Periodico di Mineralogia (2015), 84, 2, 351-371 DOI: 10.2451/2015PM0018

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY,
ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on Environment, Archaeometry and Cultural Heritage

Egyptian Smectite-rich clays for lightweight and heavy clay products

Mohamed A. Serry[1], Omar A. Hegab[2] and Ahmed G. Abd El-Wahed[2,*]

[1] Ceramic Department, National Research Center, 12622-Dokki, Cairo
[2] Department of Geology, Faculty of Science, El-Mansoura University, El-Mansoura, Egypt
[*] Corresponding author: *agomaa.eg@gmail.com*

Abstract

Suitability of three technological samples representing smectite-rich clay deposits of El-Minya, Egypt for lightweight and heavy clay products was studied. According to particle-size, mineral, and chemical composition of the clay samples, one sample was rejected due to its high content of sulphate gypsum and anhydrite minerals. Ceramic properties before firing of a sample representing the other two clays with and without addition of 40% sand grains were studied. These include rate of slaking in water and water of plasticity as well as linear drying shrinkage and drying sensitivity coefficient (DSC). The representative clay sample without addition of sand grains was assessed for lightweight bloated clay aggregate by processing its plastic pellets up to firing at 1000-1300 °C. Also, suitability of shaped plastic clay-sand bodies for heavy clay products was studied after firing up to 800-1200 °C by following their densification parameters in terms of total linear shrinkage (TLS), bulk density (BD), water absorption (WA), and crushing strength (CS). Efflorescence test was also conducted to follow up deposition of any white water-soluble sulphate salts on surfaces of the wet fired bodies after drying. The three samples of El-Minya clays contain major clay particles and lesser silt and sand particles due mainly to its high content of smectite with lesser kaolinite and illite clay minerals. In addition, variable quartz, feldspar, and hematite as well as gypsum and anhydrite non-clay minerals are detected and one of these samples was rejected due to its high content of the latter minerals. The representative sample of the other two clays is of a low-grade due mainly to its low-alumina as well as high silica and fluxing oxide contents. When 40% of sand grains was added to the clay sample, water of plasticity is decreased from ~ 51 to 25% and LDS as well as DSC were reduced from 13.3 to 8.1% and from 1.4 to 0.92, respectively. Furthermore, the shaped 60/40 clay/sand bodies were partially and fully vitrified after firing for 2 hours up to 1000 and 1200 °C, respectively. The partial and fully vitrified bodies show accepted WA, TLS, BD and CS levels, according to the Egyptian and International standards for building bricks and ceramic tiles, respectively. The fired bodies were also classified as “not-effloresced” types after testing for efflorescence. In addition, the clay sample was also processed as lightweight bloated clay aggregate with grain density of 0.7-0.8 g/cm^3 after firing up to 1300 °C. This is mainly attributed to developing of sufficient amount of a silicate liquid phase viscous enough to entrap the oxygen gas, simultaneously evolved due to partial reduction of Fe_2O_3 of the clay into FeO with the formation of magnetite (Fe_3O_4) spinel.

Key words: Ceramic; Lightweight aggregates; Clay Products; Eocene; Egypt.

Introduction

Clays are essentially applied for production of traditional clay-based ceramics and classified according to their particle-size, mineral, and chemical composition as well as ceramic properties before and after firing (Grim, 1962 and 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; El-Alfi et al. 2004; Darweesh et al. 2012 and Darweesh and El-Meligy, 2014). The ranges of particle-size composition of the clays used in production of heavy-clay products in terms of sand, silt, and clay particles were given by Winkler, (1954), applied by Jackson (1969), Dondi et al. (1992) as well as modified by Nyakairu et al. (2002). These include building bricks, roofing ceramic tiles, and masonry bricks.

Clays adequate for manufacturing building bricks and ceramic tiles have a wide range of particle size, mineral, and chemical composition. These are characterized by its balanced particle-size and mineral composition of the plastic clay minerals as well as the non-plastic quartz sand grains (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992; Nyakairu et al., 2002). Konta (1979) has reported that clays of group C with low Al_2O_3/SiO_2 ratio and high iron oxides content are satisfactory for brick-making. In addition to iron oxides, alkali, and alkaline-earth oxides (K_2O, Na_2O, CaO, and MgO) must be present as fluxing agents. These oxides control partial-densification of the building bricks and full- densification of ceramic tiles by developed silicate liquid phase up to ~ 1000 °C and 1200 °C, i.e. partial- and full- vitrification of the building bricks and ceramic tiles, respectively (Kingery et al., 1976; Clifton et al., 1984).

After reviewing composition and properties of most of the Egyptian clays, it is concluded that most of the clays exposed in the Eastern and Western Deserts are low grade smectite-rich clays (Serry, 2008). Some of these clays are currently used for manufacturing building-bricks and Portland cement after mixing with the corresponding amounts of sand and limestone, respectively. Some of these clays were also assessed in manufacturing lightweight clay aggregate due to their bloating behavior on firing up to 1300 °C (Serry et al., 1985). The lightweight clay aggregate is applied allover the world in production of lightweight building units for thermal insulation of buildings and furnaces from ambient temperature up to ~ 1100 °C (Hewlett and “Lea”, 1998; Novak, 2005).

In Egypt, there is increasing demand for production of huge amounts of the different types of building bricks, especially clay bricks, with accepted physical properties for loading and unloading walls. The clay building bricks generally show better physical properties than the other types of bricks, since it gives relatively lower bulk density and thermal conductivity as well as higher water absorption with accepted mechanical properties (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Mandour et al., 1989; Serry et al., 2007).

The aim of the present work is to study suitability of three technological clay samples, representing deposits of El-Minya clays, exposed in three sections, for production of heavy and lightweight clay products. These sections were previously investigated for their geological settings, mineralogy and geochemistry (Abd El-Wahed, 2013). The technological clay samples were investigated for their particle-size, mineral, and chemical compositions. Furthermore, one technological sample representing El-Minya clays was prepared to assess its ceramic properties before and after firing. Ceramic properties before firing were studied by determining rate of slaking in water, water of plasticity as well as linear drying shrinkage and drying sensitivity coefficient. To assess its suitability for manufacturing building bricks and ceramic tiles, the clay sample was mixed with 40% sand and water of plasticity. The plastic masses were shaped, dried and fired up to 1000-1200 ºC. Densification parameters of the fired bodies were determined by means of total linear shrinkage, bulk density, water absorption, and crushing strength. In addition, efflorescence test was conducted to follow up deposition of any white sulphate salts on the surfaces of wet fired bodies after drying. Meanwhile, the clays were utilized for processing lightweight bloated clay aggregate by firing its pellets up to 1000-1300 ºC.

Materials and Methods

Materials

The materials used in this work are mainly three technological clay samples as collected from three sedimentary sections at Gebel Qarara (GQ), El-Sheikh Fadl (SF), and Gebel El-Ahmar (GA), located East River Nile, El-Minya Governorate, Upper Egypt as exhibited in Figure 1. The three technological samples were prepared from the exposed clay beds of the three sections by mixing clay lumps, representing the clay beds of each section with amounts corresponding to its thickness. Most of the technological lump samples were crushed and ground into fine powder (- 0.1mm) for investigation of their composition and properties. Some of these lumps were left to determine particle-size distribution and rate of slaking in water.

Methods

Particle-size, mineral, and chemical compositions. Clay deposits are usually composed of particles with different sizes, including: gravel (> 2 mm), sand (2.0-0.063 mm) and silt (0.063-0.002 mm) as well as ultra-fine clay (< 0.002 mm) particles. Therefore, the particle-size distribution of clays is usually determined by a combination of wet-sieving and pipette-sedimentation methods (Grim, 1980; Folk, 1968).

The gravel and sand grains of 10g clay sample were first wet-separated on 2.0 and 0.063 mm sieves, respectively and their weight percentages were calculated relative to the original sample weight (20 g). The slurry passed through the 0.063 mm sieve, which contains the silt and clay particles was then treated several times by hydrogen peroxide (H_2O_2) solution (35%) to oxidize and eliminate organic materials. Carbonate and sulphate minerals were thereafter eliminated by mechanical stirring in hot 10% HCl solution and the residue was washed by hot water till free from chlorides.

The washed clay-silt water suspension, containing ~ 0.5% suitable deflocculating or dispersing agent, e.g. Na-hexameta-phosphate, was transferred into 1L measuring cylinder to carry out the pipette-sedimentation analysis. This method is based on Stokes law, modified by Wadell (1934), which indicates that the settling velocity of particles is related to diameter square of its perfect spheres, when subjected only to the influence of gravity according to the following

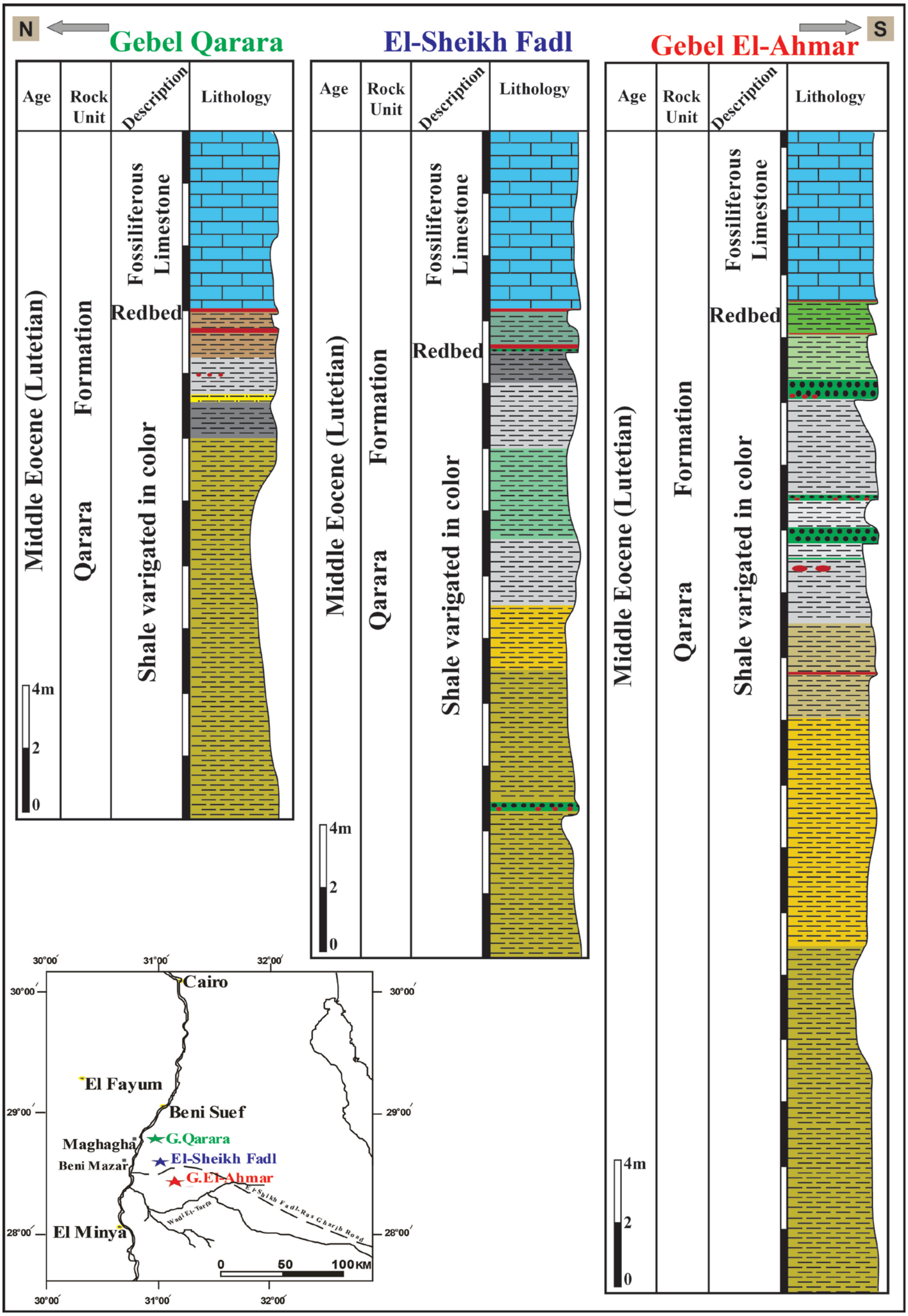

Figure 1. The three sedimentary sections including clay beds at Gebel Qarara (GQ), El-Sheikh Fadl (SF) and Gebel El-Ahmar (GA), located East River Nile at El-Minya Governorate, Upper Egypt.

equation:

$$u = \frac{2}{9} \frac{\rho_p - \rho_f}{\mu} g R^2$$

where u is the flow settling velocity (m/s), g is the gravitational acceleration (m/s^2), ρ_p is the mass density of the particles (kg/m^3), ρ_f is the mass density of the fluid (kg/m^3) and μ is the dynamic viscosity (kg/m*s).

According to Folk (1968), 20 ml of the deflocculated suspension, containing total silt (0.063-0.002 mm) and clay (< 0.002 mm) particles was immediately pipetted at a constant depth (10 cm) from the suspension surface of the 1 liter measuring cylinder. The pipetted fractions are placed in petri dishes and allowed to dry gently at 60 °C till constant weight. The percentage frequencies of silt and clay fractions of the investigated clays then calculated on the basis of the weight of the original sample (20 g).

Mineral composition of fine powders of the bulk clay samples as well as their oriented clay fractions was semi-quantitatively determined by X-ray diffraction (XRD) method, using A Philips (PW 1840) vertical diffractometer. Separation of clay fraction and preparation of samples for identification using XRD are normal routine work. Oriented, flat-layer specimens were prepared for X-ray study of clay minerals allowing few drops of clay suspension to dry out slowly on glass slides (Muller, 1967). Three oriented mounts were prepared for each sample. Air-dried preparates were analyzed from all samples, and when needed, pretreatments were utilized to distinguish overlapping XRD peaks (Hardy and Tucker, 1988). These typically include: a) heating to 550 °C, for kaolinite destruction and dehydration of smectite which potentially hide chlorite XRD peaks, b) treatment by ethylene glycol (EG) in order to reveal expandable clay minerals (Lattice expansion).

Furthermore, the major chemical constituents of the fine bulk clay samples, i.e. its chemical composition were quantitatively estimated by the recent XRF method, which is based on striking the surface of the sample with a high-energy electron beam. This leads to generate x-rays with characteristic wave lengths for each constituent. Hence, concentration of all chemical constituents could be quantitatively determined and computed by using corresponding x-ray detectors and standard samples. This was conducted by using an AXIOS, WD-XRF-SEQUENTIAL Spectrometer (PANalytical, 2005) in Acme Analytical Laboratories Ltd., Vancouver, Canada.

Ceramic properties before firing. Ceramic properties before firing of two samples of El-Minya clays, selected on the basis of their composition, with and without addition of 40% sand grains were studied. These include rate of slaking in water and water of plasticity as well as linear drying shrinkage and drying sensitivity coefficient (DSC). The rate of slaking is investigated by determining the time elapsed for complete disintegration and dispersion of the clay lumps under water (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; El-Alfi et al., 2004; Darweesh et al., 2012; Darweesh and El-Meligy, 2014).

Plasticity or workability of the clay powders and their batches was determined using Pfefferkorn test (Andrade et al., 2011). To determine linear drying shrinkage (LDS) and drying sensitivity coefficient (DSC), the clay powders and their batches were plasticized with the predetermined water of plasticity. The plastic masses were subsequently hand formed into cylindrical rods with ~ 100 mm length and 25 mm diameter and left to dry in air for few days and then in a drier at 60 °C till constant linear shrinkage and weight. During drying, LDS was measured and plotted as a function of loss in weight (Bigot's curve) (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Darweesh et al., 2012; Darweesh and

El-Meligy, 2014). The linear drying shrinkage was derived from Bigot curves and drying sensitivity coefficient (DSC) was calculated according to the following equation: DSC = [(Water content of the plastic sample) - (Water content at constant shrinkage)] / (Water content at constant shrinkage)

Ceramic properties after firing. Ceramic properties of the clay samples with or without sand additions were assessed after hand shaping of plastic masses into cylindrical samples with ~ 25 mm diameter as well as drying up to 60 °C and firing up to 1000-1200 °C. Densification parameters of the fired bodies were assessed by means of total linear shrinkage, bulk density, water absorption, and crushing strength. The test methods were carried out according to ESS No. 48-619/ 2003 as well as ISO-10545. Furthermore, efflorescence-test was conducted according to ASTM C-67 after 7-days partial immersion of the fired bodies in distilled. The test samples are classified as “effloresced” or “not effloresced” if there is evidence or not for appearance of any white powdery sulphate salts on their surfaces after drying, respectively (Sandrolini and Palmonari, 1976; Larson and Nielson, 1990; Brocken and Nijland, 2004).

Results and Discussion

Particle-size, mineral, and chemical composition

Table 1 summarizes results of particle size distribution of El-Minya technological clay samples of Gebel Qarara (GQ), El-Sheikh Fadl (SF), and Gebel El-Ahmar (GA). From Table 1, it is evident that minor amounts of sand grains (1-3%) as well as higher contents of total silt (22-34%) and major clay particles (65-77%) are estimated. Also, most of the silt fraction occurs as very fine particles (21-30% with 24% average) and only 4% average of coarse and medium particles, which increased to 6%, when it is added to the minor sand grains. In addition, the ratio of clay/total sand and silt particles is gradually increased in the order GQ (65/35) < GA (69/31) < SF (77/23) due mainly to the parallel increase of the clay particles content at the expense of total silt particles in this direction as seen in Table 1.

The clay and non-clay mineral composition is qualitatively revealed from the XRD patterns of the bulk powder samples as exhibited in Figure 2. It is evident that the clay minerals of all samples mainly comprise smectite as well as kaolinite, with minor illite. The non-clay minerals comprise major quartz with lesser amounts of feldspars. In addition to these silicate minerals, appreciable amounts of sulphate (anhydrite and gypsum) as well as hematite minerals occur in GQ sample. The presence of the latter non-clay minerals in GQ sample interprets its minimum clay/ (silt + sand) ratio (65/35), when compared with the higher ratios of GA and SF samples (69/31 and 77/23, respectively) as detected in Table 1.

The main clay minerals of the clay samples; namely smectite, illite, and kaolinite, existing within the oriented clay particles (< 0.002 µm) are calculated in Table 2 and Figure 3. It is illustrated that all samples show major smectite (54-60%), lesser kaolinite, (44-39%) and minor illite (1-3%) contents. Also, smectite is gradually increased from 54-55% in GQ and GA to 60% in SF at the cost of kaolinite, which decreases in this direction from 42-44 to 39%.

Table 3 summarizes chemical composition of El-Minya clay samples, as determined by XRF powder method. These data confirm the presence of high content of the sulphate gypsum and anhydrite minerals as well as hematite in GQ sample, beside the other silicate quartz and feldspar non-clay minerals at the expense of the smectite and kaolinite clay minerals. As a result, the latter sample shows higher contents of CaO, SO_3 and Fe_2O_3 impurities in comparison with the corresponding ranges of GA and SF samples. Meanwhile, the latter samples show higher contents of Al_2O_3 and SiO_2 as well as

Table 1. Particle-size composition of El-Minya technological clay samples of Gebel Qarara (GQ), El-Sheikh Fadl (SF) and Gebel El-Ahmar (GA).

Size fraction in mm (%)	GQ	SF	GA	Average
Total sand (2.0-0.063)	1	1	3	2
Total silt (0.063-0.002)	34	22	28	28
Coarse and medium silt (0.063-0.020)	4	1	6	4
Total sand and coarse & medium silt (2.0-0.020)	5	2	9	6
Fine silt (0.020-0.002)	30	21	22	24
Clay (< 0.002 mm)	65	77	69	70

MgO and Na_2O as compared with GQ sample. The minor potash and soda feldspars, detected in all samples (Figure 2), also contribute in the presence of limited amounts of alkali-oxides. In addition, other minor impurities; namely, TiO_2, P_2O_5 and extra-volatile Cl are also detected in all samples.

The presence of sulphate minerals in GQ sample usually leads to troubles during firing and application of their ceramic products. During firing, gypsum ($CaSO_4 \cdot 2H_2O$) is first dehydrated up to about 180 °C to anhydrite ($CaSO_4$), which persists together with the original anhydrite on further firing up to 1200 °C, before its dissociation into free lime (CaO) and SO_3 gas (Mackenzie, 1970). Cyclic wetting of the fired products leads to hydration of the sulphate salts and efflorescence-crystallization cycles, which can damage its structure (Sandrolini and Palmonari, 1976; Larson and Nielson, 1990; Brocken and Nijland, 2004).

Accordingly, GQ sample is rejected due mainly to its high content of the undesirable sulphate minerals, while, GA and SF samples were selected to represent El-Minya clays. According to the close ranges of particle-size, clay-minerals and chemical compositions of the latter samples, one sample was prepared by mixing equal weights from each. Suitability of this sample for processing heavy- and lightweight- clay products was assessed by investigation of its ceramic properties before and after firing.

For processing heavy-clay products; namely building bricks and ceramic tiles, up to 40% of the non-plastic sand grains should be added to the clay sample, while it is applied without any additions for processing lightweight products as exhibited in Figures 3 and 4, respectively. Figure 4 shows particle-size composition of the clay sample without and with 10-40% sand additions as plotted on the ternary clay- fine silt- sand and coarse and medium silt system, given by Winkler, (1954), and modified by Nyakairu et al., (2002). It is clear that 40% sand should be added to bring the clay sample within the areas defined for building bricks and ceramic roofing tiles. Meanwhile, Figure 5 also confirms suitability of El-Minya clays and its representative sample for processing lightweight clay aggregate. When chemical composition of these clays, as SiO_2, Al_2O_3 and fluxing oxides, are plotted on Riley's diagram (Riley, 1951), all points are existed within the area defined for bloated clays.

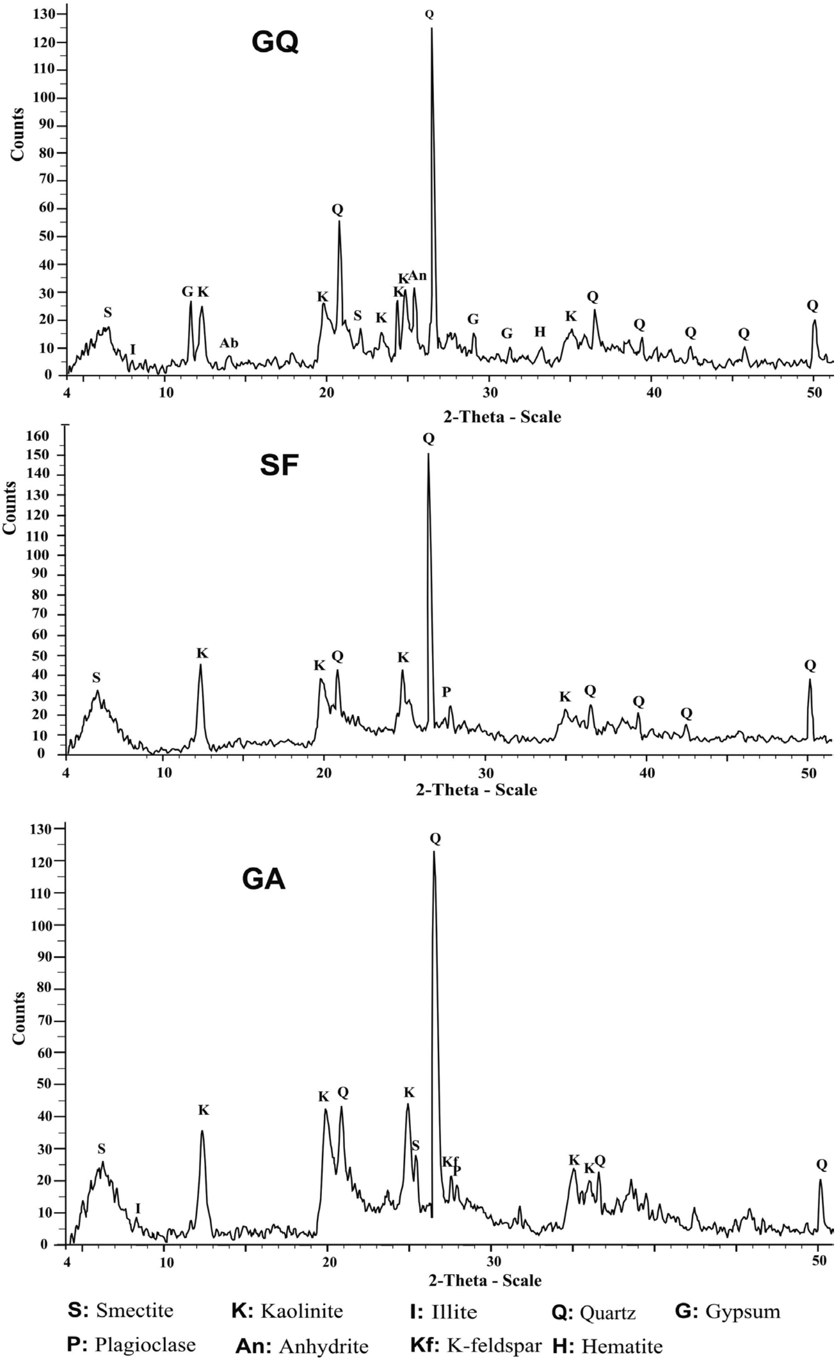

Figure 2. XRD patterns of El-Minya GQ, SF and GA clay powder samples (Cu Kα- Radiation).

Table 2. Distribution of clay-mineral composition of GQ, SF and GA El-Minya clay samples.

Clay mineral	GQ	SF	GA	Average
Smectite	55	60	54	56
Illite	3	1	2	2
Kaolinite	42	39	44	42

Ceramic properties before firing

Ceramic properties of the representative sample of El-Minya (GA-SF) clays before firing, with and without addition of 40% sand grains, were investigated by means of rate of slaking of in water and water of plasticity as well as linear drying shrinkage (LDS) and drying sensitivity coefficient (DSC).

The rate of slaking of the clay lumps in water is very fast and completely slaked into fine particles within 45 minutes as an average time. The plasticity curves of the representative clay sample and its batch with 40% sand according to Pfefferkorn are shown in Figure 6. While their linear drying shrinkage as a function of water content (Bigot's curves) are exhibited in Figure 7. It is clear that high content of water is required to render the fine clay powders plastic (~ 51%), i.e. high water of plasticity. Accordingly, when the shaped clay/water plastic masses are dried up to 60ºC, slow rate of drying with much high LDS 1(3.30%) as well as DSC (1.40), or > 1.0, i.e. sensitive on dying (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; El-Alfi et al., 2004; Darweesh et al., 2012; Darweesh and El-Meligy, 2014).

When 40% of the non-plastic sand grains were added to the clay sample, water of plasticity is decreased from ~ 51 to 25.0% and LDS as well as DSC are reduced from 13.3 to 8.1% and from 1.4 to 0.92, respectively. Hence, El-Minya clay sample becomes of moderate plasticity (25%) and un-sensitive for drying up to 60 ºC, i.e. < 1.0 (DSC: 0.92) with minimum LDS (8.1%), after mixing with 40% of the non-plastic sand grains, respectively. The higher content of clay particles is known to give higher surface area and consequently higher amount of water required for the clay batch to be plastic. Meanwhile, increasing the content of sand grains up to 40% reduces water of plasticity and provides a skeletal open microstructure, leading to improve thereby the rate of diffusion of water vapour on drying from the sample interior to its surfaces (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992).

Accordingly, El-Minya clays can be recommended for processing heavy-clay building bricks and ceramic tiles, after mixing with 40% of sand grains, shaping their plastic masses and firing up to 800-1200 ºC. Also, it can be directly utilized in production of lightweight clay aggregate after firing up to 1300 ºC.

Ceramic properties after firing

Densification parameters of the fired clay-sand bodies. In order to confirm suitability of El-Mina clay sample for manufacturing heavy-clay products, densification parameters of its bodies with and without addition of 40% sand were investigated as a function of firing temperature between 800 and 1200 ºC as shown in Table 4 and

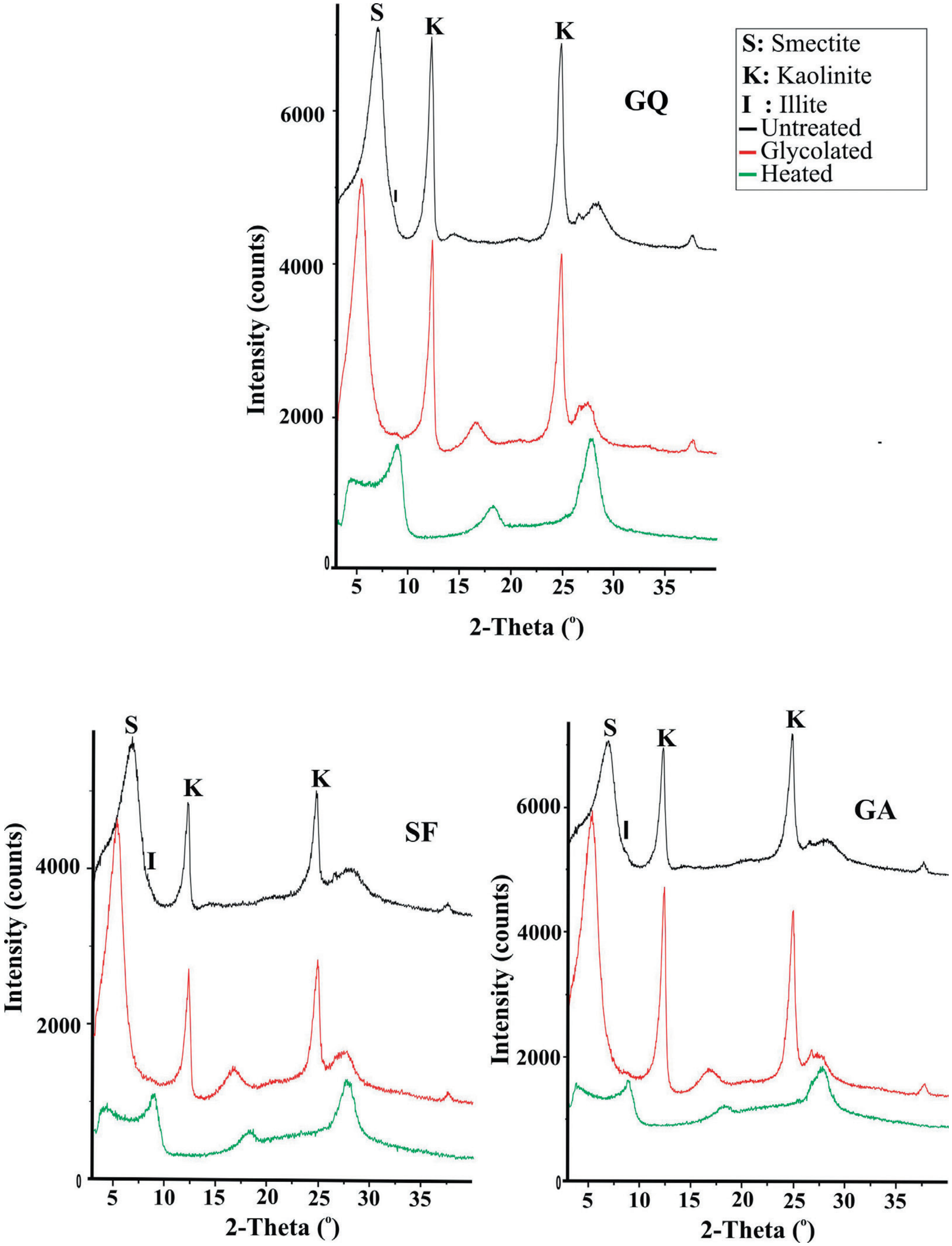

Figure 3. XRD tracing of El-Minya GQ, SF and GA clay fractions.

Table 3. Chemical composition of GQ, SF and GA El-Minya clay samples.

wt%	GQ	SF	GA
SiO_2	41.45	47.48	49.17
Al_2O_3	17.28	20.37	21.82
Fe_2O_3	14.11	8.26	6.69
TiO_2	1.13	1.27	1.34
MgO	1.96	2.90	2.47
CaO	2.52	0.94	0.62
Na_2O	0.72	1.09	0.98
K_2O	1.29	1.02	1.02
P_2O_5	0.82	0.16	0.12
SO_3	4.20	0.99	0.77
LOI	14 .49	15.51	14.98
Total	100.00	100.00	100.00
TFO	25.65	15.37	12.68
Cl	0.67	1.82	1.71

TFO = Total Fluxing Oxides; LOI = Loss On Ignition.

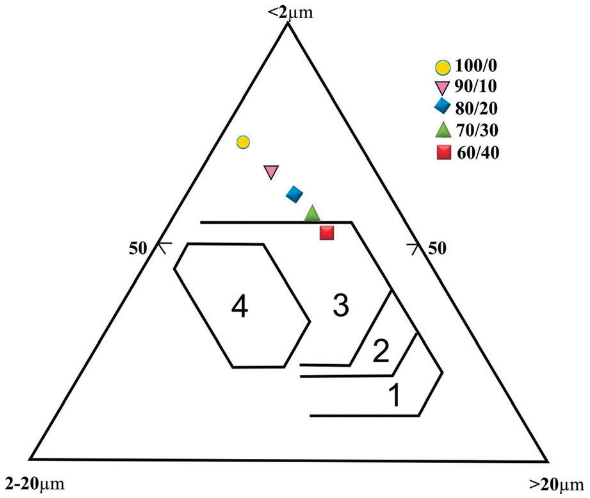

Figure 4. Particle-size composition of El-Minya clay sample without and with sand additions (0-40%) on the ternary clay - fine silt - sand and coarse and medium silt system, given by Winkler (1954) , and modified by Nyakairu et al. (2002) showing four areas for common (1) and perforated (2) building bricks and roofing tiles (3) and hollow products (4).

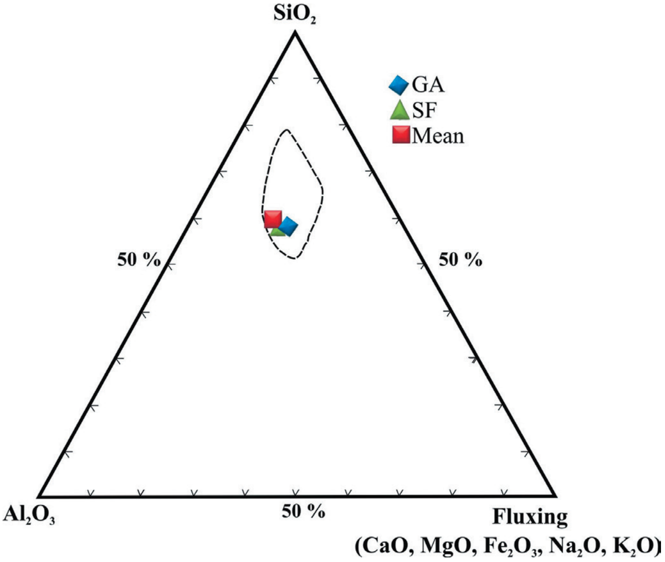

Figure 5. Chemical composition of El-Minya (GA & SF) clays and its representative sample as plotted on Riley's diagram (1951) by means of silica (SiO_2), alumina (Al_2O_3) and total fluxing oxides (TFO) on calcined basis, existing within the area of bloated clays.

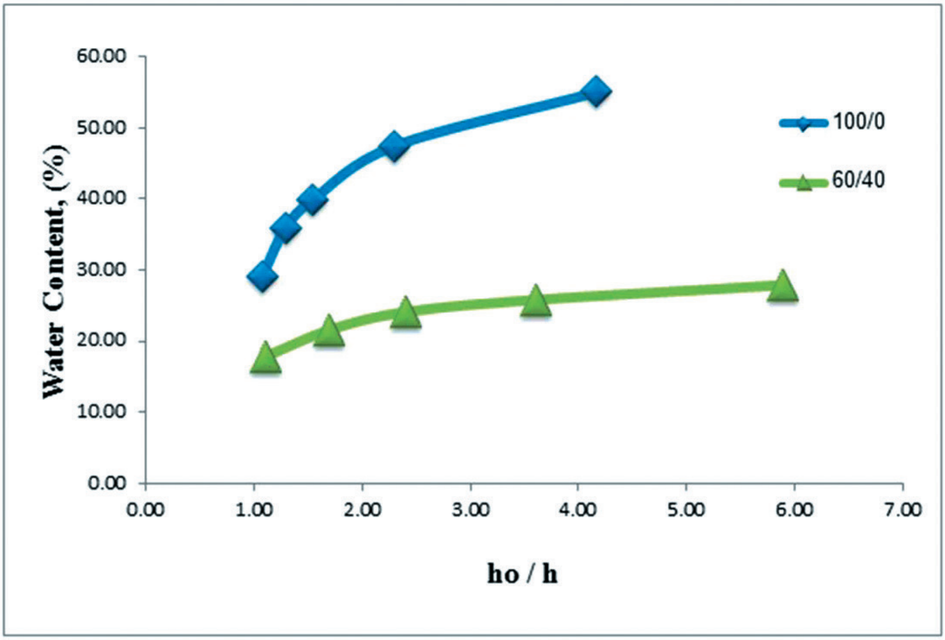

Figure 6. Plasticity curves of El-Minya representative clay sample and its batch with 40% sand grains, according to Pfefferkorn.

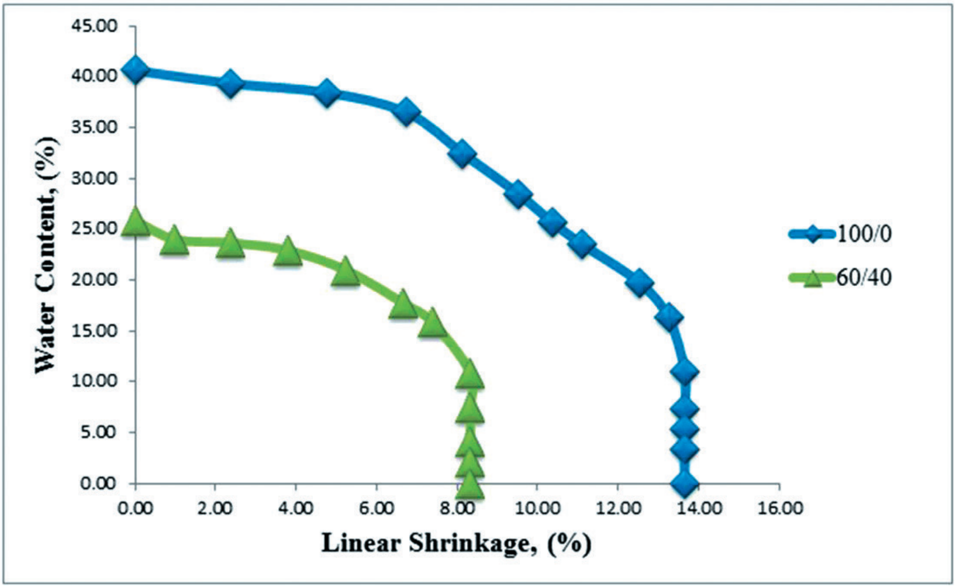

Figure 7. Bigot curves of El-Minya representative clay sample and its batch with 40% sand grains.

Figures 8 a,b as well as 9 a,b. These parameters comprise total linear shrinkage (TLS), i.e. total linear shrinkage (drying plus firing shrinkage) as well as bulk density (BD), water absorption (WA) and crushing strength (CS).

It is illustrated that firing up to 1000 ^oC generally leads to partial densification of all bodies by liquid phase, i.e. vitrification as indicated from increasing TLS, BD and CS with parallel lowering of WA at different magnitudes. Bodies without sand addition show relatively higher rate of vitrification as indicated from their much higher TLS (16.9%), BD (2.26g/cm^3) and CS (70 kg/cm^2) with lower WA (9.1%) as compared with those containing 40% sand. The latter bodies show relatively higher WA (14.2%) with lower TLS (11.2%), BD (1.89 g/cm^3) and CS (53 kg/cm^2). On rising firing temperature up to 1100 ^oC, more liquid is formed, leading to higher rate of vitrification in both bodies as indicated from lowering WA with rising TLS, BD and CS. But, the sand free bodies show partial deformation and sticking with minimum WA (4.8%) and maximum TLS (18.2%), BD (2.8 g/cm^3) and CS (83 kg/cm^2). Hence, these bodies were excluded from further firing up to 1200 ^oC. On the other side, vitrification is continued on firing bodies with 40% sand up to 1200 ^oC and show minimum WA (3.9%) with maximum TLS (12.7%), BD (2.44 g/cm^3) and CS (65 kg/cm^2) (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Kingery et al., 1976; Clifton et al., 1984; Darweesh et al., 2012; Darweesh and El-Meligy, 2014).

The onset of silica-rich liquid phase formation seems to be occurred in the fired bodies without and with sand addition as low as 800 ^oC with relatively higher amount in the former bodies than in the latter ones. This is mainly due to action of the high average amount of fluxing oxides on calcined basis (FO = 16.8%), as calculated in Table 3. In addition, FO has high average of total alkali oxides (~ 2.6%) with 1.2% Na_2O and 1.4% K_2O (Table 3), the most severe fluxing oxides on the major SiO_2 and Al_2O_3 clay components (Grim, 1962; 1980;

Table 4. Physical Properties of the fired briquettes of El-Minya clay and its batch with 40% sand grains as a function of firing temperature between 800 and 1100 °C.

Physical properties	El-Minya clay sample at (^{o}C)					Clay/sand batch (60/40) at (^{o}C)				
	800	900	1000	1100	1200	800	900	1000	1100	1200
Total linear shrinkage (%)	14.7	16.2	16.9	18.2	--	8.1	10.6	11.2	12.6	12.7
Bulk density (g/cm^3)	1.94	2.15	2.26	2.80	--	1.74	1.80	1.89	2.24	2.44
Water absorption (%)	17.6	11.3	9.1	4.8	--	20.1	17.2	14.2	9.9	3.9
Crushing strength (kg/cm^2)	66	74	76	83	--	28	39	53	59	65

Grimshaw, 1971; Norton, 1969; Konta, 1979; Kingery et al., 1976; Clifton et al., 1984). On rising firing temperature up to 1100 and 1200 ^{o}C, the liquid phase is gradually developed, diffused and closed open pore-structure, leading to full vitrification of the fired bodies without and with sand addition, respectively. On cooling, the liquid phase solidifies as a glassy bond, with decreasing WA of the former and latter bodies to minimum and increasing TLS, BD and CS up to maximum after firing at 1100 and 1200 ^{o}C, respectively. Addition of 40% sand to the raw clay is known to provide bodies with more open pore volume and lesser amount of liquid phase during firing up to 1200 ^{o}C. Hence, vitrification of these bodies could be continued up to 1200 ^{o}C as compared with that of the sand-free briquettes (1100 ^{o}C) (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992; Nyakairu et al., 2002; Kingery et al., 1976; Clifton et al., 1984).

Both of the partially-vitrified and fully-vitrified samples, fired at 1000 ^{o}C and 1200 ^{o}C, respectively are found of the not-effloresced types after testing for efflorescence, according to (ASTM C-67). No evidence of deposition of powdery sulphate salts is seen on the surfaces of the wet fired samples after partial submerging for 7 days in distilled water and drying overnight at 110 ^{o}C. This is mainly attributed to the low soluble sulphate salts contained in El-Minya SF and GA clay samples (Table 3).

It is concluded that El-Minya clays without addition of sand grains are not suitable for processing both building bricks and ceramic tiles due mainly to the excessive amount of liquid phase developed up to 1000-1200 ^{o}C. However, the 60/40 clay/sand batch can be utilized in processing building bricks due to its partial vitrification and not effloresced nature, after firing up to 1000 ^{o}C. The solid brick samples prepared in this work by hand-shaping of the plastic masses of this batch, on a lab sale, show accepted water absorption, bulk density and crushing strength, according to the [ESS: 1524, 1993] and [ISO: 10545] standards. However, industrial application of the mechanical de-airing extrusion technique for shaping and tunnel kilns for firing will be beneficial for producing varieties of perforated bricks with lower bulk density and higher crushing strength

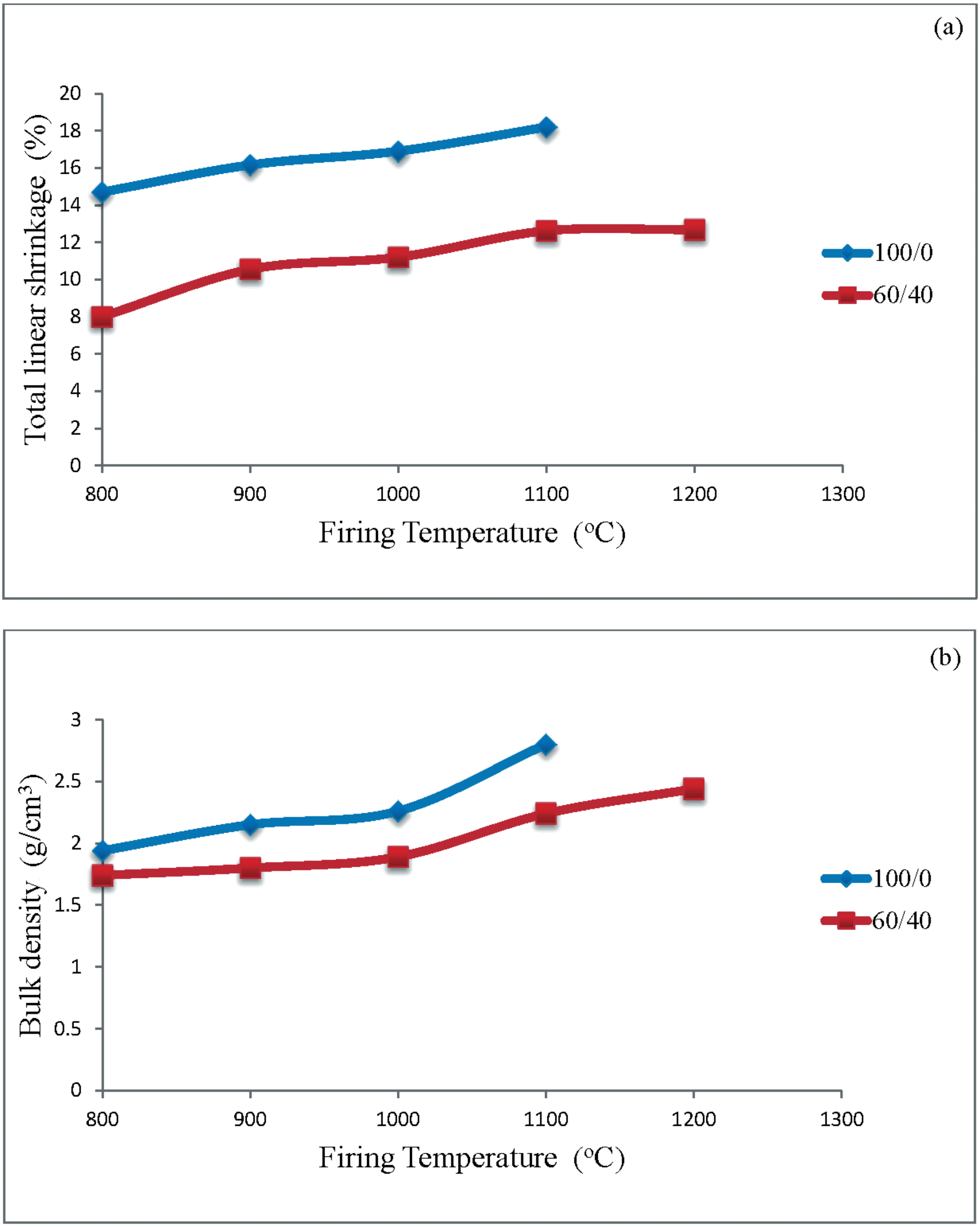

Figure 8. Total Linear shrinkage (a) and bulk density (b) of the fired briquettes of El-Minya clay and its batch with 40% sand grains as a function of firing temperature between 800 and 1100-1200 °C.

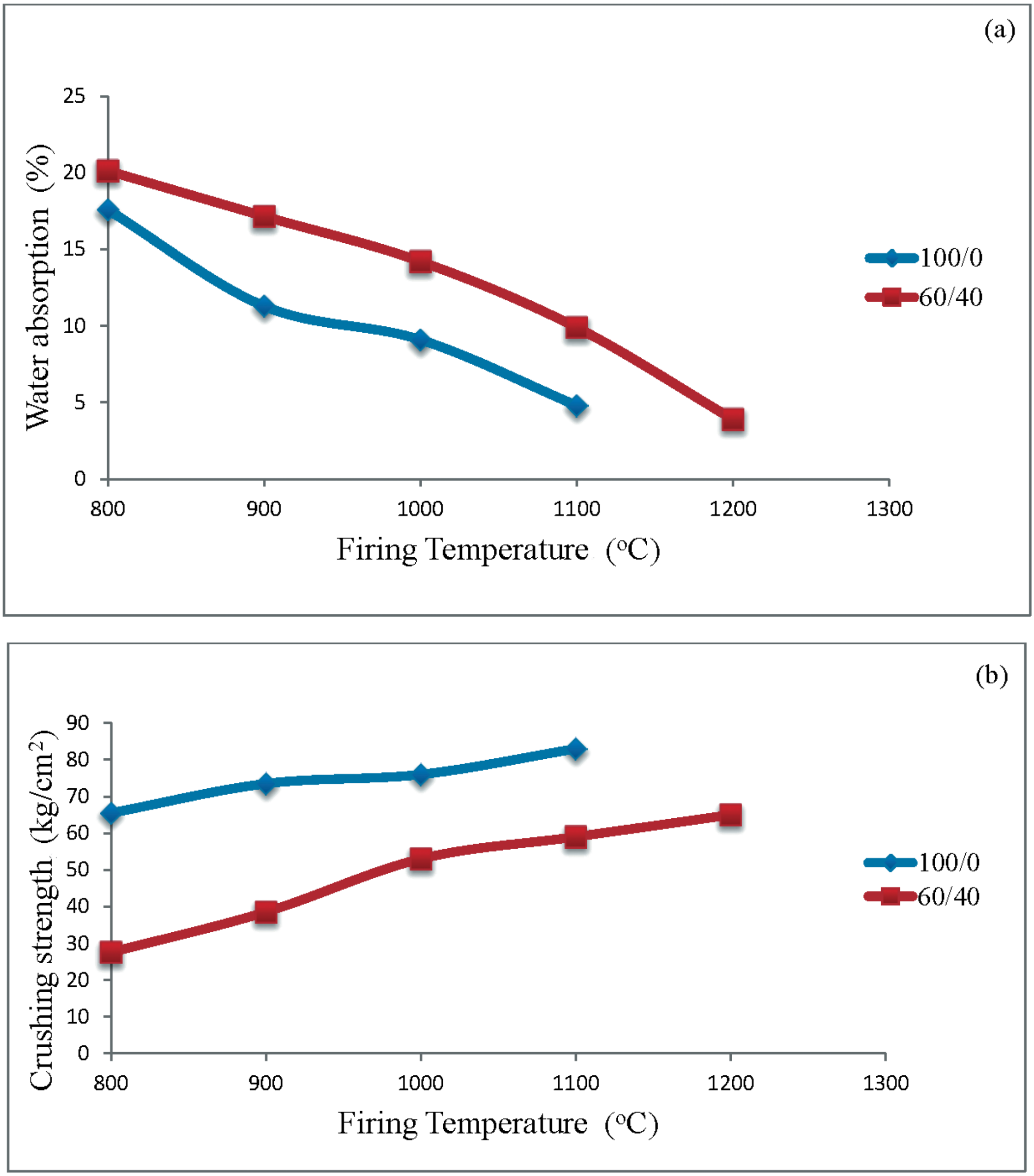

Figure 9. Water absorption (a) and crushing strength (b) of the fired briquettes of El-Minya clay and its batch with 40% sand grains as a function of firing temperature between 800 and 1100-1200 °C.

(Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992; Farag and Serry, 2000). Meanwhile, the same batch can be utilized in processing not effloresced fully vitrified ceramic tiles, after firing up to 1200 °C, with accepted water absorption, bulk density and crushing strength, according to [ESS: 3168-4, 2000] and [ISO: 10545] standards. The properties of these tiles can be significantly improved after shaping by semi-dry uniaxial pressing and fast-firing in tunnel kilns up to 1200 °C, (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992; Farag and Serry, 2000; Darweesh et al., 2012).

Figure 10 exhibits XRD patterns of the prepared partially vitrified solid building-brick (a) and fully vitrified ceramic tile (b) samples. It is shown that the building brick sample shows low-quartz as a main residual phase with minor transformed low-cristobalite and residual feldspar phases. On the other side, relatively lesser amount of low-quartz is detected in the ceramic tile sample, with appreciable amounts of low-cristobalite and transitional mullite phases. This confirms partial dissolution of the main quartz phase in the silicate liquid phase developed during full-vitrification up to 1200 °C with formation of some cristobalite and transitional mullite phases, (Kingery et al., 1976; Clifton et al., 1984).

Bloating of El-Minya clay sample. The chemical composition of El-Minya GA and SF clays and its representative sample was recalculated on calcined basis; namely, silica, alumina and fluxing oxides (FO), as previously seen in Table 3. These chemical compositions are existed within the area of bloated clays, outlined by Riley (1951) as exhibited in Figure 5. Hence, pellets of these clays are utilized for processing lightweight bloated clay aggregate after gradual firing up to 1000-1300 °C. Influence of firing temperature on degree of bloating, i.e. lowering bulk density (BD) of the fired clay pellets is plotted in Figure 11.

Figure 11 shows gradual lowering of BD from 1.87 to 1.45 g/cm^3 after firing between 1000 and 1150 °C, respectively. On increasing firing temperature to 1200 °C, abrupt decrease occurs in BD to 0.97 g/cm^3, followed by steady decrease to 0.85-0.79 g/cm^3 on further firing up to 1250-1300°C. This indicates that bloating takes place after gradual firing up to 1300 °C with three rates; a slow rate at 1000-1150 °C, highest rate at 1150-1200 °C and lowest rate between 1200 and 1300 °C. These results indicate that gradual reduction of the red ferric oxide (hematite) of the clay into its ferrous form (wuestite: FeO) starts from 1000 °C and continues up to 1300 °C. This is accompanied with a solid-state reaction of FeO with the residual hematite (Fe_2O_3) to form magnetite-spinel mineral ($FeO.Fe_2O_3$) and evolution of oxygen gas (O_2). This reaction is usually occurs on firing the bloated clays up to 1300 °C, with simultaneous formation and development of viscous silicate phase capable to entrap the evolved oxygen gas (Clifton et al., 1984; Riley, 1951; Sandrolini and Palmonari, 1976).

It seems that no sufficient viscous silicate liquid phase is formed at 1000-1150 °C to entrap the evolved oxygen gas, while the amount of liquid phase is developed at 1150-1200 °C with simultaneous increase of oxygen evolution. On rising firing temperature up to 1300 °C, the rate of evolution of oxygen may be inhibited. This led to minimize rate of bloating in spite of the higher amount of liquid phase expected at this firing temperature (Clifton et al., 1984; Riley, 1951; Sandrolini and Palmonari, 1976). Accordingly, lightweight bloated clay aggregate with minimum bulk density (0.7-0.8 g/cm^3) could be obtained due to continuation of bloating up to 1300 °C as seen in Figure 11.

Figure 12 exhibits XRD pattern of the bloated clay pellets fired up to 1300 °C. It is revealed that these pellets are mainly composed of residual quartz (SiO_2), cristobalite (SiO_2), mullite ($3Al_2O_3.2SiO_2$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and glassy silicate phase. The presence of the latter phase is indicated from the background hump occurs between 10

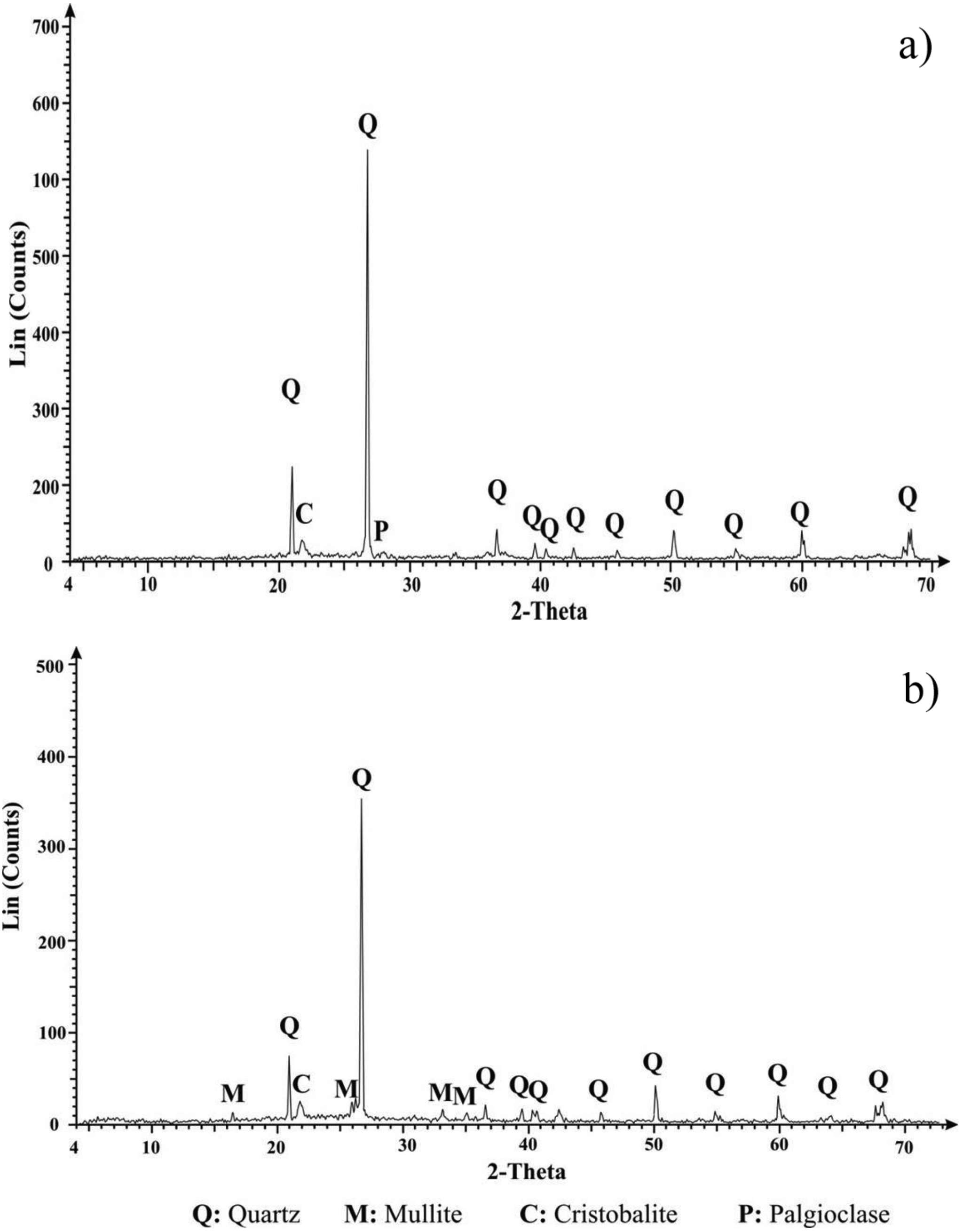

Figure 10. XRD patterns of the partially vitrified building-brick (a) and the fully-vitrified ceramic tile (b) samples, after firing up to 1000 and 1200 °C, respectively.

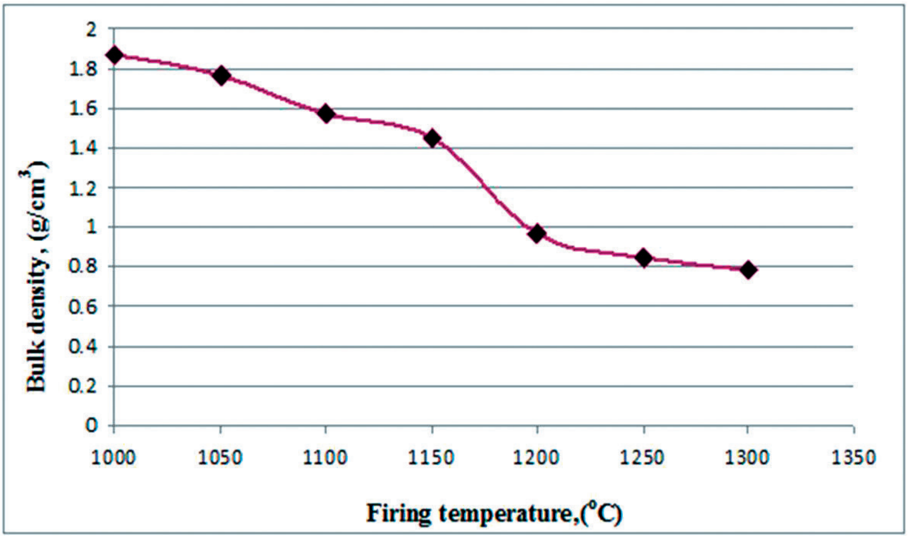

Figure 11. Rate of bloating or decreasing bulk density of El-Minya clay pellets after gradual firing between 1000 and 1300 °C.

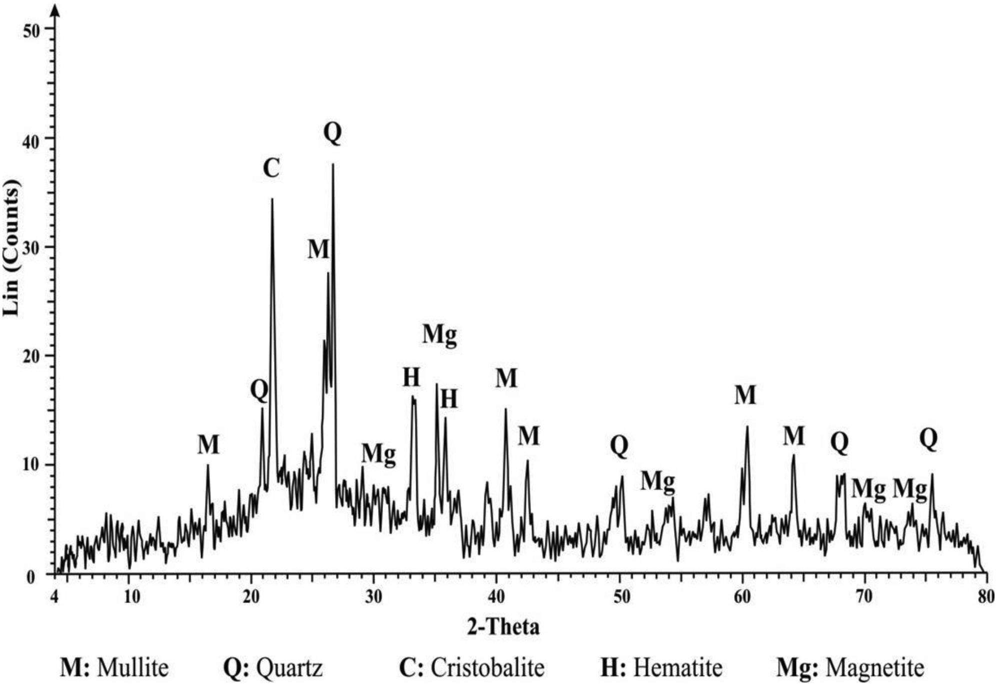

Figure 12. XRD pattern of the bloated clay pellets fired up to 1300 °C.

and 40 2θ°. Mullite is formed due to reaction between the reactive Al_2O_3 and SiO_2, liberated due to dissociation of the clay minerals on firing up to 1300 °C. Meanwhile, cristobalite is crystallized from some of the liberated SiO_2 and by polymorphic transformation of some quartz and the rest of quartz exists free. The glassy silicate phase is developed due to thee action of the fluxing oxides on the other crystalline silicate phases during firing up to 1300 °C. This led to form viscous silicate liquid phase, which is solidified as amorphous glassy phase on cooling (Grim, 1962; 1980; Grimshaw, 1971; Norton, 1969; Konta, 1979; Winkler, 1954; Jackson, 1969; Dondi et al., 1992; Nyakairu et al., 2002; Kinery et al., 1976; Clifton et al., 1984).

Conclusions

The three technological samples of El-Minya clays are smectite-rich with variable quartz, feldspar, hematite, gypsum and anhydrite non-clay minerals and one of the samples was rejected due to its high content of the latter minerals. 40% of sand grains should be added to a representative sample of the other two clays to process building brick and ceramic tile samples with minimum water of plasticity, linear drying shrinkage and drying sensitivity coefficient. The shaped clay/sand batch is recommended for manufacturing not-effloresced building bricks and ceramic tiles with accepted physical properties after firing up to 1000 and 1200 °C, respectively. The representative clay sample is also recommended for processing lightweight clay aggregate due to its bloating after firing up to 1300 °C.

Acknowledgments

I wish to express my deep thanks and gratitude to Dr. Tarek Anan, Mr. Mahmoud Lotfy, and Mr. Mohamed Youssef for their assistance in the field work. Also, I would like to express my appreciation and gratitude to Prof. Antonio Gianfagna, Dipartimento di Scienze della Terra, Università degli Studi di Roma and the anonymous reviewers for their distinct comments and kind cooperation that made this paper qualified to be published.

References

Abd El-Wahed A.G.M. (2013) - Sedimentology and assessment of the middle Eocene El-Minya clay deposits for ceramic industries on the light of their chemical, mineral and microstructure characteristics. Unpublished thesis, Department of Geology, Faculty of Science, Mansoura University, Egypt.

Andrade F.A., Al-Qureshi H.A., and Hotza D. (2011) - Measuring the plasticity of clays: A review. *Applied Clay Science*, 51, 1-7.

ASTM C67 (2005) - Standard test methods for sampling and testing brick and structural clay tile.

ASTM C860 (2005) - Standard practice for determining the consistency of refractory castable using the ball-in-hand test.

Brocken H. and Nijland T. (2004) -White efflorescence on brick masonry and concrete masonry blocks with special emphasis on sulfate efflorescence on concrete blocks. *Construction and Building Materials*, 18, 315-323.

Clifton G., Bergeron and Subhash H. Risbud (1984) - Introduction to phase equilibria in ceramics. 2nd Ed., American Ceramic Society, Inc. Columbus, Ohio.

Darweesh H.H.M., Wahsh M.M.S. and Negim E.M. (2012) - Densification and thermomechanical properties of conventional ceramic composites containing two different industrial byproducts. *Amer.-Eurasian Journal of Scientific Research*, 7 (3), 123-130.

Darweesh H.H.M. and El-Meligy M.G. (2014) - Non-Conventional Light-Weight Clay Bricks from Homra and Kraft Pulp Wastes. *Journal of Chemistry and Materials Research*, (4), 123-129

Dondi M., Fabbri B. and Laviano R. (1992) - Characteristics of the clays utilized in the brick industry in Apulia and Basilicata (Southern Italy). *Mineralogica et Petrographica Acta*, 35, 181-191.

Egyptian Standard Specifications E.S.S. 1524/1993 (1993) - The Standard Specifications for Clay Bricks.

Egyptian Standard Specifications E.S.S. 3168-

4(2000) - Standard for vitrificied ceramic tiles.

Egyptian Standard Specifications E.S.S. 48, 619 (2003) - The Standard Methods for Testing of Building Bricks, Part 1: Standard Methods for Physical Tests of Building Bricks.

El-Alfi E.A., Radwan, A.M. and Darweesh, H.H. (2004) - Effect of sand as non-plastic material on ceramic properties of clay bricks. *Interceram (International Ceramic Review)*, 53(5), 330-333.

Farag L.M. and Serry M.A. (2000) - Optimization of local technologies for drying and firing of clay bricks, final report, joint research project, academy of scientific research and technology, Cairo, Egypt.

Folk R.L. (1968) - Petrology of Sedimentary Rocks. Hamphills, Austin, Texas, 16-40.

Grim R.E. (1962) - Applied Clay Mineralogy. Mc Graw Hill Book Comp., Inc., NewYouk, Toronto, London.

Grim R.E. (1980) - Clay Mineralogy, 2nd ed., Mc Graw Hill Book Comp., Inc., New York, Toronto, London.

Grimshaw R.W. (1971) - The chemistry and physics of clays and other ceramic materials. Ernest Benn, London.

Hardy R. and Tucker M. (1988) - X-ray powder diffraction of sediments In: Tucker, M. (Ed.). Techniques in sedimentology, Blackwell, Oxford, pp. 144-153.

Hewlett P.C. and “Lea”. (1998) - Chemistry of cement and concrete, 4th Ed., John Wiley & Sons Inc., New York.

ISO 10545(1995) - Ceramic tiles.

Jackson M.L. (1969) - Introduction to white-wares. Elsevier Publishing Co.; Amsterdam, Netherlands.

Kingery W.D., Bowen H.K. and Uhlmann D.R. (1976) - Introduction to Ceramics, 2nd Ed. John Wiley and Sons, New York, London, Sydney and Toronto.

Konta J. (1979) - Properties of ceramic raw materials, Monograph 1.1.4. in: Ceramic Monographs Handbook of Ceramics, Verlag Schmid GmbH, Freiberg i. Brg.

Larsen E. and Nielsen. C. (1990) - Decay of bricks due to salt, materials and structures, 23 (1), 16-25.

Mackenzie R.C. (1970) - Differential thermal analysis, Volume 1: fundamental aspects, Academic Press Inc., First Edition, London and New York.

Mandour M.A., Taha A.S. and Serry M.A. (1989) - Ceramic properties of some Egyptian clayey deposits as related to their mineralogical and chemical composition, *Applied Clay Science*, 4, 83-94.

Muller G. (1967) - Methods in sedimentary petrology, Part I. E. Schweizerbart’scheVerlagsbuchhandlung, Stuttgart, Germany, 283pp.

Norton F.H. (1969) - Refractories, 4th Ed., McGraw Hill Book Comp., Inc., New York, Toronto, London.

Novak A.E., Editor (2005) - Refractory engineering: materials, design & construction, 2nd Ed., Vulkan - Verlag, Essen, Germany.

Nyakairu G.W.A., Kurzweil H., Koeberl C. (2002) - Mineralogical, geochemical, and sedimentological characteristics of clay deposits from central Uganda and their applications. *Journal of African Earth Science*, 35, 123-134.

Riley C.M. (1951) - Relationship of chemical properties to bloating of clays. *Journal of the American Ceramic Society*, 34, 121-128.

Sandrolini F. and Palmonari C. (1976) - Role of iron oxides in the bloating of vitrified ceramic materials. *Transactions of the British Ceramic Society*, 75 (1), 25-32.

Serry M.A., El-Maghraby M.S. and Mandour M.A. (2007) - Utilization of Egyptian waste clays for brickmaking. *American Ceramic Society Bulletin*, 86 (11), 40-43.

Serry M.A., Hegab O.A. and El-Banna M.M. (1985) - Lightweight aggregate from Wadi El-Natrun clays. *Sprechsaal*, 118 (11), 1085-1087.

Serry M.A. (2008) - Assessment of the Egyptian clayey deposits for ceramic industries: A Review Paper. *American Ceramic Society Bulletin*, 87, (1), 9101-9109.

Wadell H. (1934) - Some new sedimentation formulas, *Journal of Physics*, 5, 281-291.

Winkler H.G.E. (1954) - The ternary particle-size composition diagram (Clay-Silt-Sand) for the clays and their batches for structural clay products. *Berichte der Deutschen Keramischen Gesellschaft*, 31, 337.

Submitted, August 2014 - Accepted, May 2015