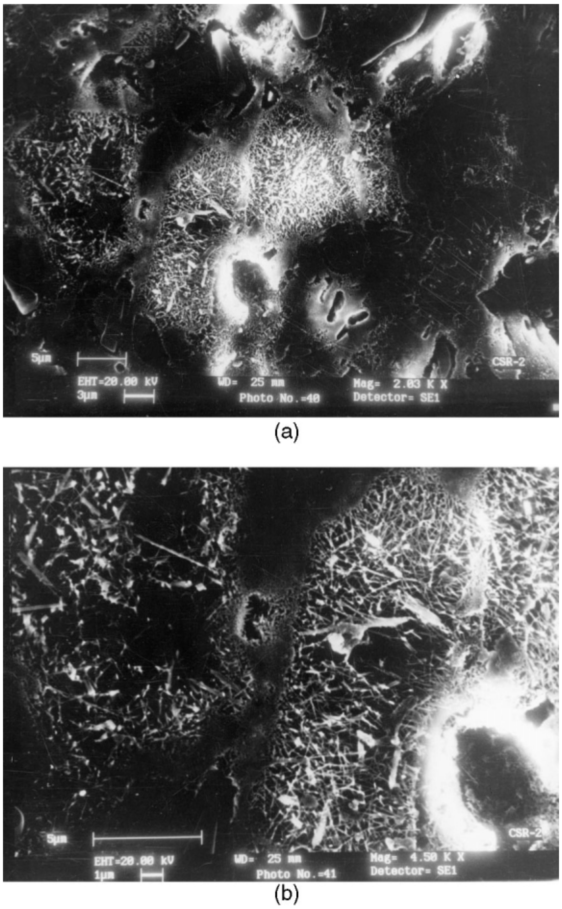

Fig. 7. (a) and (b) Recrystallized secondary mullite needles surrounded by other crystalline phases in the matrix of CSR-2 body containing 5% RHA fired at 1250°C.

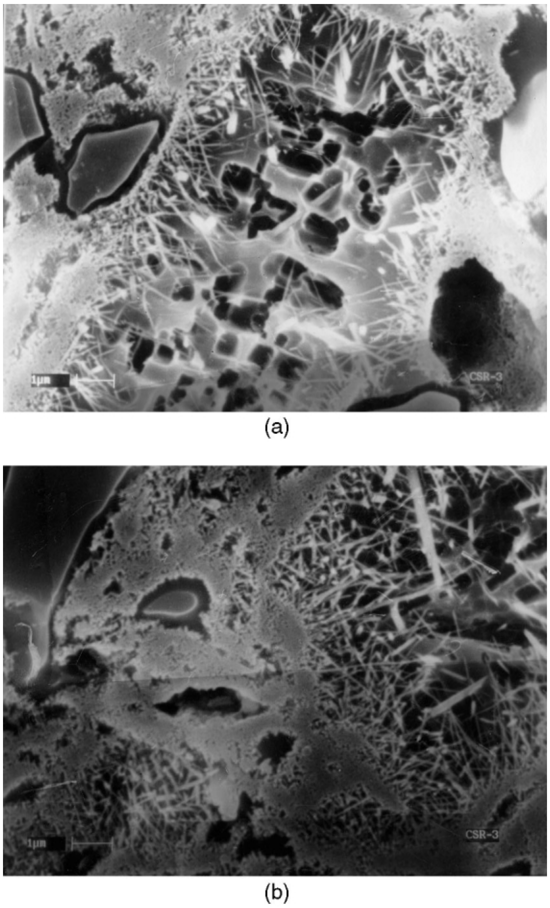

Fig. 8. (a) and (b) Recrystallized secondary mullite needles surrounded by other crystalline phases in the matrix of CSR-3 body mix containing 10% RHA fired at 1200°C.

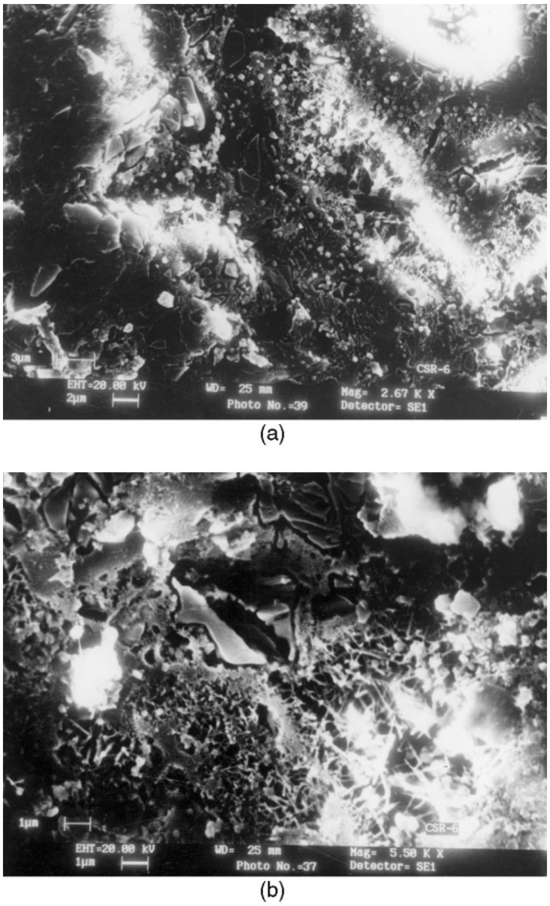

Fig. 9. (a) and (b) Crystalline phases with short mullite needles in the matrix of CSR-6 body mix containing 25% RHA fired at 1150°C.

CSR-2 (5 wt.% RHA), CSR-3 (10 wt.% RHA) and CSR-6 (25 wt.% RHA) are shown in Figs. 6–9, respectively. Fig. 6 for CSR-1 (0 wt.% RHA) shows a large amount of free quartz remained undissolved in the final microstructure, along with the occurrence of well-interlocked secondary mullite needles; which crystallised from the melt at the maturing temperature of 1250°C. The unreacted quartz grains as evident in the microstructure are responsible for the early failure of the standard whiteware mix as a result of mechanical and thermal loadings [18,29].

When quartz was partially replaced by RHA, micrographs (Figs. 7 and 8) also showed recrystallised secondary mullite needles in the matrix along with some quartz crystals which are small in size as well as less in number. Micrographs (Fig. 8) for CSR-3 containing 10 wt.% RHA showed extensively interlocked secondary mullite needles embedded in the glassy matrix. Hence, the reported improvement in the fired strength by 7.2% in CSR-3 over the reference body (CSR-1) was probably due to the well-interlocked structure of mullite needles in the microstructure.

The CSR-6 specimens (Fig. 9) also showed the presence of short as well as intensively interlocked mullite needles which appeared to be uniformly dispersed in the matrix along with a few small quartz crystallites [Fig. 9(a)] and the glassy phase.

Hence, it is evident that in all the micrographs, the major phases present were quartz and mullite, apart from the glassy phase and pores. The presence of quartz relicts decreases on replacement of quartz by RHA. It has thus been possible to eliminate, to a large extent, the inherent defects in the microstructure of a conventional whiteware, and improvement in the mechanical and thermal properties of RHA incorporated body mixes have been achieved.

## 4. Summary and conclusions

Progressive substitution of quartz by RHA in a conventional whiteware composition resulted in an early vitrification of the mixes. A reduction in the maturing temperature of about 50°C to 100°C was noticed in the body mixes containing RHA compared to the reference body. The increase in the fired strength and the substantial decrease in per cent thermal expansion of the body mixes containing RHA are attributed to the sharp decrease in the quartz content and also to the increase in the content of the glassy phase. However, the content of mullite appeared to be unaffected due to the addition of RHA in the compositions. The reduction in the vitrification temperature of the mixes would also contribute significantly to the economical production of whitewares.

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