

## **SPECTRAL CHARACTERIZATION OF ARTICULATED RED BRICKS WITH WASTES FROM ROCK INDUSTRIES**

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### **ABSTRACT**

Samples with the kaolinitic clay and red bricks rejects (in the as-received state and sintered at temperatures 900–1200 °C) were investigated through spectral studies in order to elucidate the possibility of recycling the wastes from the private bricks industry of Edappadi, Tamilnadu state, South India. A detailed attribution of all the spectroscopic frequencies in the spectra recorded in the 4000–400 cm<sup>-1</sup> region was attempted and their assignment to different minerals was accomplished. Xray diffraction analysis was performed to demonstrate the reliability of IR attributions. The indication of well-ordered kaolinite is by the band at 1115 cm<sup>-1</sup> in the raw samples which tends to shift towards 1095 cm<sup>-1</sup> in all the fired samples. The peaks at 563 cm<sup>-1</sup> and 795 cm<sup>-1</sup> can be assigned to anorthite and dickite respectively. The presence of quartz and anorthite is confirmed both by XRD and FTIR. The microstructural observations were done through the SEM images which visualized the vitrification of the fired bricks at higher temperatures. The refractory properties of the samples found through the XRF analysis are also appreciable.

Keywords: Spectral, Red Bricks, Rock Industries, XRD, FTIR

### **1. Introduction**

The rock industry generates large amounts of calcined clay wastes each year. Re-using these wastes in the same red rock industry could be a winning situation. For one hand by solving the red rock industry waste problem leading to sustainable red rock industry by reducing the use of nonrenewable resources and aggregates and the other side avoiding environmental problems related to land filling wastes. Renewed interest in the use of products that employ waste as raw materials arises due to social pressure to preserve

the natural environment combined with growing economic pressure.

The red bricks sector can incorporate large amounts of waste materials without relevant process modifications. Thermal treatment can immobilize the hazardous components into the red bricks matrix. Natural raw materials used in the fabrication of clay based red bricks products show a wide range of compositional variation and the resulting products are heterogenous. For this reason, such products can tolerate further composition fluctuations and raw material

changes which lead to the capability of incorporating a variety of waste materials [1,2] such as sediment [3,4], stone and granite rejects [5], sewage sludge and ash [6], fly ash [7] and steel slag [8] in the red rock industry. Even if this is done in small amounts, the high production rates of such red bricks products translate into significant consumption of waste materials. At the high firing temperatures generally used (>900 °C), an effective incorporation of the material into the red bricks matrix is accomplished [1], which is particularly interesting when dealing with the incorporation of red bricks wastes. According to the roles played during processing, the raw materials for the red rock industry are of three kinds: plastic components (e.g. clays), fluxing components (e.g. feldspars) and inert components (e.g. quartz sand). The red bricks wastes show non-plastic behavior due to their major constituents, expressed as oxides, silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>). These wastes generated after the firing stage of red bricks can eventually be added to clayey body in the proper red bricks processing. The pozzolanic reactivity of red bricks waste powder is also confirmed in the literature [9]. Also this non-plastic type of waste can be advantageous for the processing and quality of bricks fired at temperatures above that of the original production [10], nevertheless research carried out so far are scarce. Consequently the aim of this research is to investigate the use of red bricks rejects into the own red ROCK INDUSTRY. It is known fact that thorough chemical and mineralogical understanding of mixed clayey materials is considered the most essential step before processing them into any tailor-made product.

Thus it is very important to perform an extensive characterization of these materials in order of generating more knowledge, which can contribute for obtaining enhanced properties. Emphasis is given to chemical and mineralogical characteristics with special reference to the

suitability of these materials before manufacturing of clay based structural red bricks. In the present study, the usage of red bricks frits (CF), waste from red bricks industries is tested by characterization through FTIR, XRD and SEM. The kaolinitic clay and the red bricks frits were mixed in different proportions to prepare the test samples and the red bricks bodies obtained, both unfired and fired (900–1200 °C) were submitted to XRD and FTIR analyses in order to check the structural changes during the process. As interdependent technical tools, the application of both techniques in characterizing the samples is discussed. The microstructural observations at higher temperatures were done through SEM studies.

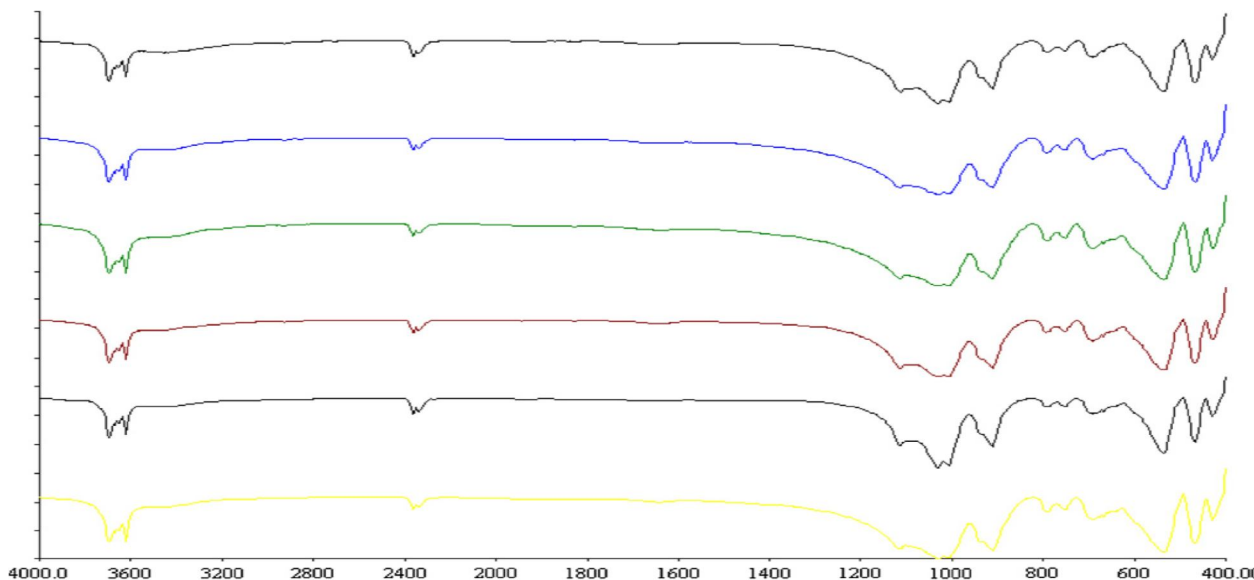
## 2. MATERIALS AND METHODS

The red bricks frits (rejects), a waste material generated while producing any type of red bricks material, is obtained from the Government red bricks industries of Vriddhachalam (located in the state of Tamilnadu, South India) and made into a fine powder in a pulveriser. The raw material (kaolinitic clay) and CF were mixed with water and the slurry was dried at 100 °C in a rotating drier until 8– 10% humidity. The dried material was then crushed and sieved to pass through a 150 mesh (100 μm) to obtain suitable powders for pressing. Unfired rectangular (90 mm × 30 mm × 30 mm) specimens in lots of 10 for each mixture were moulded using an extrusion apparatus. Six batches of samples were made in which the percentages of CF are as in Table 1. Firing was carried out in a laboratory electric furnace reaching different maximum temperatures in the range of 900–1200 °C at regular temperature intervals of 100 °C with a soaking time of 1 h at the maximum temperature needed. Cooling occurred by natural convection after it was turned off. The knowledge of chemical and mineralogical compositions is mandatory in characterization studies of clay

mixtures. The elemental composition of the starting material and rejects was analyzed by XRF (PW 1400 Philips). For FTIR analysis, dry grinding was carried out by placing 50 mg of the sample in an agate mortar. Using KBr pellet technique, the sample is mixed with KBr at 1:30

### 3. RESULTS AND DISCUSSION

The chemical composition of the kaolinitic clay and CF is presented in Table 2 which indicates that SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> as major constituents besides Na<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, CaO, etc. as minor constituents. The XRF analysis indicate that the



ratio since it gives rise to maximum transmittance [11] and the mixture is then pressed into a transparent disc in an evocable dye at sufficiently high pressure.

Using the Nicolat-Avatar 330 series FTIR spectrometer, the infrared spectra for all the samples were recorded in the region 4000–400 cm<sup>-1</sup>. The resolution of the instrument is 4 cm<sup>-1</sup> and the accuracy ±0.01 cm<sup>-1</sup>. At each and every time, this instrument was calibrated for its accuracy with the spectrum of a standard polystyrene film. The phase analysis of the samples were performed using X-ray diffractometry (SEIFERT JSO-DE BYE FLEX-2002) using Cu K $\alpha$  radiation and NaI (T1) scintillation counter detector with a scanning speed of 10\_/min. The experimental patterns were compared with the patterns obtained from JCPDS database [12].

total wt% of the fluxes present (K<sub>2</sub>O, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, TiO<sub>2</sub>) in the mixture of clay and rejects appears to be lesser than 9% which is noteworthy. Hence the refractory properties of the red bricks test samples are higher.

The FTIR spectra of the unfired red bricks test bodies (FC0–CF5) in the received state (R–S) are presented in Fig. 1a.

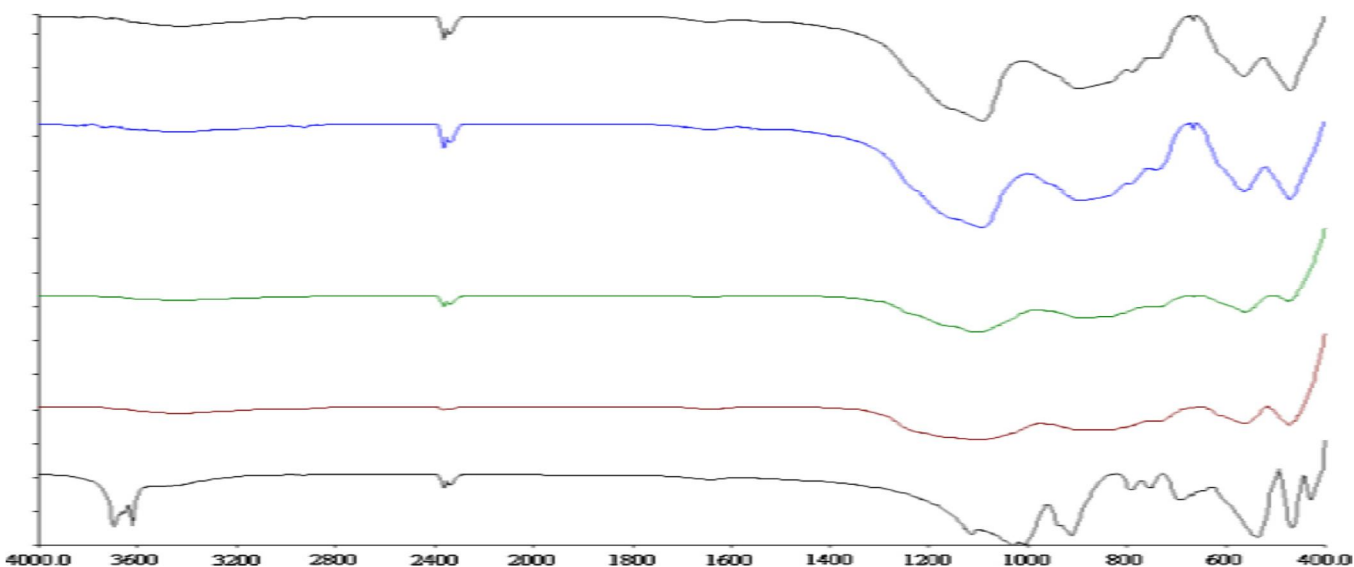
From the observation of the spectra it is clear that before sintering, the spectral characteristics of all the six samples are almost similar. This indicates the fact that any of the compositional wt% (FC1–CF5) can be assigned for the production of red bricks briquettes as these spectra correspond to well ordered kaolinite structures [13]. Kaolinite with almost Al in the octahedral positions has four absorption bands in the O–H stretching region (Fig. 1a).

The O–H stretching of inner hydroxyl group lying between the tetrahedral and octahedral sheets give the absorption band at 3620  $\text{cm}^{-1}$ . The characteristic band appearing at 3694  $\text{cm}^{-1}$  corresponds to in-phase symmetric stretching vibration whereas two weak absorptions at 3669 and 3652  $\text{cm}^{-1}$  are assigned to out-of-plane stretching vibration [14].

The IR absorption bands in the region 3800–3600  $\text{cm}^{-1}$  in the spectra of clay minerals are due

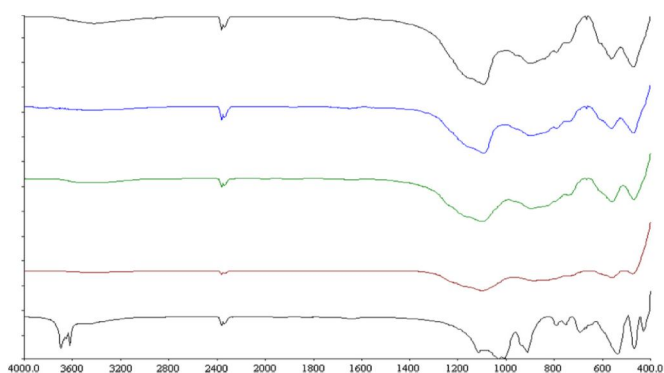
sample spectra at 1093  $\text{cm}^{-1}$  arises from asymmetric Si–O–Si stretching vibration [19] and the particle size is believed to be directly proportional to the intensity of this peak [20]. and FC1 samples (clay with 10% rejects). Only minor changes are observed which imply that a minimum of 10% red bricks rejects addition with the clay does not have strong impact in the structural changes.

Figs. 1d–1g show the spectral patterns of the clay with 20–50% rejects.



to the stretching vibrations of free hydroxyl groups present in them. The weak absorption bands at 3446 and 1636  $\text{cm}^{-1}$  are attributed to O–H stretching and H–O–H bending vibrations of adsorbed water molecules [15,16]. The dehydroxylation is partly followed by the crystal framework collapse [17] and the tetrahedral sheet disorder can be seen from the broadening of Si–O stretching band in the region 1100–1000  $\text{cm}^{-1}$ . The vibrations of aluminium hydroxyl in the octahedral sheet structure give rise to strong absorption at 913  $\text{cm}^{-1}$  [18]. The variations in the values of OH stretching and bending wave numbers from sample to sample are usually attributed to varying strength of hydrogen bonding between OH and H<sub>2</sub>O molecules and some oxygen in the structure. A peak in the fired

The strong distinct absorption bands present at 1115  $\text{cm}^{-1}$  and 913  $\text{cm}^{-1}$  in all the six spectra of the studied samples indicate the well ordered kaolinite structure. Well ordered clays are characterized by the presence of bands at 910, 1030 and 1120  $\text{cm}^{-1}$  [18,21] in which 910 and



1120  $\text{cm}^{-1}$  are due to  $\text{Al}(\text{OH})$ . They are replaced by a single band at 1030  $\text{cm}^{-1}$  as the disorder increases [22] (Figs. 1b–1g). Quartz is a non-clay mineral, which is common and invariably present in all the studied samples. The Si–O bonds are the strongest bonds in the silicate structure and can be readily recognized in the infra red spectra of such minerals. The presence of quartz can be explained by Si–O asymmetric bending vibrations at 468  $\text{cm}^{-1}$  and Si–O symmetric bending vibrations at 695  $\text{cm}^{-1}$ . These assignments are in good agreement with that reported for quartz [11,23]. The peak at 795  $\text{cm}^{-1}$  in the fired samples provides the evidence for the presence of dickite [24, 25].

The bands associated to ‘condensed’  $\text{AlO}_4$  tetrahedra expected in the range of 850–750  $\text{cm}^{-1}$  are not observable probably because of their lower intensity and broadening of the strong band belonging to  $\text{SiO}_4$  tetrahedra of the remaining phases present in the samples. The absence of the bands at 539 and 913  $\text{cm}^{-1}$  in the spectra of the fired samples can be related to the change of octahedral coordination of  $\text{Al}^{3+}$  in kaolinite [26].

The major change in the spectra in all the thermally treated samples corresponds to the disappearance of the band at 538  $\text{cm}^{-1}$  and the evolution of a band at 563–567  $\text{cm}^{-1}$  for different compositions in all the studied temperatures. These could be confidently assigned to anorthite [27] as a result of solid state reaction between CaO and clay. The rest of the spectrum is similar in its general features because the same phases are maintained.

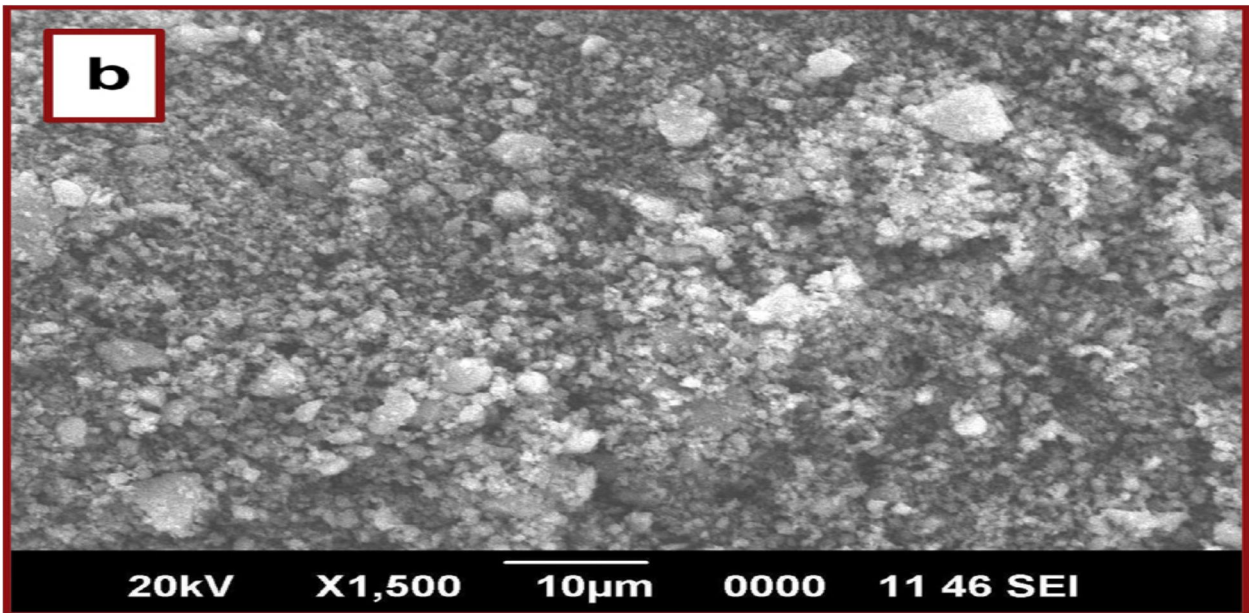
The measurements of intensity variations of characteristic XRD peaks and FTIR bands of compounds are sufficient criteria to be used in

comparison in order to obtain a trend in behavior of similar mixtures. The XRD analysis showed kaolinite (K), quartz (Q) anorthite (A) as main crystalline phases (Figs. 2a and 2b).

The presence of mullite is identified by the last reflection (1.5224 Å) with low relative intensities. The evolution of different phases with temperature in the range 900–1200 °C is studied. The kaolinite becomes progressively less crystalline by dehydroxylation to form metakaolinite (amorphous) at a low temperature around 500 °C. It was not possible to accurately establish the complete dehydroxylation by this technique because XRD can reveal little about the occurrence of the poorly ordered material.

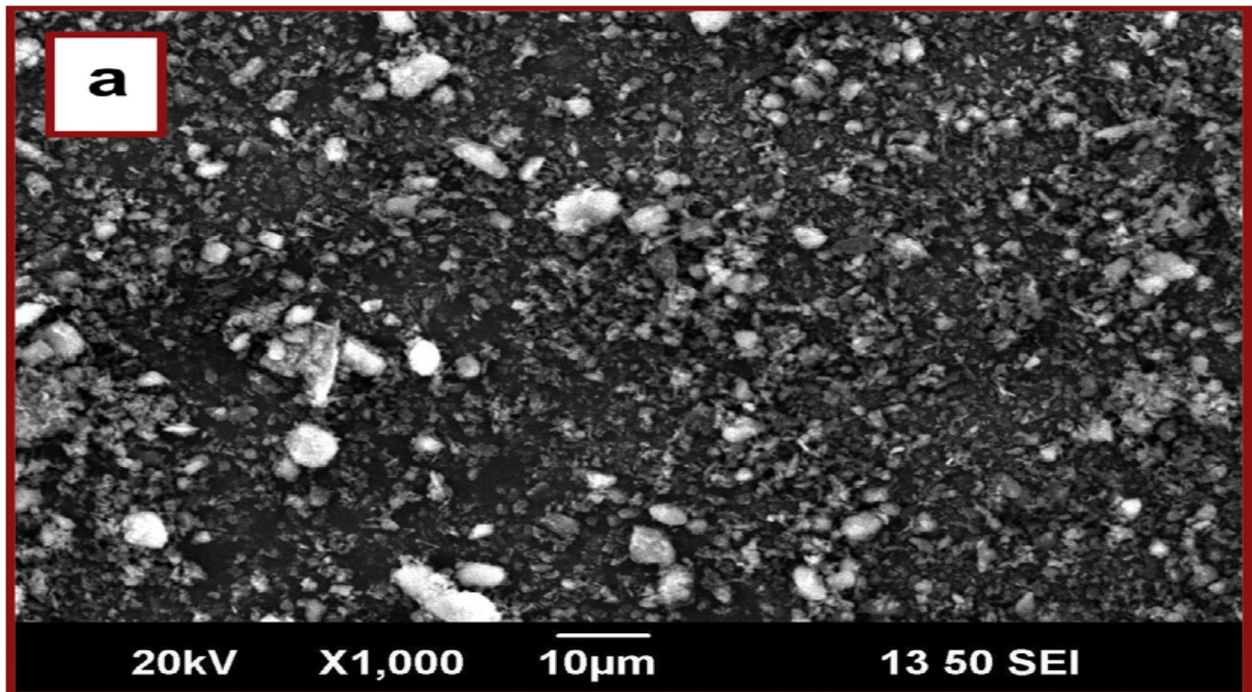
The XRD patterns of the fired CF5 samples indicated the presence of tridymite, dickite, eskolaite and greenalite along with quartz, kaolinite and anorthite. The intensity of tridymite is decreasing with the increasing CF and remains intact with the fired temperature. The minerals like tridymite, eskolaite and greenalite are identified only in XRD analysis which indicates their crystalline order in spite of their meagre presence. However, the major minerals quartz and anorthite are present invariably in all the test samples [28]. The anorthite content of the compositions increases at the expense of the mullite content as the addition of alkaline oxides ( $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ ) in CF will actually reduce the amount of mullite formed during firing [5,7].

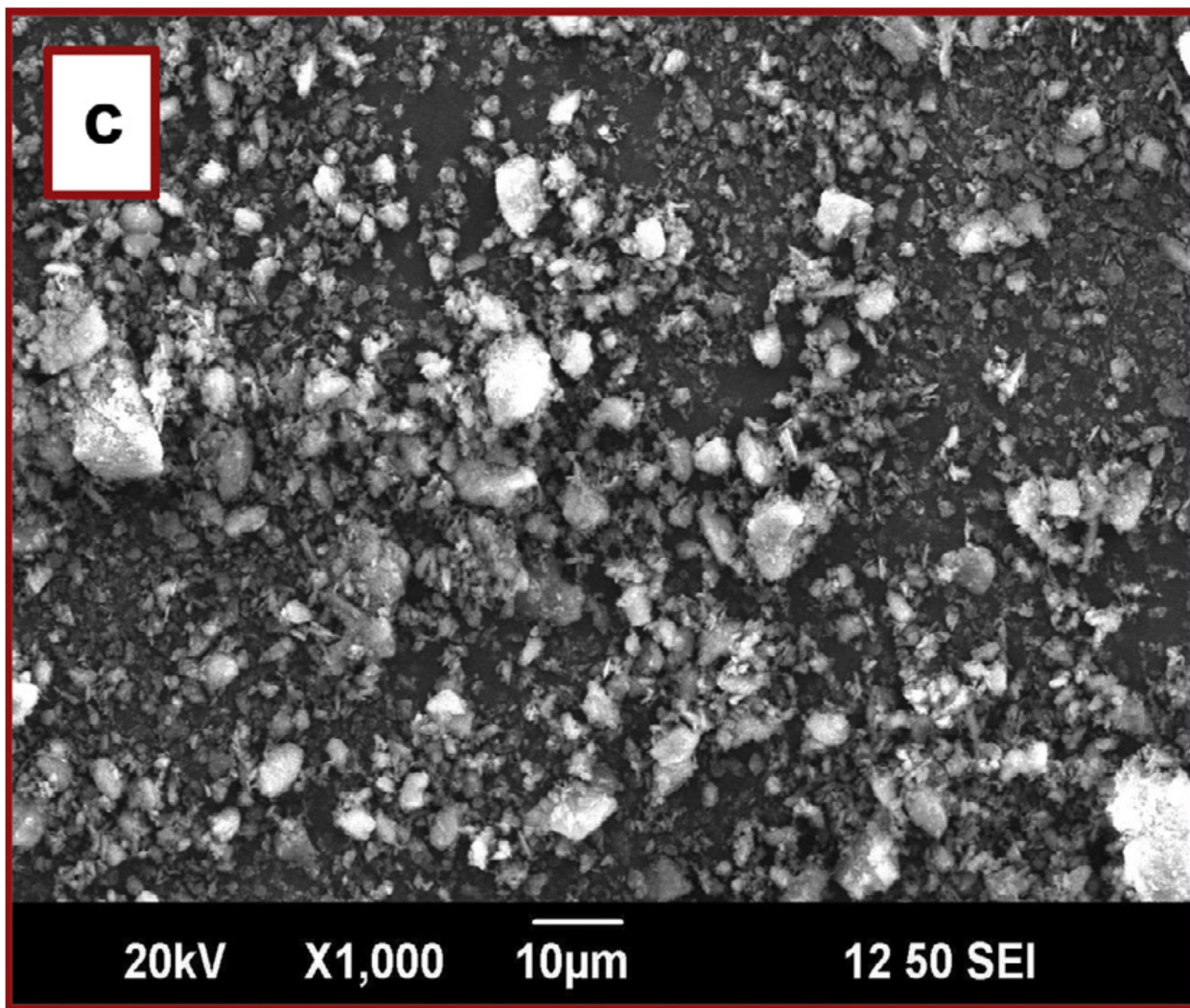
The amorphous/glassy phase, crystalline phase, porosity and overall structure of the products were investigated by SEM studies. The SEM studies show that high K-bodies have a considerable amount of amorphous/glassy phase (Fig. 3a).



50% rejects (CF5) indicated a denser more sintered microstructure. When compared with FC0, the sintered sample CF5 shows a dense matrix containing some isolated small voids (Figs. 3a–3d).

The microstructure of the red bricks bricks with





The morphological changes observed by SEM with rising sintering temperature are similar to those commonly described in the literature. Significant vitrification occurs only above 1000 °C. Quartz grains and significant amount of pores can be clearly seen at the highest firing temperature. Rounded quartz grains were also identified which was in good agreement with the XRD results. When compared with the SEM micrographs of unfired samples (Figs. 3a and 3c), the samples fired at 1200 °C have smaller particles with sizes in the range of 2–4 µm as shown in Figs. 3b and 3d. This indicates the

denser microstructure which is desirable for red bricks brick strength.

#### 4. CONCLUSIONS

Based on the chemical and mineralogical characterization of the CF additive samples, it can be observed that they have characteristics similar to the conventional raw materials. Anorthite formation implies a change in the coordination polyhedral from AlO<sub>6</sub> towards AlO<sub>4</sub> tetrahedra in the firing phases. The trend observed for the crystalline nature of the main mineral quartz through XRD very well matches with the results of FTIR. The study indicated that

changes in the brick production process were not needed. Higher amount of rejects can also be used in the red bricks brick production (40–50%) with higher sintering temperatures (1100 and 1200 °C) as no major changes in the mineralogical and structural behavior were observed. This could be accounted by the presence of almost similar composition of alumina and alkali ions in the clay and reject material. Thus the red bricks wastes from the red bricks industries can be recycled in the red bricks bricks to reduce the production cost which is the main industrial application of the present study. From the results, the use of red bricks wastes instead of conventional nonplastic raw materials can be accomplished yielding a reduction in the energetic costs of the red bricks process.

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