

Phase evolution and microstructure-property relationship in red clay bricks

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Clay brick is one of the oldest and commonly used clay products in construction industry in Khyber Pakhtunkhwa (KP) Pakistan. In spite of its widespread use, studies regarding the manufacturing standards and quality of locally made bricks are much less in comparison to those of technologically advanced countries. The aim of the present study was to investigate the chemistry and phase constitution of the raw materials used in local brick kilns. Phase and microstructural analyses of fired bricks from local kilns were performed and compared with those of the laboratory made bricks. X-ray diffraction of raw materials revealed the presence of illite, quartz, clinocllore and albite while calcite was identified as a minor phase in all the investigated samples. Diopside, anorthite and quartz were observed as major phases in the kiln-fired samples, and only diopside and quartz in the laboratory-fired samples. The presence of albite and clinocllore, although in small concentrations, in the kiln-fired samples indicated that the employed temperature was too low to completely dissolve the initial ingredients. Consistent with X-ray diffraction results, semi-quantitative energy dispersive spectroscopy revealed the presence of silicon, aluminum, calcium, magnesium, iron and potassium along with a small amount of sodium in these samples. An increase in firing temperature decreased porosity which resulted in substantial increase in compressive strength and decrease in water absorption. The optimum mechanical properties were achieved at 1000 °C.

Key words: Clay bricks, Phase constitution, Microstructure, Diopside, Kiln.

Introduction

Red clay bricks are mainly used in construction industry. Its production process involves forming of red clay into rectangular blocks of a standard size, followed by firing to temperatures ranging from 900 to 1200 °C [1]. It is one of the oldest building materials and probably the first to be manufactured by man, first as Sun-dried bodies and then as kiln fired bricks. Red clay brick is still popular as a construction material mainly because of its structural properties, easy availability, relatively cheaper raw materials and architectural distinctiveness [2]. The Regional Wood Energy Development Programme (RWEDP) in Asia estimates that there are approximately more than 3000 brick manufacturing plants / kilns in Pakistan. The industry appears to be growing at an annual rate of about 3% resulting in the setting up of new factories; however, many factories are also going out of business for various reasons. The industry is facing a number of problems. The first and probably the most important problem is the supply of affordable fuel in the form of fuel wood as well as coal. Secondly, this industry is not well organized and technically speaking, very little is known about it in this part of the world; consequently, relatively few engineers / scientists have taken an interest in this industry [3].

The quality of fired bricks strongly depends on the type, composition and phase constitution of the raw materials (i.e. clay, feldspathic minerals and quartz etc.) [4]. In addition to an increase in compressive strength, the presence of certain carbonates reduce shrinkage and anisotropic behaviour during firing [5-7]. The control of firing temperature may be less critical in the case of calcareous clays, since their morphology remains essentially unchanged over a wide range of temperature [8].

Properties of a ceramic product are not only related to the type, proportion and mineralogical composition of the constituent raw materials, but also to the processing conditions, for example, pressing, drying, firing, and thermal gradients in the kiln [9-12]. Consequently, in addition to chemical and mineralogical analyses of the representative raw materials, a number of studies have been carried out to investigate the phase and microstructural evolution of clay bricks [13-16].

Conventionally, temperatures above 900 °C are taken as being the minimum for firing clay-based ceramics [12, 17, 18]. For ceramics, the densification process during sintering is closely related to the grain growth; therefore, the solid-state diffusion mechanism using geometrical parameters was proposed to explain the consolidation of clay particles into a dense body [19, 20]. Furthermore, the mineralogical composition is considered a key parameter in achieving the desired microstructure of clay bricks, which in turn influences the mechanical properties and durability of the product [21-24]. Sintering at an appropriate temperature transforms

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as-formed / green clay bodies into a rigid, contiguous (although porous) ceramics via a complicated succession of physical and chemical changes [25], can be briefly described as follows:

1. Dehydration occurs at ~ 100 °C which is followed by dehydroxylation of clay minerals at ~ 450 - 750 °C, depending upon the type and purity of the clay [26]
2. Decomposition of initial ingredients and loss of CO_2 , S and hydrocarbons at ~ 400 - 650 °C, again depending on the type of the flux and other raw materials used
3. Alpha/beta-quartz conversion at 573 °C
4. Solid state minerals reactions and the beginning of vitrification at ~ 1050 - 1150 °C; however, the melt formation may begin at temperatures as low as 985 °C, depending on the eutectic temperature of the mixture [27]

In clays, water may be bonded chemically in the form of OH ions or loosely attached surficial water. The dehydration / dehydroxylation of comparatively pure clay minerals takes place over different ranges of temperature depending on the clay minerals present. Chlorite loses its water at a relatively higher temperature, usually beginning at ~ 750 , but this temperature again depends on the mineral chemistry. The transformation of illite (mica) begins with its dehydration at ~ 100 - 150 °C, followed by dehydroxylation at ~ 600 - 700 °C [28]. The carbonate minerals lose carbon dioxide on heating, for example, calcite decomposition begins at ~ 650 °C. The phase transformation temperatures vary from sample to sample because of its dependence on a number of factors such as the minerals grain size, heating rate, and how easily the evolved carbon dioxide can be lost to the atmosphere [29].

At ~ 573 °C alpha / low quartz undergoes a structural phase transition into beta / high quartz. As this transition involves rotation rather than the breaking of bonds, the reaction is reversible, so that any high quartz present after the high temperature soak will invert to low quartz during the cooling part of the firing cycle. The brick expands during the rise in temperature; however, if the cooling rate is too fast, then highly damaging micro-cracking can occur [2].

Keeping in view the previous studies on bricks, it can be concluded that the main factors affecting the quality of bricks are related to the mineralogy of the constituent raw materials and processing conditions. An appropriate firing temperature and optimum particle size of the raw materials produce more vitrification, less porosity and relatively higher density. The higher the fired density of the product the better will be the mechanical properties; however, improvement in density is 'in general' accompanied by a reduction in the insulating behaviour of the brick [30]. Previous studies of clay bricks from Punjab (Pakistan) reported that the main phases identified in the raw materials of these bricks

included; illite, chlorite, quartz, albite and calcite [31, 32]. In contrast, there are a number of brick factories throughout the province of KP; however, to authors knowledge, these bricks have not been investigated. The aim of the present study was to investigate the microstructure property relationship for clay bricks from local brick manufacturing plants and compare these with the laboratory made clay bricks.

Materials and Methods

Initially, representative samples of locally used raw materials such as soil and processed bricks were collected from various brick manufacturing sites of Peshawar, KP, Pakistan. These raw materials and pieces of brick samples were separately ground to fine powders using pestle and mortar. Phase analysis of these samples was carried out using a Philips 1700 series (Netherland) X-ray diffractometer ($\text{CuK}\alpha$ radiations with $\text{K}\alpha = 1.5418$ Å) operating at 40 kV and 30 mA at $2\theta = 5$ - 60 °, at the Department of Materials Science and Engineering, University of Sheffield (UK) and Centralized Resource Laboratory (CRL), University of Peshawar (UoP), Pakistan. For microstructural investigation, a JSM-5910 (JEOL, Japan) scanning electron microscope (SEM) was used at CRL, UoP, Pakistan. SEM samples were prepared by cutting small pieces ($3 \times 5 \times 40$ mm³) from the bricks and finely polishing with a twin prep ³TM grinding / polishing machine. The smooth polished surfaces were chemically etched with 5% HF for one minute at Materials Research Laboratory (MRL), Department of Physics, UoP. Finally, the samples were mounted onto aluminum stubs with silver paint and gold coated in order to avoid charging in the SEM.

Soil samples collected from the same local kiln sites were used as raw materials for making of the laboratory made bricks. The raw materials were processed using a stainless steel mould and hand pressing into $3 \times 5 \times 40$ mm³ rectangular bars. The shaping technique used for the laboratory scale bricks was almost similar to that of the local industrial processing. After forming, the test pieces were subjected to drying and firing operations in order to enhance their mechanical strength and durability properties. To study the influence of heating, freshly shaped samples were placed in a drying oven at 110 ± 2 °C for over 4 h to attain equilibrium residual moisture content in the clay bodies. Dried samples were placed directly in an electric furnace and were sintered at temperatures ranging from 500 to 1000 °C at a heating rate of 10 °C/min. After reaching the maximum temperature, the samples were soaked for 1h at the maximum temperature and then allowed to cool down naturally inside the furnace. In the present investigations, an attempt was made to understand the relation between the firing process and the resulting properties, such as phase development, microstructural changes, compressive strength and water Absorption. Compressive strength and water absorption

were measured for both the factory made and laboratory manufactured brick samples. Compressive strength was determined using a UTM at CRL. Water absorption (expressed as percentage) of these samples was measured by submersing the bricks into water for 24 h.

Results and Discussion

Fig. 1 shows the room temperature XRD patterns recorded for three red clay samples collected from various brick manufacturing sites, Peshawar, KP, Pakistan. The interplanar spacings (d-values) and relative intensities corresponding to the observed XRD peaks indicated the presence of illite, quartz, albite and clinochlore while calcite was identified as a minor phase in all the investigated samples. Fig. 2 shows XRD patterns of fired brick samples collected from various locally available kilns, Peshawar, KP, Pakistan. The exact firing temperature of these samples is not known but Sun-dried bricks are stacked and fired in

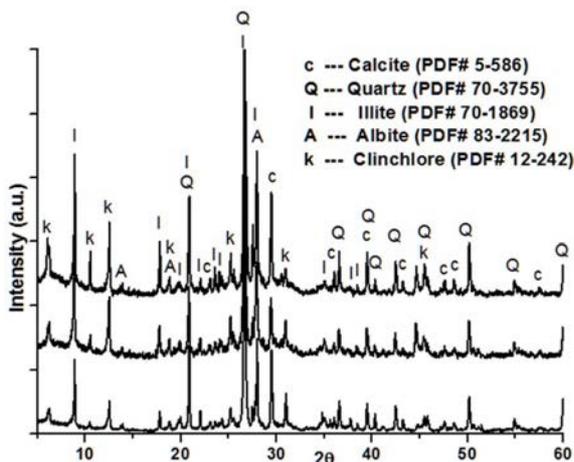


Fig. 1. Room temperature XRD patterns of three red clay samples collected from various brick manufacturing sites, Peshawar, KP, Pakistan.

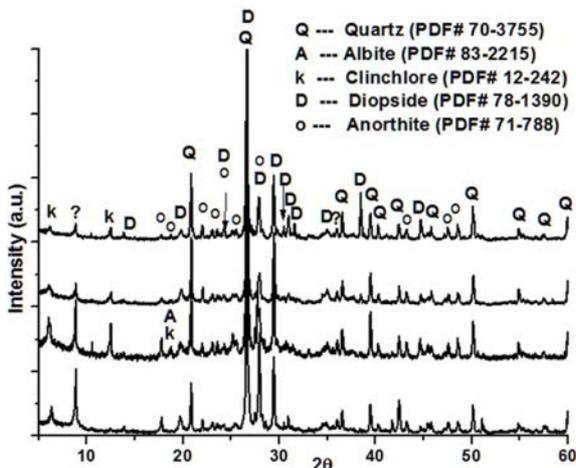


Fig. 2. Room temperature XRD patterns of fired brick samples collected from local kilns, Peshawar, KP, Pakistan.

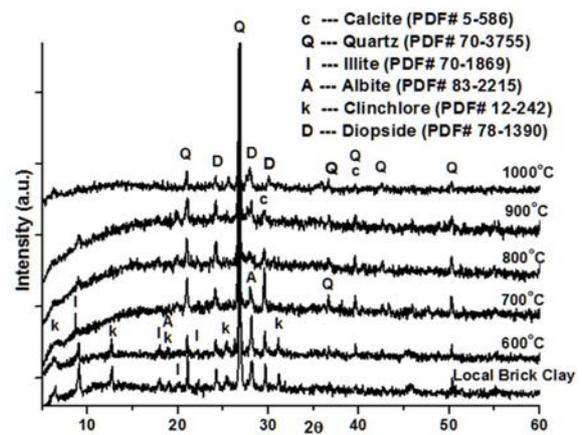


Fig. 3. Room temperature XRD patterns of laboratory made clay bricks samples fired at 500, 600, 700, 800, 900 and 1000 °C. The bottom plot is the XRD pattern from the unfired sample shown for comparison.

locally made kilns and the firing temperature is estimated to be in the range of 900 °C to 950 °C. XRD detected the presence of diopside ($\text{CaMgSi}_2\text{O}_6$) along with the major quartz phase consistent with a previous study [33]. A few low intensity XRD peaks matching albite and clinochlore, and some unidentified peaks probably due to untransformed initial ingredients were also detected. The presence of these peaks indicated that the firing temperature was too low to melt / transform these low melting phases. The observed low intensity of the peaks due to albite, clinochlore and other initial ingredients demonstrated that with an increase in firing temperature, the concentration of these phases decreased due to their partial dissolution and / or transformation into other phases upon firing. The presence of quartz grains prevents shrinkage and warping of bricks during firing. In addition to uniformity of shape, quartz grains act as crack diversion flaws [34]. The absence of XRD peaks due to mullite indicated that the kilns temperature was too low for mullite formation. The formation of mullite in burnt clays is usually indicative of firing at elevated temperatures (well above 1000 °C) [10]. According to Iqbal and Lee [27], small (~7 nm in length) mullite needles could be identified in triaxial porcelain bodies fired to 1100 °C but via transmission electron microscopy.

Fig. 3 shows the room temperature XRD patterns recorded from the laboratory made clay brick samples fired at 600, 700, 800, 900 and 1000 °C. The XRD pattern at the bottom of Fig. 3 was recorded from the soil sample. As mentioned earlier, the unfired samples comprised quartz, illite, albite, clinochlore and calcite. It is evident from a close inspection of Fig. 3, that at temperatures < 700 °C, with the exception of quartz, XRD peaks due to the initial ingredients persisted. At temperatures ≥ 700 °C, peaks due to illite almost disappeared while the concentration of calcite, albite and clinochlore decreased with increasing firing temperature

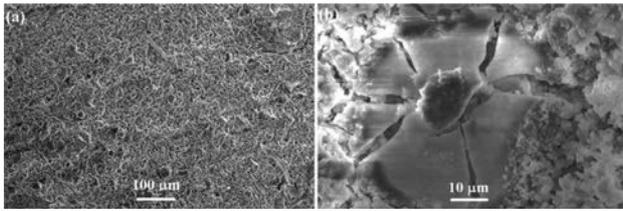


Fig. 4. SEI a) showing the grass view of locally made clay brick samples b) a chemically etched locally made clay brick sample, showing cracked anorthite grains.

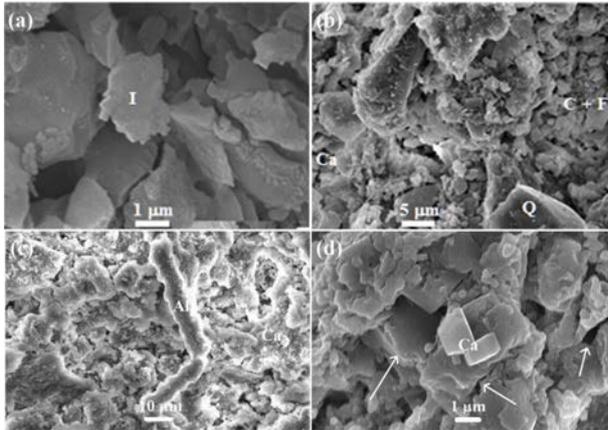


Fig. 5. SEI (a-b) from chemically etched sample of low-fired clay brick samples collected from local plant (District Peshawar, Pakistan), showing poor density; and SEI (c-d) recorded from chemically etched clay brick samples fired at relatively higher temperatures showing rod-shaped albite grains with deformed edges and rectangular calcite crystals. Note the denser microstructure of these samples than that shown in Fig. 5(a-b).

Table 1. Mean values of compressive strength and water absorption.

Types of locally manufactured clay bricks	Mean value of compressive strength (MPa)	Mean value of water absorption (%)
First class brick	30	11
Second class brick	14	25

at the cost of diopside. XRD peaks due to diopside emerged at temperatures above 800 °C. As the raw materials commonly used in brick-making are mostly impure and the positions of the peaks due to the new emerging phases and initial ingredient coincide in some cases, it was difficult to clearly distinguish the emergence of peaks due to new phases and disappearance of the peaks due to the diminishing phases. As evident from Fig. 2, some peaks could be also matched with anorthite and according to Taskiran et al. [35], high crystallinity of anorthite enhances compressive strength. Anorthite is an end member of the plagioclase series (AlbiteAnorthite). Hence, in addition to other factors mentioned above, the reported increase in compressive strength, decrease in porosity and cracking with an increase in firing temperature can be associated with anorthite formation [36].

Fig. 4a shows the general area secondary electron SEM image (SEI) of brick samples collected from local plants.

General area EDS indicated the presence of silicon (Si), aluminum (Al), calcium (Ca), magnesium (Mg), iron (Fe) and potassium (K) along with a small amount of sodium (Na) in this sample. Semi-quantitative SEM EDS supported by XRD indicated that the raw materials comprised illite, quartz, calcite and low melting feldspathic minerals such as albite and clinocllore. The weight% composition (18% Al, 37% Si and 45% Ca) of the cracked micro-region (Fig. 4b) derived from the corresponding EDS spectrum was close to anorthite. The observed cracking may be due to the mismatch of the thermal expansion coefficient of anorthite and the neighbouring micro-regions [37].

Fig. 5a shows the microstructure of a clay brick sample showing the presence of unreacted initial ingredients which indicated that the firing temperature was probably lower than the other samples. Consequently, the strength of such type of bricks was much lower (Table 1) than the optimally fired bricks. The elemental composition of the irregular-shaped grains / agglomerates (Fig. 5a) was close to illite i.e. 46% Al, 37% Si, 8% K, 3%Mg and 4% Fe. EDS peaks due to oxygen and carbon were present on all the spectra but were not included in semi-quantitative analysis as these may come from carbon-coating / chemical etchants. The microstructure of another micro-region of the same sample, shown in Fig. 5b, comprised sharp-edged large quartz grains, a mixture of small feldspar and clay grains / particles and some rectangular calcite grains labelled as “Q”, C + F and Ca, respectively, consistent with the present XRD results (Fig. 1). Some elongated grains (Fig. 5c) with composition close to albite were also seen in the microstructure of this sample, showing incomplete sintering. Semi-quantitative SEM EDS of grains with bright contrast observed in the microstructure of another micro-region of the same sample showed calcium in high concentration which may be lime (CaO) coming from the decomposition of calcite, consistent with the present XRD results. The presence of carbonates in the initial ingredients cause an increase in porosity upon firing as a result of decomposition of, for example, calcite into CaO and CO₂, at ~ 800 °C [24]. Fig. 5d shows some voids (marked with arrows) which may be the result of poor packing density and sintering at relatively lower temperature.

In the presence of water, calcium oxide combines with hydroxyl ions forming portlandite (Ca(OH)₂). The latter finally converts to CaCO₃ in the presence of atmospheric carbon dioxide. These reactions result in an increase in volume and lead to the formation of cracks, a phenomenon often called as “lime blowing” [38], which causes further increase in porosity. Such problems cause severe implications in ceramics made of raw materials rich in carbonates, particularly, with grain size > 1 mm [6]. These problems can be controlled by increasing the firing temperature which neutralizes the expansion forces exerted by the portlandite, via forming

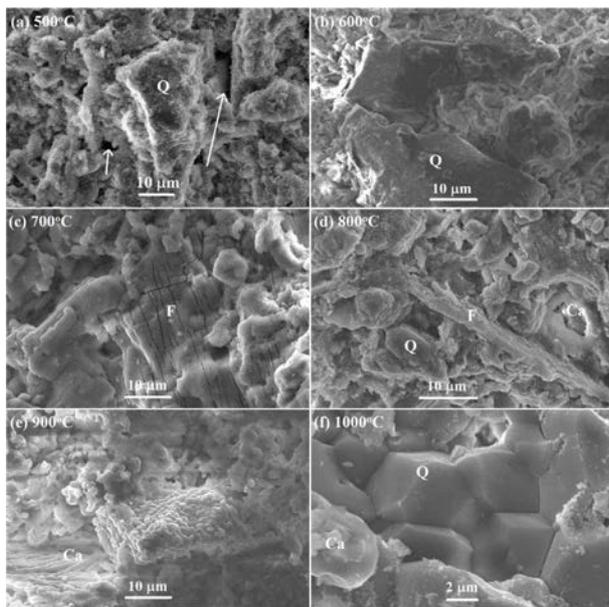


Fig. 6(a-f). SEIs from chemically etched laboratory made brick samples sintered at a) 500 °C, b) 600 °C, c) 700 °C, d) 800 °C, e) 900 °C and f) 1000 °C. The large grains in Fig. 6b were quartz grains as confirmed by SEM EDS which remained unaffected at temperatures up to 1000 °C.

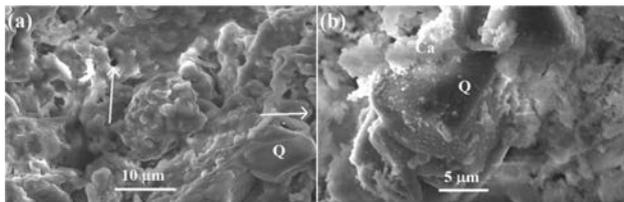


Fig. 7 (a-b). SEI from chemically etched laboratory made brick samples fired at 1000 °C for 1 h, showing some calcium-rich micro-regions and quartz grains.

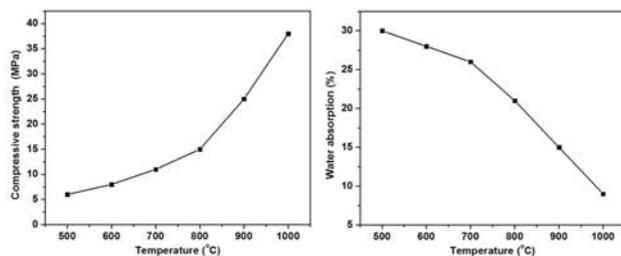


Fig. 8. a) Variation in compressive strength with temperature and b) variation in water absorption with temperature.

an outer reaction rim of high temperature phase(s) around the CaO grains, thus hindering the access of water vapour and the formation of portlandite [4].

Fig. 6(a-f) shows the microstructure of laboratory made bricks fired in the temperature range ~ 500 °C to 1000 °C. The voids observed in the microstructure of the samples fired at ~ 500 °C may be due to low packing density of unreacted initial ingredients at such a low firing temperature (Fig. 6a). The microstructure of samples fired at 600 °C, comprised of large quartz grains and mixtures of clay and feldspar grains / agglomerates (Fig. 6b). At this temperature, the brick

has not yet experienced the solid state sintering process. As the sintering temperature was increased to 700 °C and then 800 °C, the interconnectivity of the grains caused a reduction in the number as well as size of the voids but grains of the initial ingredients could be still distinguished from one another (Fig. 6c-d). At this stage, the apparent colour of the brick turned reddish, indicative of the presence of Fe.

At 900 °C, the clay mineral grains coalesced as expected at the early stage of vitrification and the microstructure appeared more continuous due to the beginning of vitrification (Fig. 6e) in comparison to the samples fired at temperatures ≤ 800 °C. The phyllosilicates deform and tend to join together at ~ 900 °C; the surface as well as edges of the grains become smoother. Additionally, during the evaporation process, deformation and cracking are observed. The values of water absorption were observed to decrease for the specimens sintered at 1000 °C/1 h, which indicated liquid phase formation and hence densification via liquid phase sintering. The liquid penetrates into the pores and voids to fill the voids. The liquid surface tension and capillarity action help in bringing the small pores closer together and hence, cause a decrease in porosity. In the final stages of vitrification, the pores join together to form new pores, which result in further decrease in porosity [39-41]. Thus, the presence of glass / liquid phase (Fig. 7a), fills the spaces among different grains, leading to further densification of the sample [42, 43]. SEM EDS demonstrated that the large grains observed in the microstructure of the present samples were quartz as only silicon could be detected in these grains (Fig. 7b) which remain unaffected at temperatures up to 1200 °C

The compressive strength of clay based products is strongly influenced by the constituent mineral phases, texture, crack pattern and porosity level. With the exception of the constituent minerals / chemical composition, all the other parameters can be controlled via processing. As there is no temperature control in the traditionally used kilns, the following three different types of bricks are normally produced in such kilns:

i) The first class bricks: These bricks have sharp edges, low water absorption and good strength. These bricks are recommended for construction purposes

ii) Under-burnt bricks: These bricks are highly porous due to low firing temperatures and termed as under-burnt bricks with relatively higher water absorption and lower strength. These bricks are relatively cheaper and are commonly used by the low income group for construction of residential buildings.

iii) Over-burnt bricks: These are the bricks fired to relatively higher firing temperatures, typically dark brownish in colour and irregular in shape due to warping. These bricks are much harder but not recommended for construction purposes.

The mean values of mechanical strength and water

absorption for locally manufactured clay bricks are given in Table 1. The compressive strength of the bricks in the present study was determined for full size bricks. The compressive strength and water absorption of laboratory made clay bricks fired at different temperatures are shown in Fig. 8. Compressive strength of a brick can be remarkably improved by firing it at an optimum temperature, depending upon the nature and grain / particle size of the initial ingredients. In the present study, compressive strength was observed to increase and water absorption decreased with an increase in firing temperature (Fig. 8). The observed sharp increase in the strength of bricks fired at 900 °C and above may be attributed to the appropriate vitrification of constituent raw materials (Fig. 8a). Compressive strength increases with firing temperature due to the consequent decrease in porosity and increase in bulk density.

Conclusions

The major conclusions based on the experimental investigations carried out in the present study can be summarised as follows:

1. All the soil samples used in the local brick industry have almost similar composition, predominantly quartz, illite and feldspar along with calcite as a minor phase.
2. Brick samples collected from local industry were found more porous, and exhibited relatively poorer mechanical properties due to improper and non-scientific method of processing and heat treatment in the local kilns.
3. The cracks observed in the microstructure of some bricks might be due to abrupt changes in temperature, thermal expansion mismatch of the neighbouring micro-regions and inappropriate processing.
4. Vitrification could be clearly detected in the microstructure of samples fired at temperatures ranging from 900 °C to 1000 °C.
5. The mechanical strength significantly improved and water absorption decreased at the peak firing temperature (1000 °C) and soaking time at the peak temperature.

Acknowledgments

The authors acknowledge the financial support (ADP No. 130314) extended by the Khyber Pakhtunkhwa Government through the Directorate of S&T, Peshawar for the up-gradation of Materials Research Laboratory, University of Peshawar.

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