7.1 Introduction

Ceramic tile industries in India are the third biggest producer and also the third leading purchaser of ceramic tiles in the world (Baraldi, 2016). This tiles market is acquiring faster around 15% compared to the global tiles production at an annualized rate of 11% (Ceramic tiles industry statistics). Tile consumption in India is lowest only 0.59 m^2 among the top countries. This will provide the immense potential to grow the tile industry in association with demographic and growing urbanization in India. A number of ambitious announcements like "Smart Cities Mission", "Sanitation for all by 2019", "Housing for all by 2022" and "Urban Transformation" are launched by Government of India (GOI) in the last three years. It will act as a potential demand for the ceramic tile industries in India (Patel *et al*., 2016).

Almost all ceramic tiles are made from a mixture of clay, soil, sand and other natural ingredients as raw materials, followed by casting the raw materials into the required shape, drying and sintering at a high temperature in a kiln. The extensive consumption of natural ingredients in the ceramic tile industry has caused an alarming deficit level of these natural resources (Pappua *et al*., 2007). In this aspect, tile industries also have inspiring environments for the implementation of waste utility systems (Almeida *et al*., 2016). Therefore, many researchers are working to develop new compositions for tiles manufacturing from various waste materials. A wide spread diversity of waste materials such as blast furnace slag (Ozturk and Gultekin, 2015), electric arc furnace slag (Teo *et al*., 2014), steel plant dust (Zhang *et al*., 2014b), paper mill sludge (Maschio *et al*., 2009), petroleum waste (Pinheiro and Holanda, 2013), rice husk ash (Silva and Surangi, 2017), rice straw ash (Guzmán *et al*., 2016), sugarcane bagasse ash (Schettino and Holanda, 2015), coffee husk ashes (Acchar *et al*., 2013), fishbone ash (Awaad *et al*., 2015), fly ash (Castellanos *et al*., 2017; Wang *et al*., 2017; Luo *et al*., 2017; Ji *et al*., 2016), ceramic waste (Tarhan *et al*., 2016; Ke *et al*., 2016) and glass waste (Dondi et al., 2009; Kima *et al*., 2016) have been studied for tiles production.

Turkmen *et al*. (2015) have been studied the effect of sintering behaviour on wollastonite ($CaSiO_3$) addition of ceramic porcelain body. Wollastonite powder is added by replacing the K-feldspar up to 5 wt% and higher strength is obtained at lower sintering temperature. He *et al.* (2012) have prepared sintered bricks by incorporation of yellow river silt (Jinan, China) with Red mud.

This study has investigated the feasibility of using river silt as an alternative raw material for the manufacturing of ceramic tiles by replacing quartz. Additionally, this research also studies the effect of waste derived wollastonite addition in place of feldspar on the physical and mechanical performance of tiles with different sintering temperatures. The inspiration behind this work is to use wastes (river silt (Kosi River, Bihar, India), eggshell, rice husk ash) to produce high strength and low cost sustainable ceramic tiles.

7.2 Experimental procedure

The procedure and outsize discussion about wastes derived para-wollastonite (1100°C calcined) was described in the previous chapter 3 and chapter 5, respectively. In the present work, different types of samples were prepared by different compositions with partially and fully replacement of quartz and feldspar by river silts and wollastonite, respectively. Initially, all ingredients were weighed according to the batch composition, as shown in Table 7.1. First five samples were prepared by replacing of quartz through the silt and last three were prepared by adding of wollastonite in the place of feldspar. Mixing was done in 2 steps, first in dry condition for 20 min with 300 rpm in a ball mill and next 10 min in the semi-dry process by adding least amount of water. Then, semi-dry powder was poured into different size of steel moulded for different shape and compressed by the uniaxial hydraulic press at a pressure of ~200 MPa to yield a green tile. The green body was dried in an electric laboratory air oven at 110°C for 12 h. The sintering was done in a laboratory electric furnace in an air atmosphere at different temperatures, i.e., 1000°C, 1100°C, and 1130°C with heating and cooling rate were 2°C/min and soaking period was 6 h to yield a vitrified or semi vitrified unglazed tile body, as shown in Figure 7.1(a).

Table 7.1 Sample's nomenclature and composition for tile samples.

Samples	Ball clay (wt.%)	Quartz (wt.%)	Feldspar (wt.%)	Silt (wt.%)	Wollastonite (wt.%)
k-0	50	20	30	-	-
k-1	50	15	30	5	-
k-2	50	10	30	10	-
k-3	50	5	30	15	-
k-4	50	-	30	20	-
kw-1	50	-	20	20	10
kw-2	50	-	10	20	20
kw-3	50	-	-	20	30

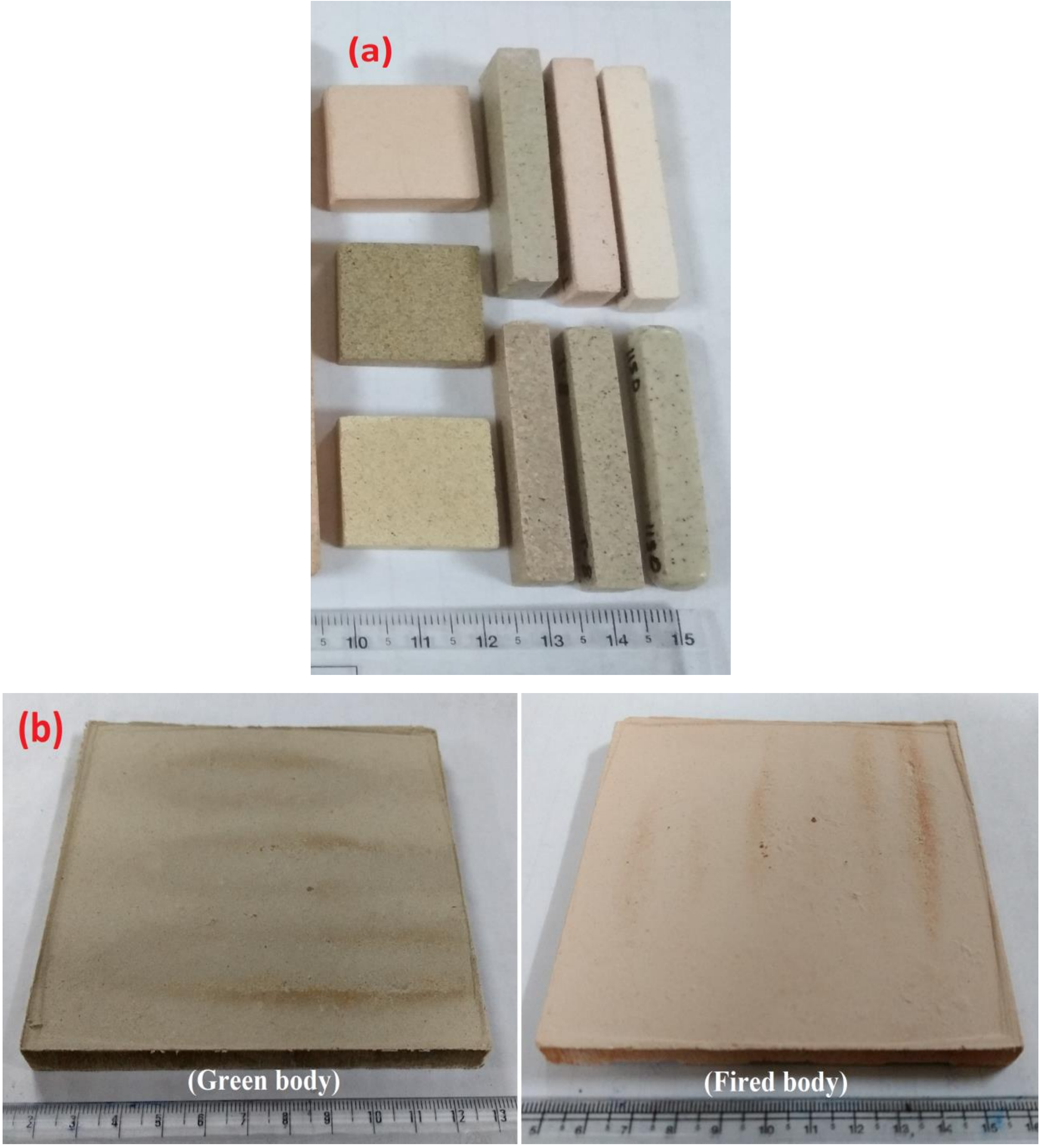


Figure 7.1 Image of (a) different size sintered tile samples and (b) Pilot sample.

7.3 Results and discussion

The visible imperfections and dimension tolerances of the tile samples are examined after sintering by the naked eye. No significant deformities on the size and shape with any visible flaws are identified for all samples. However, colors of the samples are changed with increasing silt or wollastonite in the composition and sintering temperature, as shown in Figure 7.2(a-b), respectively. Figure 7.2(a) shows that the colors of the samples become dark for the sample k-0 to k-4 due to the increasing impurity (Fe_2O_3) content in the system through the silt. Subsequently, this darkness is dissolved into whiteness (kw-1 to kw-3) with the increasing of wollastonite as it acts as a whitening agent (Sen, 1992). Colors of the samples are also changed with firing temperature, as represented in Figure 7.2(b) for sample kw-3. It may be due to the change of phase and microstructure with temperature.

The densification behaviour of some selective green samples, i.e., k-0, k-4 and kw-3 up to 1200°C are illustrated in Figure 7.3. All samples are displayed slight dissimilar sintering curves. At first, a slow gradual thermal expansion is observed for all three samples. It may be attributed to the release of absorbed and adsorbed water. After that, the expansion is rapidly increased. Higher expansion shows in k-0 sample may be due to the higher content of quartz in the composition. This expansion is accompanied by the transformation of α-quartz to β-quartz, happened in the range of 550°C to 600°C. After that, the dimensional variations rate is gradually decreased and densification is begun in between 900°C and 1000°C. Consequently, the composition kw-3 shows the faster sintering rate than the other. It may be ascribed to the present of higher amount wollastonite. Above 1000°C, clay starts to break down and develops higher density mullite crystal with the combination of SiO_4 and AlO_6 groups (Torres *et al.*, 2009). The fluxing ions (Na^+, K^+ and Ca^{2+}) present in feldspar, clay, and silt forms liquid phase which accelerates the sintering phenomena. However, high wollastonite based sample (kw-3) shows little deformation during firing at 1130°C. The densification curve (Figure 7.3) described the sintering temperature of different composition is different according to expansion values. Based on the expansion results, it is found that for silt based samples (k-0 to k-4) sintering temperature is optimized at 1130°C and for wollastonite base samples (kw-1 to kw-3) sintering temperature is optimized at 1100°C. Though, we have sintered all the samples at three different temperatures, i.e., 1000°C, 1100°C and 1130°C.

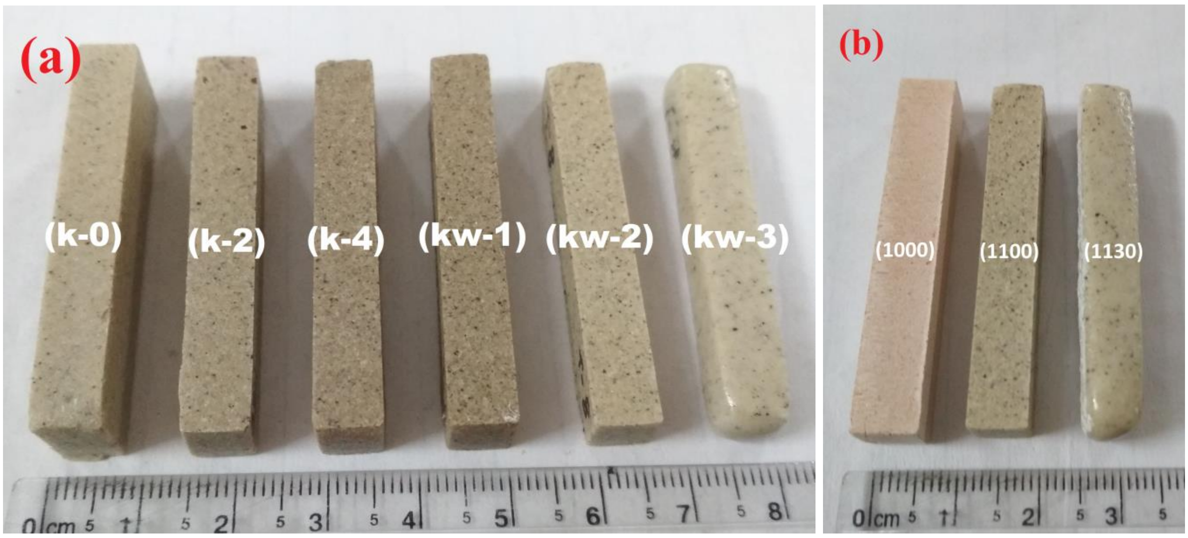


Figure 7.2 Color changing of samples with (a) composition and (b) temperature.

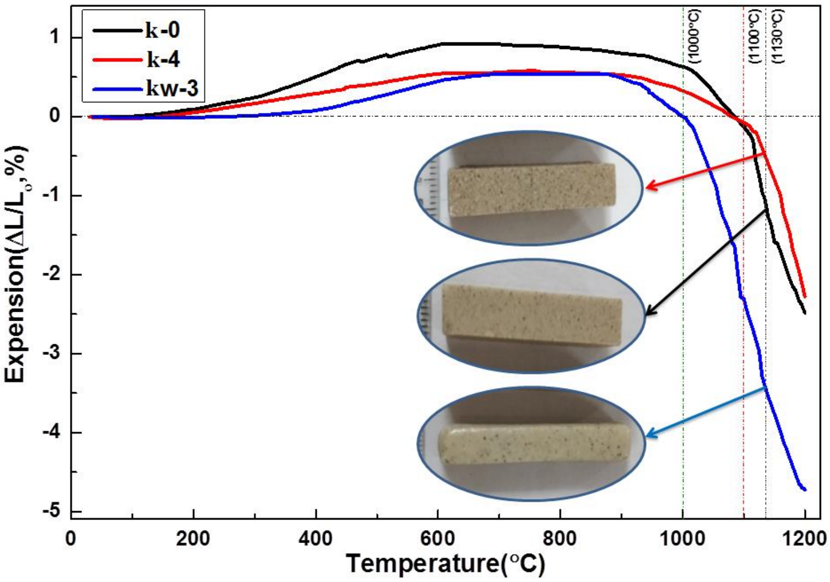


Figure 7.3 Sintering curves of tile samples.

The XRD analysis of three different compositions (k-0, k-4 and kw-3) fired at different temperatures are investigated in the room temperature, as shown in Figure 7.4. It has been seen that both k-0 and k-4 bodies are contained mainly quartz, sanidine ($K_{0.47}Na_{0.43}Ca_{0.1}Al_{1.1}Si_{2.98}O_8$), microcline ($KAlSi_3O_8$) and a small amount of larnite

(Ca_2SiO_4), as a crystalline phase at 1000°C. With increasing the firing temperature, sanidine and microcline phase are dissolved through the formation of high-temperature phases as mullite ($Al_6Si_2O_{13}$) and glassy phase. Consequently, with the addition of wollastonite in place of K-feldspar (kw-3 specimen), anorthite ($CaAl_2Si_2O_8$) phase is formed along with quartz, wollastonite (unconverted) and mullite for 1000°C. At high temperature, the intensity of anorthite phase is slightly increased for wollastonite based samples. This result may be occurred due to alumina silicates, which are reacted with wollastonite released CaO. Therefore, number of crystalline mullite peaks is decreased in Figure 7.4. Moreover, total numbers of crystalline peaks are reduced at 1130°C for kw-3 specimens due to glassy phase formation in the system. The glassy phases formed at high temperature may be due to the presence of alkaline elements along with some trace impurities presence in the silt or may be due to the dissolution of quartz reacting with wollastonite. Turkmen *et al.* (2015) is reported the same behavior of wollastonite in their research.

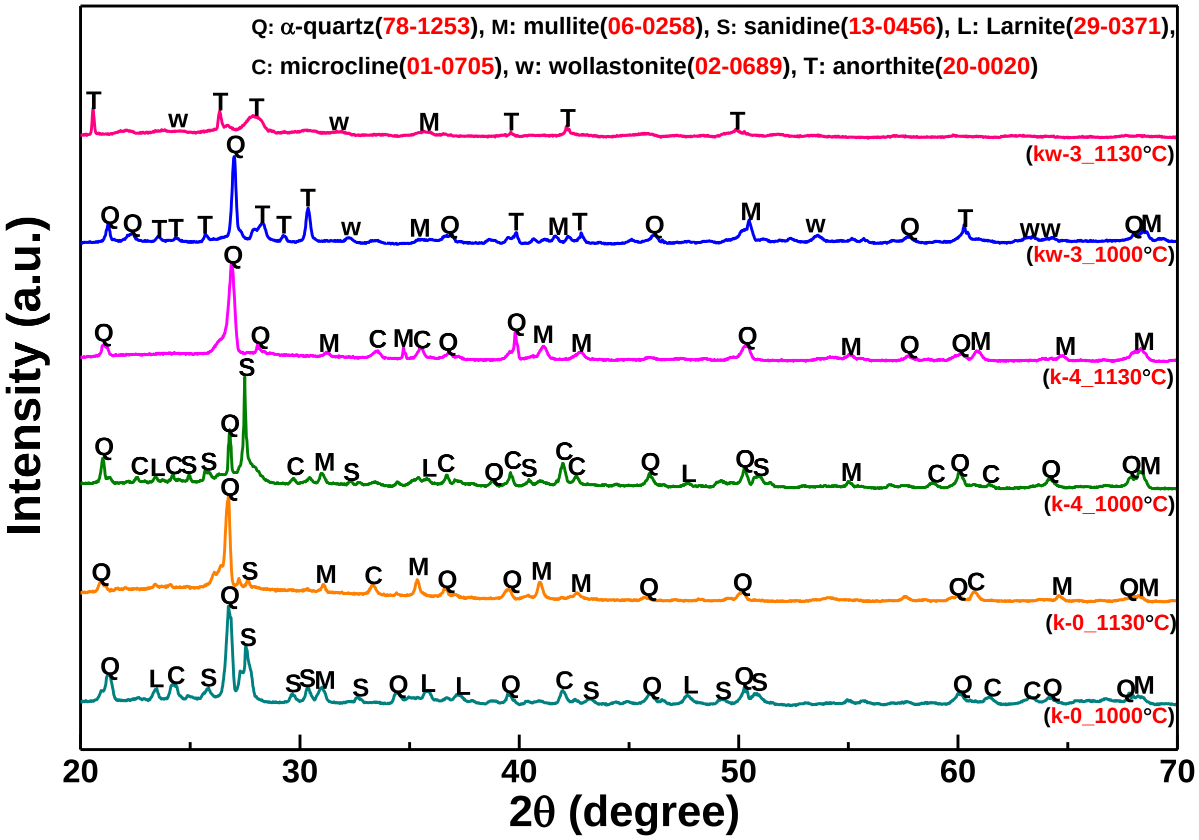


Figure 7.4 XRD patterns of sintered tile samples.

Figure 7.5 exhibits the SEM micrograph of the fractured cross-sectional surface of sintered tile specimens. The SEM analysis indicates that the unmistakable characteristic morphology for 1000°C fired samples with a few numbers of closed pores and no preferential shape or orientation of grains. It is also seen that the wollastonite addition and firing temperature mark influences on the vitrification through the formation of the glassy network. Therefore, 1100°C fired kw-3 sample shows the fully vitrified dense structure without any close pores and grain boundary.

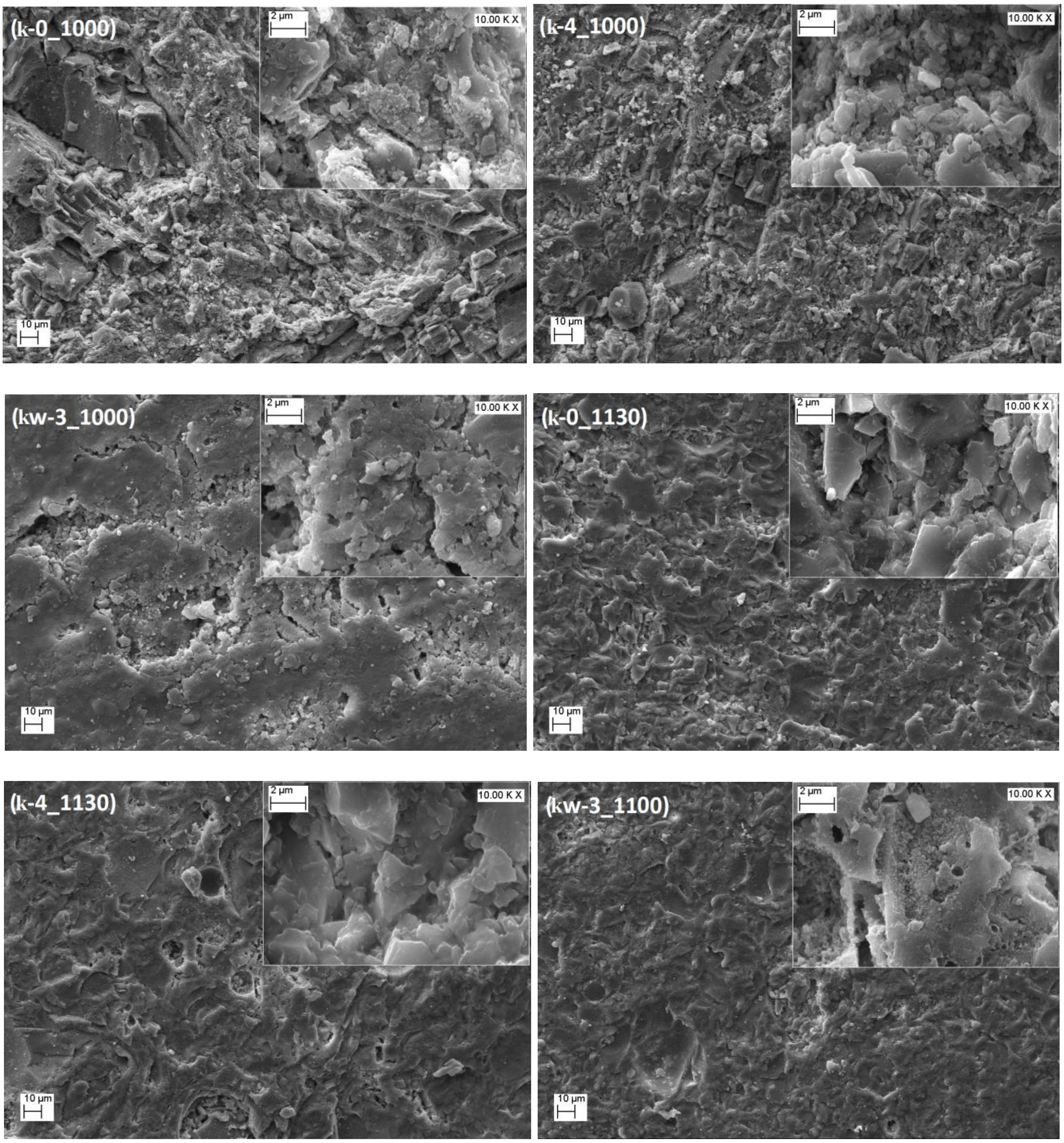
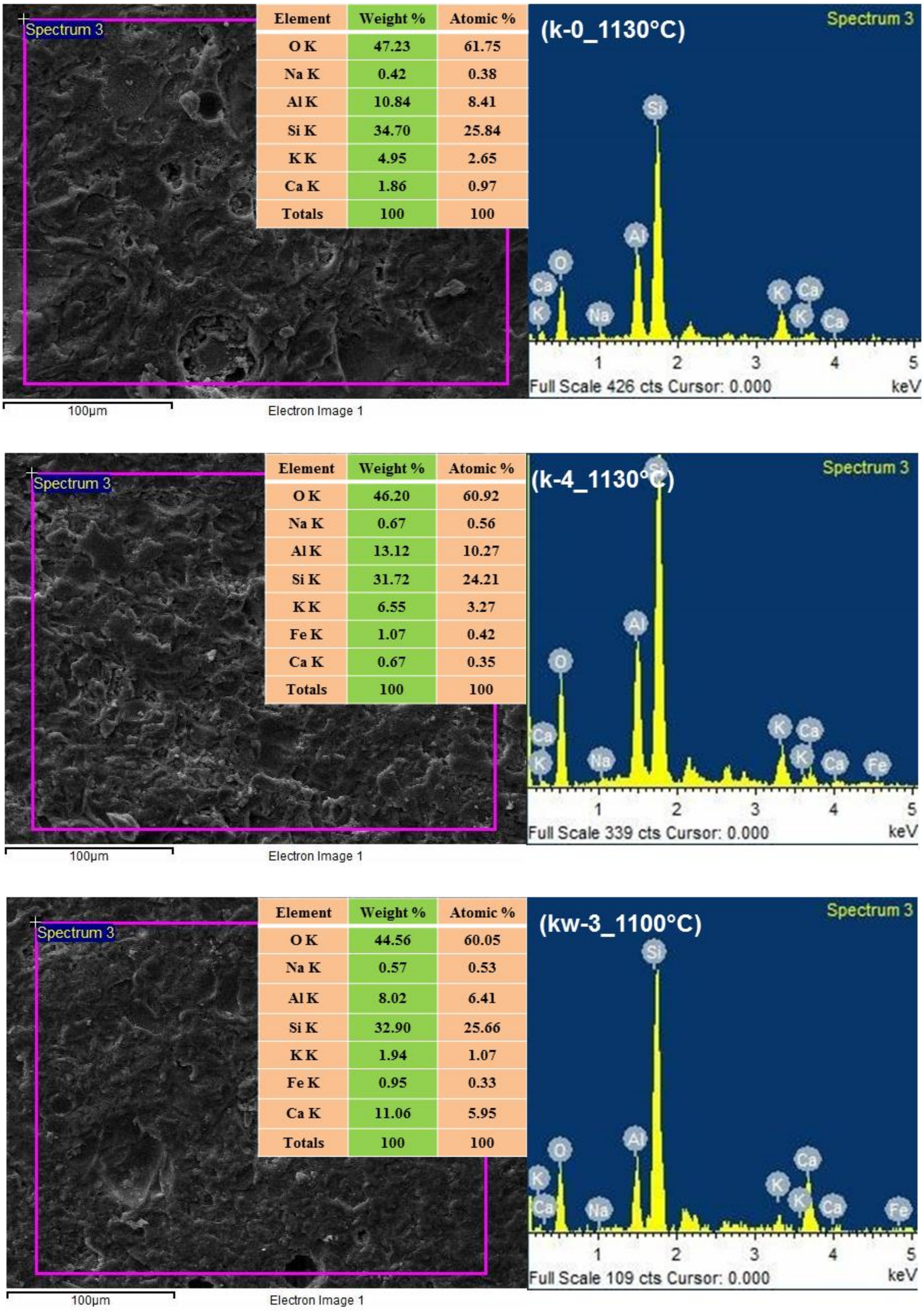


Figure 7.5 SEM micrograph of fired k-0, k-4 and kw-3 samples.

The EDX studies are accomplished to find out the elemental composition of the sintered specimen. Figure 7.6 displays the EDX investigation of k-0, k-4, and kw-3 fired samples. It specifies the qualitative existence of Si, O, Al, Ca, K, Na and Fe elements only, but doesn't detect any harmful and heavy metal elements in the accuracy limit of EDX.



Element	Weight %	Atomic %
O K	47.23	61.75
Na K	0.42	0.38
Al K	10.84	8.41
Si K	34.70	25.84
K K	4.95	2.65
Ca K	1.86	0.97
Totals	100	100

Element	Weight %	Atomic %
O K	46.20	60.92
Na K	0.67	0.56
Al K	13.12	10.27
Si K	31.72	24.21
K K	6.55	3.27
Fe K	1.07	0.42
Ca K	0.67	0.35
Totals	100	100

Element	Weight %	Atomic %
O K	44.56	60.05
Na K	0.57	0.53
Al K	8.02	6.41
Si K	32.90	25.66
K K	1.94	1.07
Fe K	0.95	0.33
Ca K	11.06	5.95
Totals	100	100

Figure 7.6 EDX analysis of fired k-0, k-4 and kw-3 samples.

Table 7.2 shows the mean values of AP and BD of different sintered samples. It has been seen that at 1000°C the AP is slightly increased and BD is decreased for batch k-0 to k-4 samples due to incorporate river silt in place of quartz. This effect may be ascribed due to the presence of volatile compounds (~5.25 wt.%) in the silt. These compounds are burnt or decomposed up to 1000°C (Figure 3.3(a)), which are formed pores in the system. Another effect may be due to uneven shape of particles as shown in Figure 3.2(c). Therefore, the probability of imperfection is higher in the packing density with river silt. Additionally, the softening temperature of the samples may be increased with increasing silt, may be due to the increment of high refractoriness phase i.e. Al_2O_3 (~17 wt.% of silt). On the other hand, it is found that the AP significantly decreases from 22.43 to 12.94% with the substituting feldspar by the wollastonite at 1000°C. It is proposed lower firing temperatures through the contributing more amount of CaO and SiO_2 in the glassy phases, which aids densification by viscous flow. Alternatively, the sintering kinetics is increased with the increasing of firing temperature. Therefore, the size of pores is shrunk and the packing efficiency is increased, results in higher density and lower porosity, as shown in Table 7.2.

Table 7.2 Apparent porosity and bulk density of sintered tile samples.

Samples	Apparent porosity (%)						Bulk density(gm/cc)					
	1000°C		1100°C		1130°C		1000°C		1100°C		1130°C	
	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.	Mean	s.d.
k-0	18.38	0.82	5.64	0.27	2.39	0.17	2.177	0.056	2.276	0.034	2.337	0.026
k-1	18.87	0.56	5.97	0.34	2.66	0.16	2.146	0.045	2.258	0.031	2.324	0.027
k-2	19.24	0.79	6.74	0.41	2.92	0.24	2.123	0.036	2.240	0.026	2.312	0.019
k-3	20.13	0.67	7.83	0.38	3.14	0.30	2.108	0.021	2.236	0.025	2.294	0.016
k-4	22.43	0.83	9.16	0.54	3.26	0.28	2.085	0.018	2.226	0.022	2.288	0.024
kw-1	20.45	0.57	6.31	0.43	1.77	0.18	2.114	0.022	2.263	0.015	2.369	0.017
kw-2	17.56	0.92	2.76	0.28	1.23	0.19	2.155	0.024	2.353	0.013	2.372	0.009
kw-3	12.94	0.64	0.68	0.23	0.45	0.21	2.237	0.014	2.407	0.011	2.411	0.017

The mean values of water absorption (WA) for the tile samples with the function of silt and wollastonite at different temperatures are represented in Figure 7.7. It’s seen that the values of water absorption are slightly increased with the incorporation of silt in the place of quartz for 1000°C and 1100°C fired samples. It is happened due to the development of open porosity. The water absorption is deeply related to the open porosity and pore volume, which demonstrates a linear relationship. However, the values of water absorption are abruptly decreased with increasing the firing temperature up to 1130°C for all samples. At high temperature, particles are acquired more activation energy and started to diffuse each other or developed liquid phase, which are accelerated the sintering degree. Therefore, number of pores is decreased or volume of pores is shrunk.

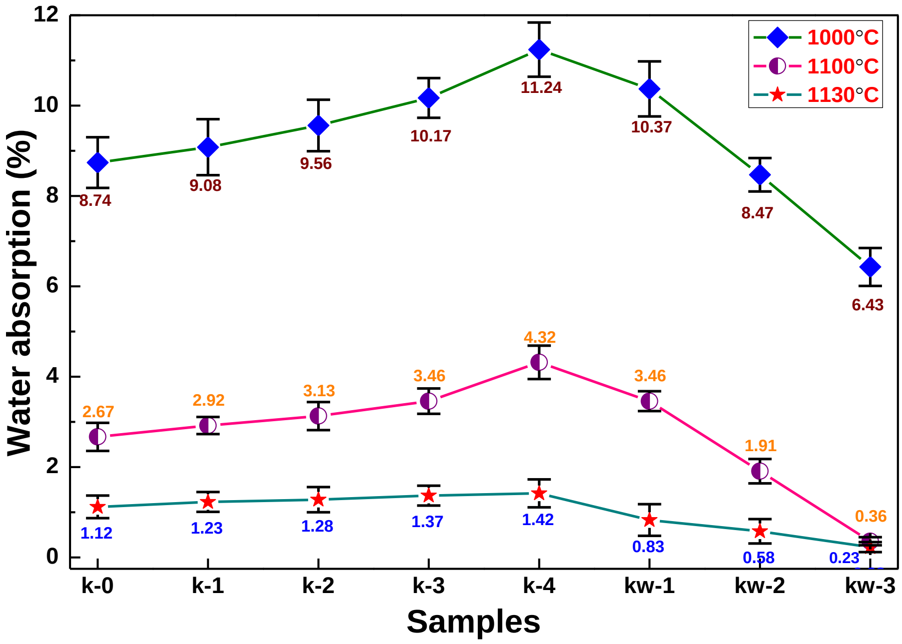


Figure 7.7 Water absorption of different sintered tile samples.

Subsequently, for kw-3 sample fired at 1100°C has the lowest water absorption ~ 0.36 %, which is lower than ISO 13006 standards (≤0.5 wt.%) (Ke *et al.*, 2016). The replacement of virgin K-feldspar with wollastonite provides a higher quantity of CaO, which decreases the viscosity of glassy phases at high temperature in the system. It makes to a higher degree of vitrification by increasing the viscous flow into the inter-granular pores (Turkmen *et al.*, 2015).

Shrinkage is also an imperative characteristic for ceramic tiles and its alteration causes the variations in mechanical behaviour. Table 7.3 is illustrated the mean value of linear shrinkage and L.O.I of tile pieces as a function of different composition and sintering temperatures. At 1130°C sintered samples are exhibited linear shrinkage values between 6.32

to 9.13%, which is acceptable values for industrial production of stoneware floor tiles (Schettino *et al*., 2015; Acchar *et al*., 2013). It has also been observed that the linear shrinkage of the sample doesn't significantly affect with the replacement of quartz by the silt. Conversely, the wollastonite addition in place of feldspar expressively influences the shrinkage values. As per expectation, the firing shrinkage is increased with the increment of the degree of vitrification up to an optimum densification through the enhancement of sintering temperature. It can be explained by the closing of pores in the body with the diffusion of grains or forming of viscous phase. The values of L.O.I are enhanced through the silt addition. The weight loss is happened due to the burning of an organic compound, decomposed of carbonate and remove of adsorbed water present in the clay minerals and other ingredients. Consequently, the wollastonite incorporation decreases the L.O.I. It is occurred due to calcined wollastonite which does not contain any organic and volatile compound (Table 3.1).

Table 7.3 Linear shrinkage and loss on ignition of fired tile samples.

Samples	**Linear shrinkage (%)**						**Loss on ignition (%) at 1100°C**	
	1000°C		**1100°C**		**1130°C**		**Mean**	**s.d.**
	Mean	**s.d.**	**Mean**	**s.d.**	**Mean**	**s.d.**		
k-0	3.97	0.027	5.82	0.034	6.85	0.044	9.25	0.018
k-1	3.95	0.016	5.73	0.037	6.69	0.047	9.47	0.024
k-2	3.94	0.032	5.65	0.026	6.58	0.036	9.61	0.026
k-3	3.92	0.028	5.54	0.019	6.46	0.032	9.73	0.022
k-4	3.86	0.017	5.42	0.033	6.32	0.039	9.96	0.027
kw-1	4.17	0.019	6.22	0.041	7.15	0.034	9.75	0.032
kw-2	4.78	0.027	7.78	0.035	8.57	0.033	9.34	0.042
kw-3	5.24	0.029	8.26	0.036	9.13	0.42	9.03	0.027

The mechanical properties of fired tiles are greatly depended on the crystalline phases developed after sintering and microstructure characteristics, i.e., porosity, size and shape of pore and grain size of samples (Cheng *et al*., 2012). Figure 7.8(a-c) shows the mean values of BS, CCS and the maximum displacement at the elastic curve of some selective tile samples at room temperature. After correlating of Table 7.2 and Figure 7.8, it is seen that the higher porosity tends to reduce the mechanical strength of the samples due to presence of high concentration of pore, which aids to crack propagate in the non-ductile body with less value of stress (Teo *et al.*, 2014). The lowest BS values are 14.36 MPa to 30.74 MPa for 1000°C sintered samples. Probably higher porosity is the responsible for lowering the values of strength. It may be attributed by the presence of a higher amount of incomplete fusion fluxing agent in the system at low firing temperature. Therefore, the lake of strong bond in the structure is introduced. However, the addition of wollastonite is significantly increased the strength value due to the enhancement of fluxing characteristic of body. Consequently, both bending and CCS gradually decreases with the replacement of quartz by silt at 1000°C samples. Furthermore, at a higher temperature, no remarkable effect is observed with silt addition. It may be due to the formation of a higher amount of high strength phases by the alumina present in silt. As per expectation, the strength values are increased with the increasing of sintering temperature. The highest bending and CCS values are observed for kw-3 (1130°C) sample around 50.36MPa and 72.67MPa, respectively. It can be attended by the formation of a large number of glassy phases, which reduce the porosity (Table 7.2) and pore size, as shown in SEM micrograph (Figure 7.5).

The acid–alkali resistance test is necessary for ceramic tiles to study the effect of prolonged exposure to chemical constituents that are normally used in the domestic purpose for scrubbing as well as other more severe conditions, i.e., lavatories, medical, food counters. 1100°C sintered k-0, k-4, and kw-3 specimens are used for the performances of the acid–alkali resistance test. After 24 h of interaction of samples with the testing solution, the specimens are examined by visual evaluation, i.e., color differences between the treated and untreated area, texture from multiple angles and loss of glossiness. The test results show that the surface doesn’t react with both the solutions. Consequently, several pencil lines are drawn on the treated and untreated area of the test specimen. But pencil lines are removed with a damp cloth from both surfaces. So, samples are passed for chemical resistance test according to ASTM C650-04 (2014).

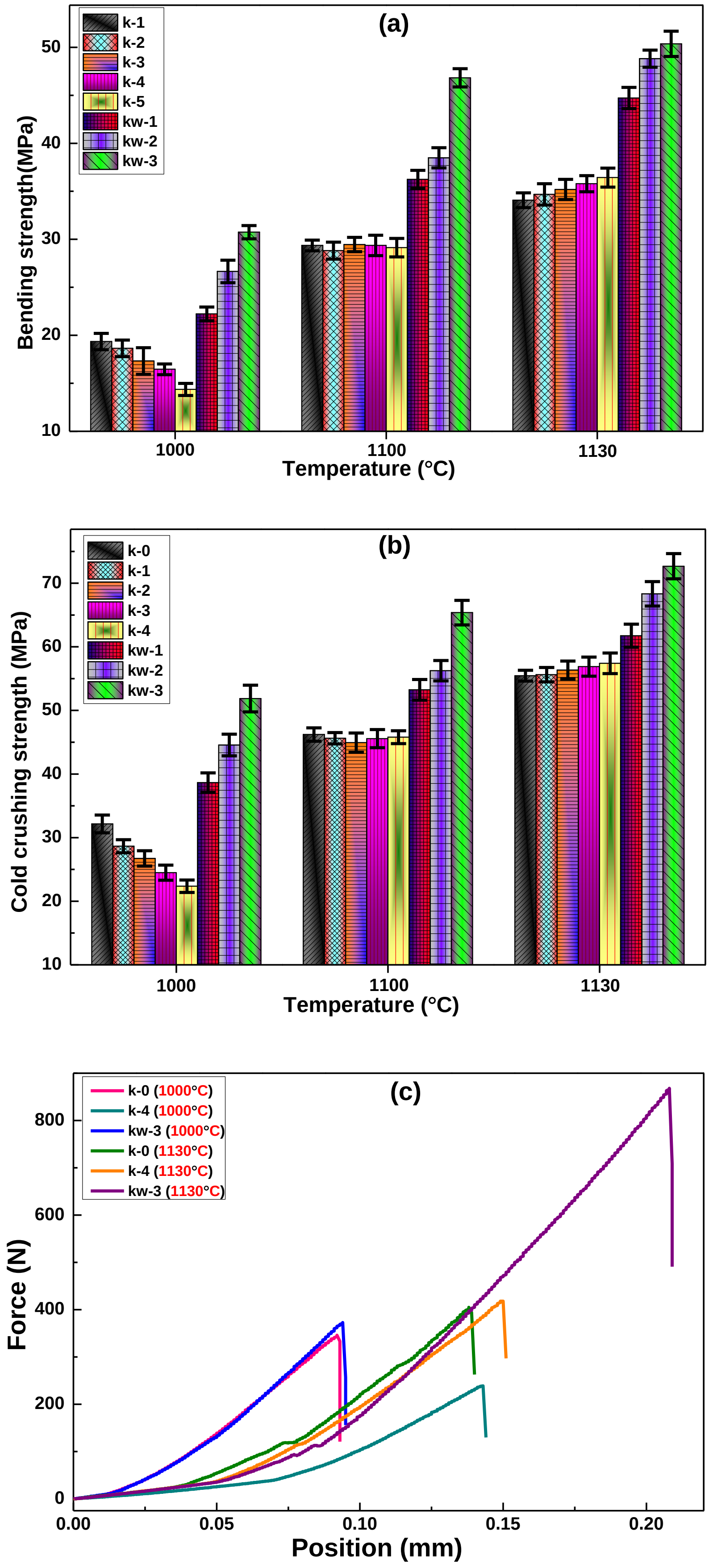


Figure 7.8 (a) Bending strength, (b) cold crushing strength and (c) the maximum displacement at the elastic curve of sintered tile specimens.

7.4 Summary

Recently, waste utilization has gained much attention in the area of ceramic product formulation. This study confirms the possibility of utilization of wastes in place of natural ingredients for tiles preparation. The physico-mechanical properties of the wastes incorporated tiles have been analyzed. The physical and mechanical properties of the tile samples are reduced with the incorporation of river silt in the place of quartz for low-temperature sintering but at high-temperature mechanical properties don't have significant influence through this substitution. Subsequently, all the properties are improved with wollastonite addition in place of K-feldspar. The color of the sample is changed from light to darkness with silt addition. However, this brightness is recovered through the addition of wollastonite in place of feldspar. The substitution of K-feldspar by wollastonite is reduced the sintering temperature at 30°C. The fully quartz replaced, 1130°C fired k-4 sample can be used as unglazed ceramic wall tiles. Consequently, 1100°C sintered kw-3 sample fulfills the main desired properties of porcelain stoneware tile bodies as per ISO 13006.

We have prepared pilot size sample (based on kw-3 composition) (Figure 7.1 (b)). The surface and texture are fully satisfactory. The values of water absorption and BS are 0.36% and 49 MPa, respectively. It is exhibited better performance than standard (ISO 13006). This study confirms the feasibility of Kosi river silt and waste derived wollastonite for sustainable tiles manufacturing. It leads to the environmental and economic benefits in the ceramic industries.