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ORIGINAL PAPER

Recycling and Utilization of some Waste Clays for Production of Sintered Ceramic Bodies

M. F. Zawrah[1] · **Hayam A. Badr**[1] · **R. M. Khattab**[1]

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Abstract

The recycling of industrial waste clays for production of an interesting ceramic product is the main goal of the present research work. Ceramic bodies were prepared using Feeders or Cyclons waste clays, sand and feldspar. 0.0, 15, 20, and 25 wt.% of sand were added at the expanse of kaolin (75-50 wt.%). Constant mass percent (25 wt.%) of feldspar was added for all ceramic compositions. The designed batches were sintered at 1200–1400 °C. Physical properties were determined by water displacement method. Phase composition and microstructure were investigated by x-ray diffraction and scanning electron microscope, respectively. The compressive strength was also determined. The results indicated that the ceramic bodies prepared from Cyclons' waste clay exhibited higher physical and mechanical properties than that prepared from Feeders' clay after sintering at 1400 °C. The addition of sand enhances the porosity, water absorption, bulk density and mechanical strength after sintering at 1400 °C due to the formation of mullite network and glassy phases.

Keywords Ceramic products · Waste clays · Sintering · Properties

1 Introduction

Recently, due to the relatively high cost of raw materials, a new economic trend is acted to utilize and partially replaces the waste materials instead of raw materials for fabrication of many products while maintaining the required properties [1–9]. Traditional ceramics or white wares are normally fabricated by special processing of clay (kaolinite), feldspars and sand with the ratio around 50, 25 and 25 wt.%, respectively. The effect of each component of these raw materials on the physico-mechanical properties of the end product has been investigated by many researchers [10–15]. The utilization of industrial solid wastes as alternative sources for alumino silicate and fluxing minerals (kaolin, feldspar and sand) has been investigated by several workers [16–23]. In principle, the clay gives the plasticity to the ceramic slurry while flint or quartz maintains the shape of formed body and gives the strength during firing. Feldspar is a common material in the earth's crust and it is a vital raw material for ceramic/glass industries. Owing to its fluxing characteristics, it is also operated as a crucial material for porcelain, hardware, vitreous china [24]. Heat effects on the clay and many reactions are occurring during firing. Physically adsorbed water is removed at <200 °C while dehydroxylation with removal OH^- ions from the crystal lattice is carried out at 450–600 °C; this leads to formation of amorphous metakaolin ($Al_2O_3.2SiO_2$) phase. At temperature higher than 900 °C, recrystallization is occurred with the formation of mullite phase (Al2O3 .2SiO2) [25–28]. On the other hand, feldspar also suffers changes under heating with the formation of leucite ($K_2O.Al_2O_3.4SiO_2$) in case of potash feldspar and sanidine ($3K_2O.Na_2O.4Al_2O_3.24SiO_2$) in case of mixed feldspar. At higher temperature, the feldspar decomposes until melting leading to the formation of viscous liquid [29–31]. Furthermore, quartz also undergoes a series of changes throughout heating. These changes effect on thermal expansion property, crystal structure and physical properties as density. At 573 °C, the room temperature form of quartz (alpha-quartz) changes into the high temperature one (beta-quartz). When the later phase is subjected to extra heat, reconstructive transformations are occurred. It is well known that quartz is stable until 870°, before it transforms into tridymite which is stable until 1470 °C before it changes into cristobalite [32].

✉ M. F. Zawrah
mzawrah@hotmail.com

[1] Refractories, Ceramics and Building Materials Department, National Research Centre, 12622-Dokki, Cairo, Egypt

It is well known that after crushing and storing the raw kaolin with size 20 cm to be ready for calcination and used for refractory production, and as a result of violent collision, fine kaolin with size less than 3 mm is produced as a waste material; this called as Feeders kaolin. This waste cannot be introduced into the rotary kiln since it can escape out of chimney during calcination process and cause a voluminous pollution of air. So it is important to separate it before the inlet of rotary kiln at the beginning. On the other hand, during the calcination process of kaolin in the rotary kiln, and as a result of extra frictions, very fine waste calcined kaolin is produced. This called Cyclones kaolin since it moves with a high jet of hot air and collected on cyclones (like filter) to separate it out of air as possible before chimney. It is consider as semi-calcined kaolin where it subjected to temperature within the rotary kiln for few minutes. Its Loss of ignition reaches about 4.5–7.5%. On national and worldwide scales, a huge amount of these waste clays are produced as a by-product after preparation of clays for refractory production. These wastes can be recycled and used in many industries.

This work focuses on utilization and recycling of waste clay materials (as Cyclones and Feeders clays) instead of raw clays for production of sintered conventional ceramic bodies. Effect of increasing the sand percentage at the expense of clay on physico-mechanical properties is also investigated.

2 Materials and Experimental Methods

In the present study, two kaolin waste materials; namely Feeders and Cyclones kaolin were supplied from Asfour Company for refractory, Egypt. Their particle sizes were ranged between 75 and 150 μm. These waste clays were used in addition to Feldspar and sand in production of conventional ceramic bodies. Eight different batches were designed as illustrated in Table 1. These ceramic bodies were prepared by common ceramic processing. Typically, the mixtures of raw materials for designed batches were homogenized for 4 h in a planetary mill with alumina grinding balls. The powders were uniaxially pressed under a load of 100 MPa in stainless steel die to produce pellets with dimension of 2.54 × 2.54 × 2.54 cm^3. The compacted samples were sintered at different firing temperatures, i.e. 1200, 1300 and 1400 °C for 1 h in a lab furnace with maximum temperature of 1600 °C. The densification parameters in terms of apparent density (AP), bulk density (BD) and water absorption (WA) were determined by using the Archimedes water displacement method according to ASTM C20(2015) and employed to characterize the quality of sintered bodies. After sintering, the phase composition of formed crystalline phases was identified by X-ray diffraction technique (XRD Bruker D8 diffractrometer) using nickel-filtered CuKα radiation. The microstructural characteristics of sintered pellets were examined by scanning electron microscope (SEM) equipment type Philips XL30 after coating the surface of sample with gold thin film. The mechanical property in terms of compressive strength for sintered bodies was measured by using automatic hydraulic testing machine, type SHIMADZU of maximum capacity 1000 kN by rate of 0.025 kN/mm^2/s, according to ASTM C773–88(2016).

Table 1 Batch composition of designed ceramic bodies

Designed Samples	Compositions, wt.%			
	Feeders' Kaolin	Cyclones' kaolin	Feldspar	Sand
50 F	50		25	25
55 F	55		25	20
60 F	60		25	15
75 F	75		25	0.0
50 C		50	25	25
55 C		55	25	20
60 C		60	25	15
75 C		75	25	0.0

3 Results and Discussion

3.1 Chemical Composition of Raw Materials

The chemical compositions of starting materials (waste clays, Feldspar and sand) are illustrated in Table 2. It is indicated that waste clays are composed mainly of alumina and silica with some impurities like Fe_2O_3 and TiO_2 in presence of other oxides. On the other side, feldspar constitutes of silica,

Table 2 Chemical analysis of starting materials

Oxide	Wt%			
	Feeders' Clay	Cyclones' clay	Feldspar	Sand
Al_2O_3	35.08	36.681	16.37	0.53
SiO_2	47.71	48.320	71.23	98.04
TiO_2	2.46	3.665	0.02	0.12
Fe_2O_3	1.35	1.478	0.44	0.48
MnO	0.01	0.011	0.00	0.00
MgO	0.16	0.158	0.09	0.08
CaO	0.43	0.883	1.10	0.39
Na_2O	0.10	0.107	2.38	0.09
K_2O	0.06	0.073	8.21	0.06
P_2O_5	0.12	0.117	–	0.07
SO_3	0.12	0.123	–	0.13
Cl	0.06	0.037	–	0.05
ZrO_2	0.17	0.253	–	0.06
LOI	11.97	7.52	0.31	0.38

alumina, K_2O, Na_2O with trace amounts of other oxides, while the sand is composed mainly of silica and trace amount of other oxides.

3.2 Phase Composition of Sintered Ceramic Bodies

Phase composition for some selected ceramic batches (50F & 60F) and (50C & 60C) sintered at 1200 and 1400 °C are shown in Figs. 1 and 2, respectively. Generally, both ceramics bodies prepared from Feeders and Cyclones' clays form same phases (quartz and mullite) with comparable crystallinity and quantities. At 1200 °C, XRD patterns of both ceramics exhibit quartz as predominate phase with a little amount of mullite. The quantity of quartz increases with increasing of sand in the batch i.e. 50F has quartz amount more than 60F and 50C has more amount than 60C. On the other side, at 1400 °C, the patterns display mullite as the major phase with a little amount of quartz since most of quartz is consumed in mullite and glassy phase formation. As confirmed for the patterns, the ceramics bodies prepared from Feeders waste clay exhibit more mullite formation than that prepared from Cyclones waste clay. Also, the amount of mullite increases with increase of the amount of sand in the batches i.e. 50F has mullite amount more than 60F and 50C has more amount than 60C. These results confirm the data published on alumina-silica system. In the present study, according to the designed batches, the system inclines to be reaching in silica. So, the formed phases are mainly quartz and mullite with the presence of some liquid phases which increase with increasing densification temperature and quartz amount. According to the batch compositions and phase diagram of alumina-silica system, no evidence for formation or coexistent of alumina phase either from clays or feldspar at equilibrium [33]. Also, it was expected to find some cristobalite in the batches due to the phase transformation of quartz since it starts to transform into cristobalite above 1000 °C. This is probable due to the nature of added silica which is natural sand exists as quartz phase. Also, when the temperature has increased into 1400 °C and in the presence of fluxing materials from feldspar and kaolin, the possibility for precipitation of mullite is higher than of cristobalite. The presence of feldspar leads to decrease the melt temperature and viscosity of glassy phase. This tends to nucleation and growth of secondary mullite and consequently raises the density of ceramic bodies. The reaction mechanism for these systems is supposed to be as follows: at 980 °C, metakaolin transforms into amorphous silica and spinel ($2Al_2O_3.3SiO_2$) like phase or mullite ($3Al_2O_3.2SiO_2$) with the presence of original added quartz. At >1100 °C, pyrophllite [$3(Al_2O_3.4SiO_2)$] or spinel transforms also into primary mullite and amorphous silica. With increasing temperature, liquid phase starts to be formed. At 1300 °C, almost all feldspar in the form is in the liquid state and the dissolved alumino-silicate phases in the formed liquid phase are precipitated as mullite [34].

3.3 Physical Properties of Sintered Ceramic Bodies

The densification parameters in terms of bulk density, apparent porosity and water absorption for ceramic bodies sintered at different firing temperatures up to 1400 °C, are shown in Figs. 3, 4 and 5, respectively. Generally, for all batches of both ceramics fabricated from Feeders and Cyclones' waste clays, the apparent porosity and water absorption decrease while bulk density increases with increasing sintering temperature up to 1400 °C. This is attributed to solid-solid interaction and particles' diffusion with the formation of liquid phase after rising the densification temperature. This liquid phase enhances the grain sizes, reduces the pore volume and results in improved density values [35, 36]. Moreover, the ceramics prepared from Cyclones' waste clay are better than that prepared from Feeders' waste clay since they exhibit improved

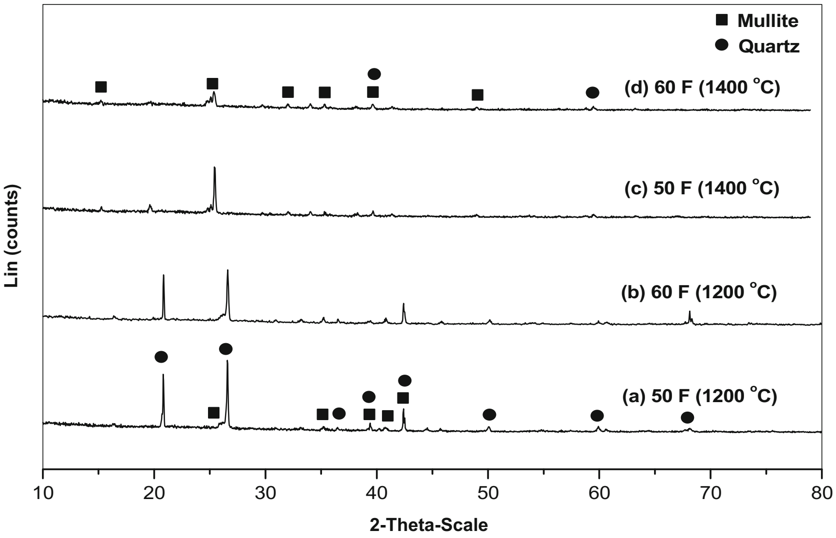


Fig. 1 XRD patterns of 50F and 60F ceramics sintered at 1200 and 1400 °C

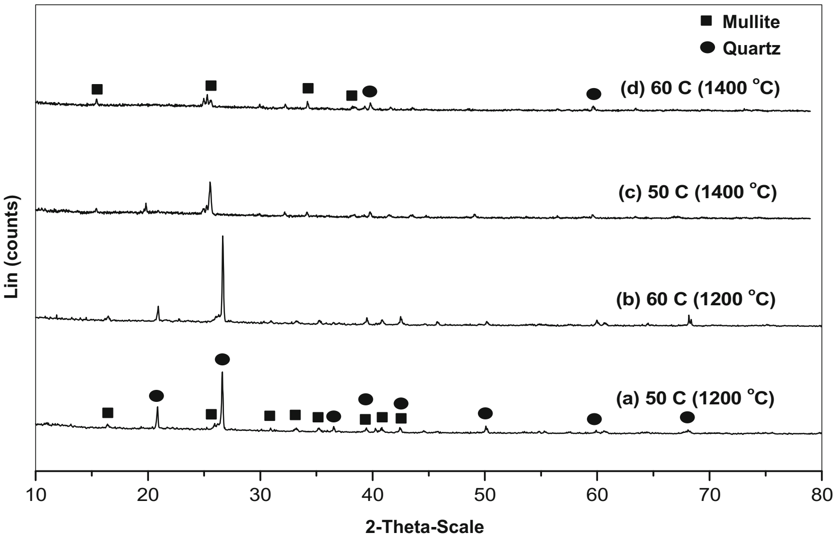


Fig. 2 XRD patterns of 50C and 60C ceramics sintered at 1200 and 1400 °C

densification parameters (lower porosity, lower water absorption and higher density) at all sintering temperatures. This is owing to the nature of Cyclones' waste clay since it is very fine, semi-crystalline i.e. highly reactive and it has a relatively lower ignition loss. Also, in both types of ceramics, with increasing the amount of waste clays in the batches at the expanse of sand, apparent porosity and water absorption decrease when the ceramics sintered at 1200 and 1300 °C. At these lower temperatures, the sand-quartz is still partially unreacted to form mullite or liquid phase so the samples that contain higher amount of sand exhibit higher porosity and water absorption while the samples that contain higher amount of waste clays display lower porosity and water absorption. Moreover, the samples having higher clays form some liquid phases coming from the clay itself and feldspar. On the contrary, at 1400 °C, the apparent porosity increases with increasing the amount of waste clay in both ceramics prepared from Cyclones' and Feeders' clay wastes. At this higher temperature, the specimens having higher amount of sand form more mullite and liquid phases; so they exhibit lower porosity as compared with that contain higher waste clays [37]. In all cases, the best two samples are those prepared from Cyclones' clays (50 C and 55C), they exhibit the best densification parameters. In some published works, the authors reported that the crystallization of mullite delays the complete densification at elevated temperatures [33–39].

3.4 Microstructure of Sintered Ceramics

Figures 6, 7, 8, and 9 depict SEM images (different magnifications) of some selected ceramic bodies (50F and 60F) and (50C and 60C) sintered at 1200 and 1400 °C, respectively. Generally, the microstructure of ceramics sintered at 1200 °C show higher porosity than that sintered at 1400 °C. Also, the ceramics prepared from Cyclones' waste clay form denser and compact microstructure. Although the ceramics prepared from Cyclones' waste clay form lower amount of mullite (needle-like or elongated grains) with shorter size and aspect ratio than that prepared from Feeders waste clay, they exhibit compact and denser microstructure. Moreover,

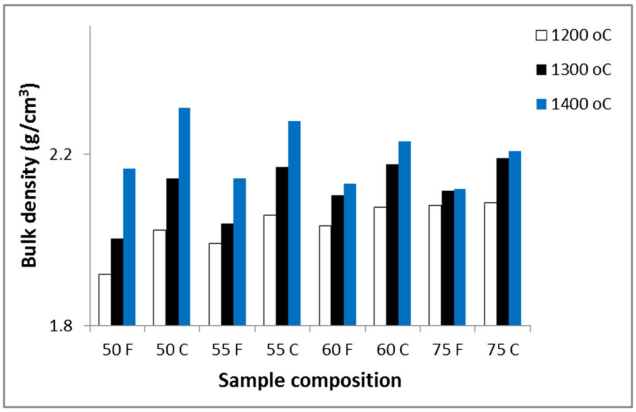


Fig. 3 Bulk density of all ceramic compositions sintered at different temperatures

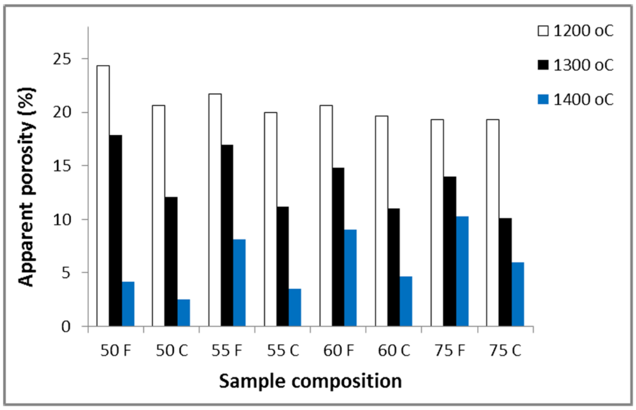


Fig. 4 Apparent porosity of all ceramic compositions sintered at different temperatures

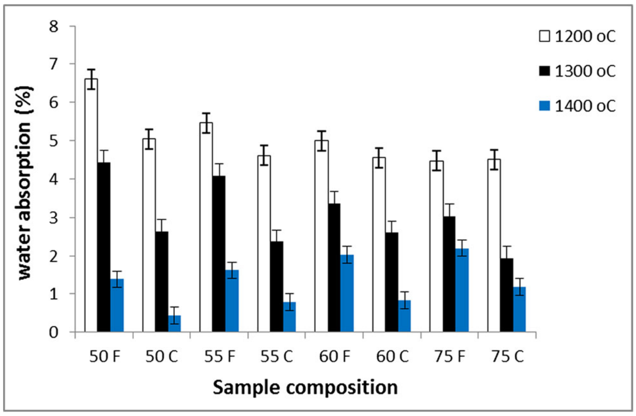


Fig. 5 Water absorption of all ceramic compositions sintered at different temperatures

according to the obtained microstructure features, the grain sizes of ceramics prepared from Feeders' waste clay are bigger than that prepared Cyclones' waste clay. The quartz grains are detected as edged or deformed-rounded grains while the mullite is appeared elongated grains. It is well known that retardation of anisotropic mullite grain growth sometimes happens at a sintering temperature around the eutectic point of mullite-silica system. The ceramic bodies fabricated from both ceramics sintered at 1200 °C (Figs. 6 and 7) contain mainly quartz grains with some liquid phases and little amount of mullite. Also, all ceramic samples sintered at 1400 °C (Figs. 8 and 9) exhibit needle-like mullite grains embedded in glassy phase matrix without any sign for the presence of quartz grains. These results confirm the data obtained from XRD patterns.

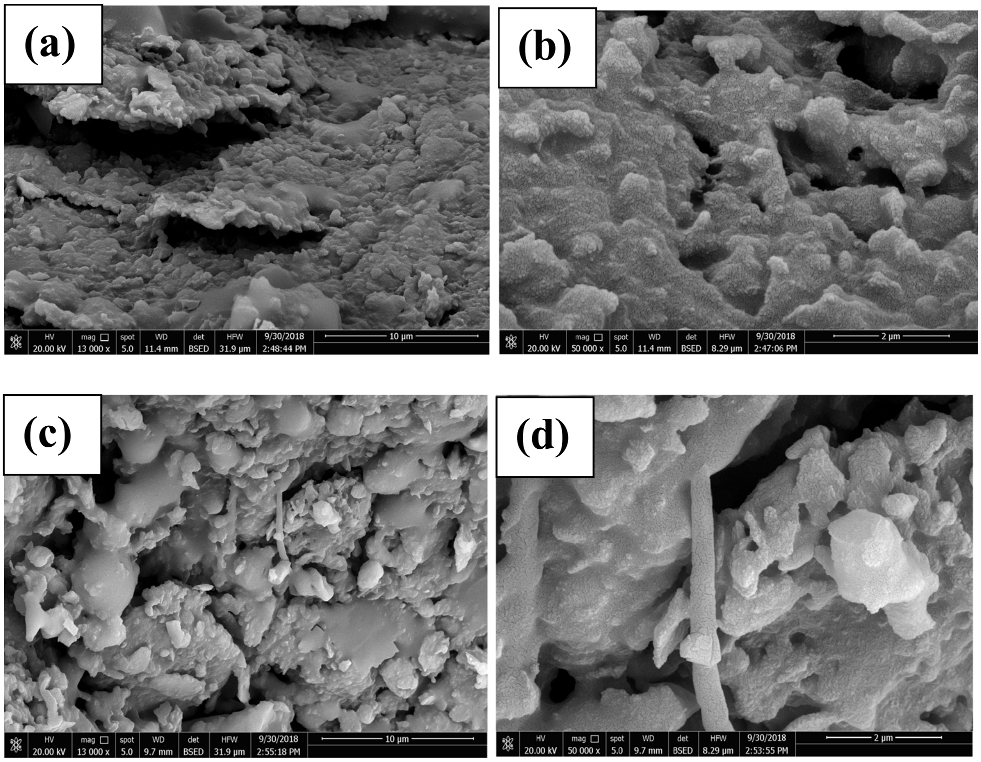
3.5 Compressive Strength of Sintered Ceramics

The compressive strength of all ceramic compositions sintered at 1400 °C is shown in Fig. 10. It is well known that the mechanical properties are affected by many parameters such as porosity, grain size, morphology of grains, type of materials and sintering temperature. As indicated from the figure, the compressive strength of sintered ceramics prepared from Cyclones' waste clay is higher than that prepared from Feeders' waste clay. This is attributed to their lower porosity and dense microstructure with the formation of fine mullite elongated grains networks as confirmed from SEM images and XRD results. The best compressive strength is obtained for 50C ceramic. Furthermore, the compressive strength decreases with increasing the content of waste clays. This is owing to the lower amount of formed mullite and the higher porosity content.

4 Conclusion

- In the present study, kaolin which is the major ingredient for making traditional ceramics was successfully replaced by recycled Feeders' and Cyclones' waste

Fig. 6 SEM images of 50F (**a** & **b**) and 60F (**c** & **d**) ceramics sintered at 1200 °C



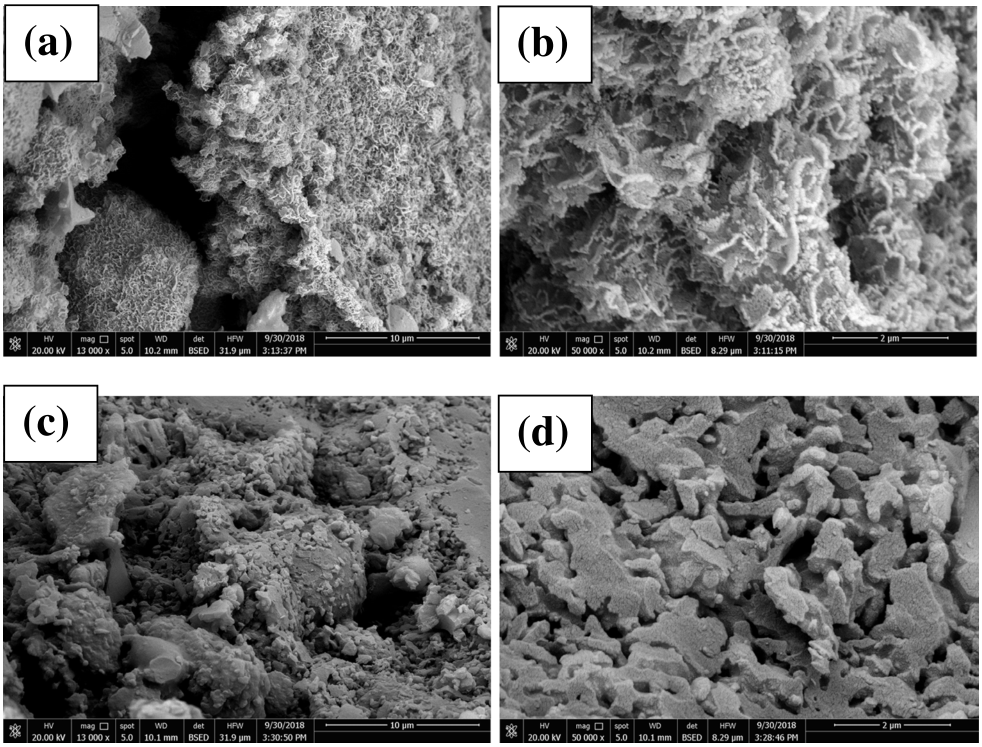


Fig. 7 SEM images of 50C (**a** & **b**) and 60C (**c** & **d**) ceramics sintered at 1200 °C

clays. In the presence of constant amount of feldspar and variable quantities of sand, ceramic bodies with improved physical and mechanical properties have been obtained after sintering at 1200-1400 °C. The optimum properties were obtained after sintering at 1400 °C.

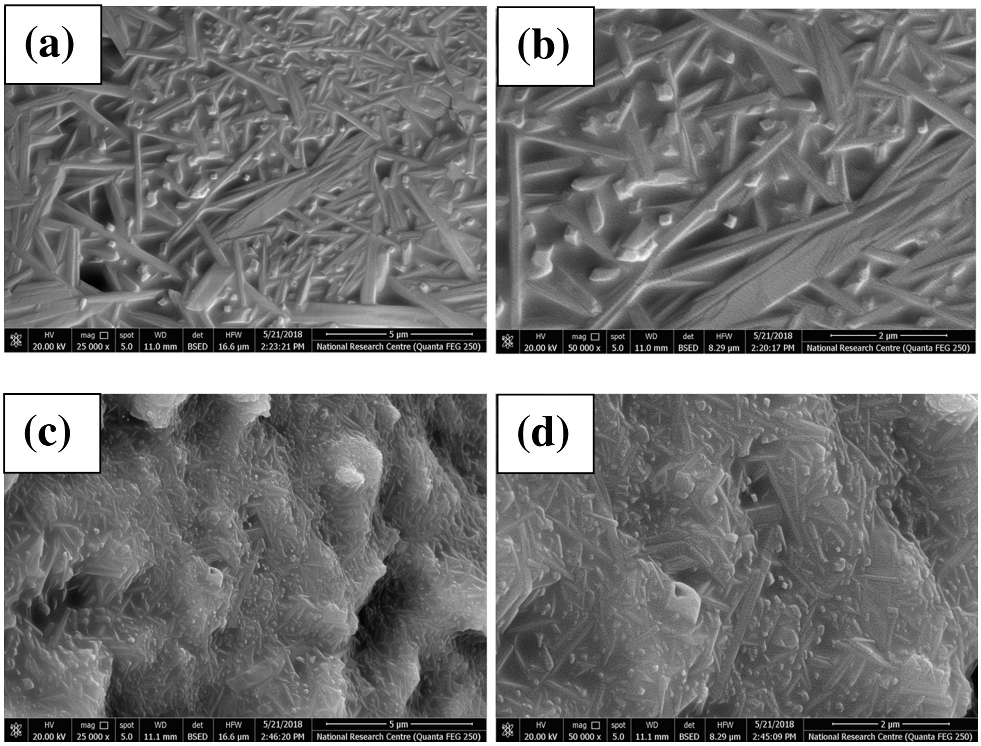


Fig. 8 SEM images of 50F (**a** & **b**) and 60F (**c** & **d**) ceramics sintered at 1400 °C

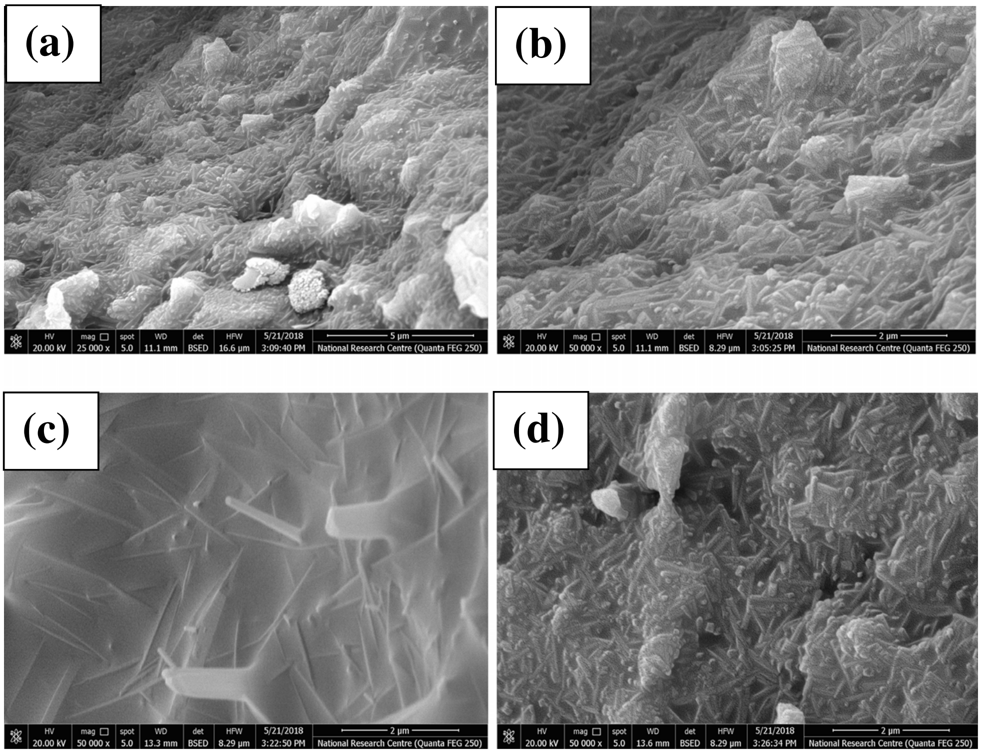


Fig. 9 SEM images of 50C (**a** & **b**) and 60C (**c** & **d**) ceramics sintered at 1400 °C

- The sintered ceramic bodies fabricated from Cyclones' waste clays exhibited better properties than that prospered from Feeders' waste clay.
- The small grain size and higher reactivity of starting Cyclones' waste clay as well as the addition of sand led to produce ceramic bodies having low porosity and improved properties. This is due the formation of fine mullite needle-like grains and glassy phase. These consequently were the keys factors for production of improved ceramic bodies using that starting material.
- The physical and mechanical properties were enhanced after sintering at 1400 °C and addition of sand. The best sample was that contains 25% sand (i.e. 50C)

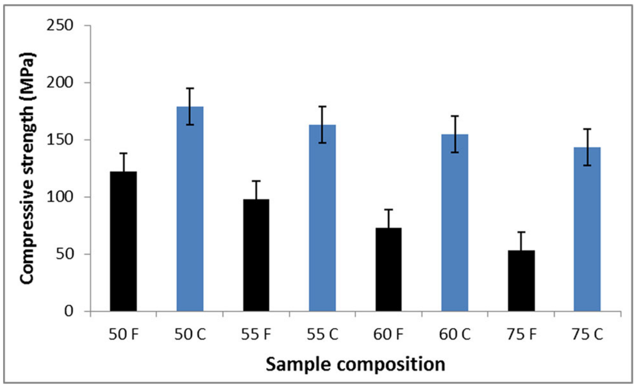


Fig. 10 Compressive strength of all compositions sintered at 1400 °C

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