

Densification and Thermomechanical Properties of Conventional Ceramic Composites Containing Two Different Industrial Byproducts

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Abstract: The influence of the leached cement kiln dust waste (LCD) and Homra (H) as new raw materials on the densification and thermo-mechanical properties of conventional ceramic body has been studied. The results showed that as the firing temperature increases, the densification and mechanical properties evidently improved and enhanced up to 10 wt. % LCD content at all firing temperatures, but more than 10 wt. % LCD have inverse behavior. The dry shrinkage was unchanged with the substitution of the LCD up to 20 wt. %, while the firing shrinkage slightly increased at 1050 and 1100°C, but sharply at 1150°C. The samples with higher porosity showed a greater dimensional stability and therefore they can be used as wall tiles, whilst those with low porosity can be used as floor tiles. So, the optimum body batch was that containing 10 wt.% LCD and 5 wt.% H fired at 1150 °C, which achieved the best data of densification and mechanical properties. The XRD analysis showed that the detected final phases are quartz, anorthite (CAS₂), traces of hematite and cyclo-wollastonite and calcium-rich silicate phases which played an important role to improve the various characteristics of the fired articles.

Key words: Ceramic body • Homra • LCD • Densification parameters • Flexural and crushing strengths • Dry and firing shrinkage • XRD

INTRODUCTION

The reutilization of the various industrial wastes or byproducts collected from the various sectors of industry in useful applications is recently the common trend all over the world because these wastes often cause many environmental and health hazard problems. The cement factories discard very great amounts of cement kiln dust as a waste material, particularly with the new production techniques of dry process, where the dry process emits cement dust waste three times more than the wet process [1-4]. Moreover, very huge quantities of this waste material are accumulated behind the electrostatic precipitator kiln filters. So, this problem has become worse than before. In Egypt, the cement factories often discard more than 2.5 million tones of that waste material annually. This waste material contains large ratios of sulfates, chlorides and alkali oxides that make it too difficult to

utilize, especially for recycling to the cement industry [5]. Therefore, it is necessary to look for another field of application to utilize this hazardous material.

On the other hand, most ceramics possess high strength, particularly at elevated temperatures, but inherently brittle [6]. The transition from the traditional slow double-firing to the fast single processes in firing technology has required some changes in the production techniques as well as in the raw materials used. These must have very constant chemical and mineralogical compositions as well as low quantities of impurities in order to avoid the formation of defects during firing [7]. Many investigators [8-10] used some industrial byproducts in ceramic wall and floor tiles. The broken waste material of the fired bricks, which is industrially known as "Homra", was also used in the current study. The Homra can be used as a fluxing material in the ceramic industry. Hence, the main objective of this paper is to

study the effect of partial substitution of the leached cement kiln dust (LCD) and Homra on the densification and thermo-mechanical properties of ceramic products at different firing temperatures.

MATERIALS AND METHODS

Raw Materials: The clay sample (TC) was taken from Toshka region. Toshka region is located on latitude 20° 30' N and longitude 31° 53' E at 250 km south of Aswan which was related to the Upper Cretaceous age. The selected clay deposit is belonging to El-Dakhla Shale Formation. About 50 kg clay was collected from the 85th km north of Aswan/Abu-simple asphaltic road. It is a dark yellowish grey. The clay sample was crushed, ground and quartered to have a representative sample, which was fine ground to pass a B.S. 100 mesh sieve. Feldspar (F), sand (S) from El-Hekma firm, limestone (L) from Samalout district were supplied by the Arab Ceramic Company (Aracemco), Cement kiln dust (CKD) which was provided by Helwan Portland Cement Company and a broken fired brick waste with the commercial name Homra (H) from a brick-making factory, Egypt. Firstly, the CKD sample was subjected to a simple leaching process using hot water to eliminate or reduce as possible most of the soluble deleterious constituents before its use (LCD).

Constituents of Raw Materials: Table 1 shows the chemical analysis of the raw materials. The original ceramic base batch was composed of T-Clay (TC), Feldspar (F), sand (S), limestone (L) and Homra (H) by 46.27, 18.75, 18.10, 9 and 7.28 wt. %, respectively. The base batch was then partially substituted by 0, 5, 10, 15 and 20 wt. % leached cement kiln dust (LCD).

Table 1: The chemical composition of raw materials, wt. %

MaterialsOxides	T-Clay(TC)	Feldspar(F)	Sand(S)	Limestone(L)	Homra (H)	Leached C. Dust (LCD)
L.O.I	9.72	0.67	1.78	42.63	-	24.51
SiO ₂	53.47	75.37	93.63	0.08	58.22	12.84
Al ₂ O ₃	26.78	13.62	3.64	0.03	28.25	1.86
Fe ₂ O ₃	3.99	0.41	0.08	0.04	8.16	1.53
CaO	0.60	0.53	0.18	56.84	0.79	52.51
MgO	1.38	---	---	0.10	0.46	1.84
MnO	0.03	0.03	0.02	---	---	---
K ₂ O	1.18	5.84	0.14	0.05	1.46	1.65
Na ₂ O	1.15	3.44	0.17	0.12	1.32	0.83
TiO ₂	1.12	0.05	0.16	0.01	1.34	---
SO ₃	---	0.02	0.14	0.02	---	2.43
P ₂ O ₅	0.51	---	---	---	---	---
Cl	---	0.02	0.06	0.08	---	---

Preparation of Samples: The cement batches were mixed well in a gate ball mill for one hour using the wet method, dried at 105°C for 48 hours and then ground to pass 200 mesh sieve in order to obtain the same homogeneity of all batches. Five disc-shaped samples of 1cm diameter and 1 cm thickness, five rod-shaped samples of 1x1x7 cm³ dimensions, 1 cm diameter and 3 cm height were cast for each batch. The moulding of specimens were carried out under a shaping pressure of 18 KN/mm² using water as a binder. The prepared specimens were let to dry in air for 48 hours and then in a dryer at 105°C for another 48 hours. The firing was carried out in a slow rate furnace Mod. VECSTAR with a heating rate of 5°C/min. The firing temperature was ranged between 1050-1150°C with one hour soaking time.

Methods of Investigation: The 1 cm diameter / 1 cm thickness disc-shaped specimens were subjected to densification parameters [11], namely water absorption (W.A), bulk (B.D) density and apparent porosity (A.P) from the following relations:

$$W. A, \% = (W1-W2) / (W3) \times 100 \quad (1)$$

$$B. D, g/cm^3 = (W3) / (W1-W2) \quad (2)$$

$$A. P, \% = (W1-W3) / (W1-W2) \times 100 \quad (3)$$

where, W1, W2 and W3 are the weights of soaked samples in water, suspended samples in air and dry weight, respectively. The 1 x 1 x 7 cm³ rod-shaped specimens (Figure1), were subjected to flexural strength (F.S) [12-14] by the following equation:

$$F. S, kg/cm^2 = 3 (PL) / 2 (b) (d^2) / 10.2 Mpa \quad (4)$$

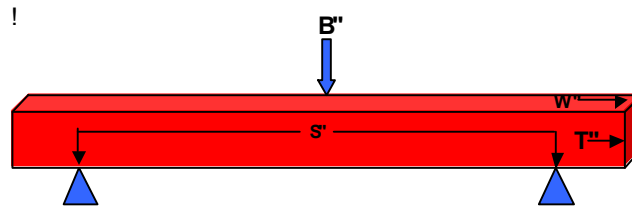


Fig. 1: Schematic diagram of three points system for bending or flexural strength, B: Bending load, S: Span, W: Width and T: Thickness

where, P: the load of rupture, kg, L: span or the distance between the two lower beams (5 cm), b: width of sample, cm and d: thickness of sample, cm.

The 1 cm diameter / 3 cm height cylinder-shaped samples were subjected to crushing strength (C.S) [15, 16] by the following equation:

$$C.S, \text{ kg/cm}^2 = (D) / (L) \times (w) / 10.2 \text{ Mpa} \quad (5)$$

where, D: the load, kg; L: length of sample, cm; W: with of sample, cm. The drying and firing shrinkage [17] were also measured on the rod-shaped specimens using the following relation:

$$F.S, \% = (L_0 - L) / (L_0) \times 100 \quad (6)$$

where, L_0 and L: are the measurements before and after firing, respectively. The optimum firing temperature and the optimum batch composition were identified by comparison of results. The phase composition was further investigated by X-ray diffraction analysis (XRD) which was employed by a Philips X-Ray Diffractometer of Mod. P.W. 1390 with Ni-filtered Cu-K α radiation.

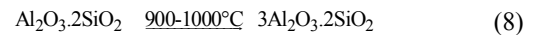
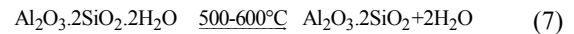
RESULTS AND DISCUSSION

Characterization of T-clay, LCD and Homra Samples:

The physical properties of the T-clay and LCD samples as particle size distribution, slaking time and nomenclature according to Triangular Folk Diagram [18-20] are summarized in Table 2. It is clear that the LCD is finer than clay, but has no slaking or clay characteristics.

The XRD patterns of the T-clay (A) as well as LCD (B) and Homra (H) waste materials are shown in Figure 2, respectively. The main clay mineral (A) is the montmorillonite-kaolinite mixture, while the Illite-Montmorillonite is that of the LCD sample (B) as traces. The quartz is the only non-clay mineral impurity in both. The LCD sample contains also abundant calcite and traces of some clay minerals. The H sample (C) composes mainly of silica quartz, hematite and albite.

The DTA analysis of the T-clay and LCD samples are shown in Figure 3. The endothermic peak at the temperature range of 700-900°C is due to the calcination of limestome. The two endothermic peaks at the temperature range 100-120°C and 500-600°C are due to the evaporation of the absorbed and structural or hygroscopic water, respectively. The endothermic peak at the temperature range 500-600°C is due to the conversion of kaolinite ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot \text{H}_2\text{O}$ or AS_2H_2) to metakaolin ($\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or AS_2), which in turn is converted to mullite phase ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ or A_3S_2) at 980 -1000°C as follows:



Densification Parameters: Generally, as the firing temperature increases the densification parameters of the fired products in terms of water absorption, bulk density and apparent porosity evidently improved which in turn reflected positively on the mechanical properties [21, 22].

Figures 4-6 show the results of water absorption, bulk density and apparent porosity of the various fired ceramic products at different firing temperatures, respectively. Both water absorption and apparent porosity decreased as the firing temperature increased, while bulk density increased [13]. On the other side, as the LCD content increased up to 10 wt. %, the water absorption and apparent porosity also decreased whilst the bulk density increased. The same trend was displayed with all firing temperatures. This is mainly due to the formation of new phases resulting from the thermal reactions during firing either through decomposition and/or recombination changes [23]. This means that during firing, the main crystalline phases in the green bodies were completely replaced by the development of new amorphous and crystalline phases [7, 13], in addition to the melting action of feldspar which controls the reactions of body components with each others in the liquid phase [23]. Furthermore, the presence of high amounts of fluxing oxides increased the rate of thermal

Table 2: The physical properties of Toshka clay (TC) and Leached cement kiln dust (LCD) samples

Preparation Property	Toshka clay sample (TC)	L. Cem. K. Dust(LCD)	Homra(H)
Particle size	wt. %	wt. %	wt. %
>63	1.43	---	---
63-16	1.68	---	---
-16-8	3.96	---	---
-8-2	9.14	11.32	10.65
<2 (clay)	83.79	88.68	89.35
Total	100 %	100 %	100 %
Nomenclature according to (Triangular Folk Diagram)	Clay	----	---
Slaking Time	H min.	----	---
1 30	----	----	---

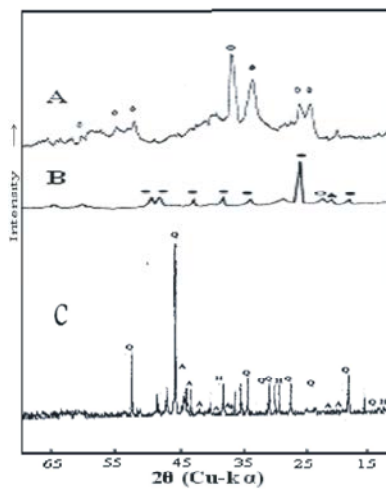


Fig. 2: The XRD patterns of clay and Leached Cement kiln Dust waste. A: T-Clay (o: Quartz, •: Kaolinite, ▲: Montmorillonite) and B: LCD (o: Quartz, ▲: Kaolinite, •: Limestone, Δ: Illite-Montmorillonite) and C: Homra waste (H). (o: Quartz, A: Albite, H: Hematite)

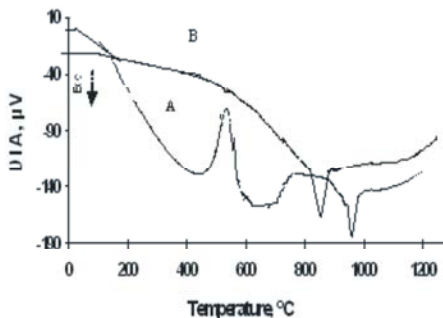


Fig. 3: The DTA thermograms of (A) T-clay and (B) Leached Cement kiln Dust waste (LCD)

reactions and liquid phase, which in turn flows directly and settled inside the pore structure of the fired products. On solidification, a product of more compact and glassy structure with a minimum porosity resulted. This tends to

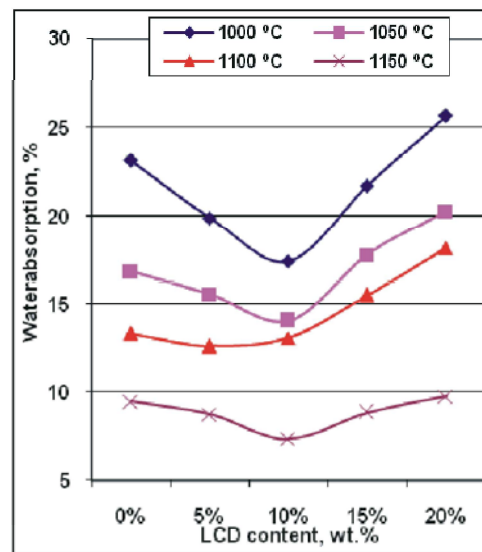


Fig. 4: Water absorption of ceramic products with various LCD content, %

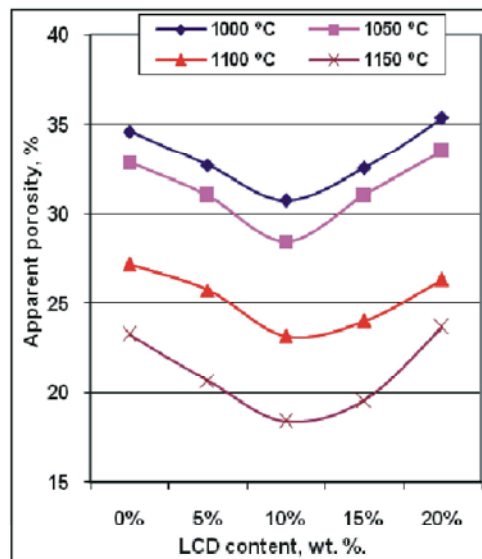


Fig. 5: Apparent porosity of ceramic products with various LCD content, %

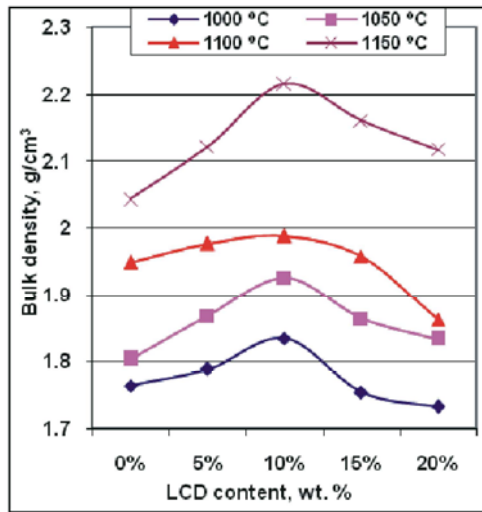


Fig. 6: Bulk density of ceramic products with various LCD content, %

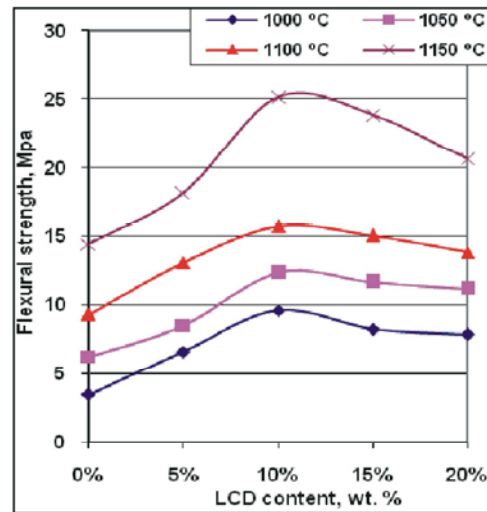


Fig. 7: Flexural strength of ceramic products with various LCD content, %

improve and enhance all the densification parameters of the produced ceramic articles [20-22]. The ceramic bodies containing more than 10 wt. % LCD, the water absorption and apparent porosity tended to increase while bulk density decreased. The same property was also displayed even with the increase of firing temperature. This is essentially attributed to the creation of a more pore structure resulting from the evolution of gases through the matrix of articles which results from the enhancement of the thermal decomposition of some components during firing [4]. This means that the addition of high amounts of LCD into the ceramic bodies is undesirable due to its adverse action on the physical properties of ceramic products.

Flexural Strength: The Flexural strength of the ceramic products containing various ratios of LCD fired at different firing temperatures is represented in Figure 7. It is obvious that the Flexural strength increased with firing temperature. This is due to the fact that as the firing temperature increases, the rate of densification properties improves and enhances resulting in the formation of a ceramic product having good mechanical characteristics on cooling [13, 21, 22]. Therefore, it could be estimated that many strengthening mechanisms of ceramic articles took place simultaneously during firing of the green bodies. Furthermore, the good compaction of samples during moulding using a high shaping pressure permits a suitable contact between the various ingredients to react with each other forming new phases, which contribute to the high Flexural strength [21, 22]. The Flexural strength

of the ceramic products increased with LCD content up to 10 wt. % due to that the presence of cement dust with the ceramic ingredients, particularly feldspar, increases the rate of glassy phase formation and reduces its viscosity during sintering. On cooling, the glassy matrix solidifies and cements all the unmelted particles together. As a result, a ceramic product of high mechanical properties could be obtained compared with those containing no LCD. This means that the presence of CaO, Fe₂O₃, Al₂O₃, MgO and alkali oxides (Na₂O and K₂O) in LCD helps to form sufficient quantities of liquid phase which promotes the crystallization of Ca-rich phases, especially with mullite phase [13, 21, 22]. On the other hand, as the LCD content increased than 10 wt. %, the Flexural strength of all ceramic products gradually decreased even with the increase of firing temperature. This may be due to that the higher amounts of LCD may be prevent and hinder the suitable contact between the various ceramic particles and those of LCD to react normally with each other. This in turn led to a reduction in the glassy phase formation. Hence, the new phases that responsible for the enhancing of mechanical strength were reduced. In addition, the migration of high rate of gases through the matrix created a ceramic body with high porosity. So, the mechanical properties diminished [22-24]. Accordingly, the optimum ceramic products are those containing 10 wt. % LCD fired at 1150°C.

Crushing Strength: The crushing strength of the ceramic products containing various ratios of LCD fired at different firing temperatures is plotted as a function of

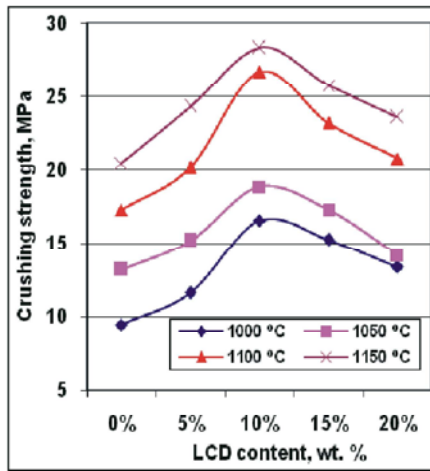


Fig. 8: Crushing strength of ceramic products with various LCD content, %

LCD content in Figure 8. The crushing strength of the prepared ceramic products increased with LCD content only up to 10 wt. % and then decreased. This is due to the fact that the presence of LCD with the ceramic ingredients especially feldspar increases the formation rate of glassy phase and reduces its viscosity during sintering. On cooling, the glassy matrix solidifies and cements all the unmelted particles together. As a result, a ceramic product of high mechanical properties could be obtained compared with those containing no LCD. Also, the crushing strength increased with the increase of firing temperature up to 1150°C. This is mainly due to the increase of glassy or liquid phase that improves the reaction processes between the various ingredients. This leads to the formation of well-developed crystals [21, 22]. On the other side, as the LCD content increased more than 10 wt. %, the crushing strength of all ceramic products gradually decreased even with the increase of firing temperature up to 1150°C. This may be attributed to that the higher amounts of LCD prevent and hinder the suitable contact between the various ceramic particles to react normally with each other and with those of LCD. This in turn led to a reduction in the rate of the formed glassy phase. So, the new phases that responsible for the enhancing of mechanical strength were reduced. In addition, the migration of gases through the matrix created a ceramic body with high porosity, which reflected negatively on the mechanical properties [22, 25]. Hence, the results of densification properties of all samples are in a good agreement with those of mechanical strength. Accordingly, the optimum ceramic products are those containing 10 wt. % LCD fired at 1150°C.

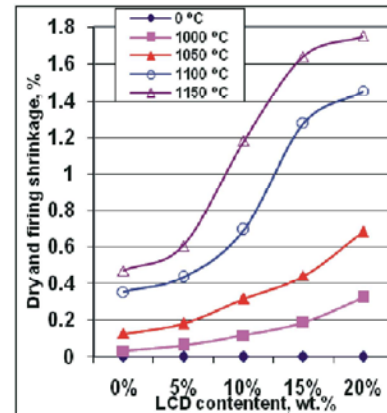


Fig. 9: Dry and firing shrinkage of ceramic products with various LCD content, %

Dry and Firing Shrinkages: Figure 9 shows the dry and firing shrinkages of the ceramic products containing various ratios of LCD fired at different firing temperatures. The dry shrinkage of all ceramic bodies seemed to be equal to zero. This means that all dimensions of the prepared green ceramic bodies are unchanged on drying, but as the firing temperature increased, the firing shrinkage increased slightly at 1050 and 1100°C and increased more at 1150°C [26]. The same trend was displayed by all samples [4]. The ceramic products containing no LCD exhibited the lowest values of firing shrinkage and those containing 20 mass % LCD achieved the highest values nearly at all firing temperatures. The lower values of firing shrinkage are mainly due to the removal of residual and combined water contents, but the higher values are due to the migration of gases from the dissociation of carbonates (CO_2) and sulfates (SO_3) [27], respectively. Moreover, the presence of larger amounts of CaO and alkali oxides in LCD tends to lower the melting point of the fired articles that contributes to the formation of large amounts of glassy phase. This is the principal cause of the sharp increase of the total firing shrinkage of ceramic bodies containing 20 mass % LCD. However, the firing shrinkage of ceramic bodies containing 5-10 mass % LCD lies in the permissible limits in all-standard specifications. Accordingly, the optimum body batch is that containing 10 mass % LCD. So, the dry and firing shrinkage of ceramic bodies are also in a good agreement with those of densification and mechanical properties.

X-Ray Analysis: The XRD patterns of the various ceramic products containing various ratios of LCD fired at 1150 °C are shown in Fig. 10. The major phases were anorthite

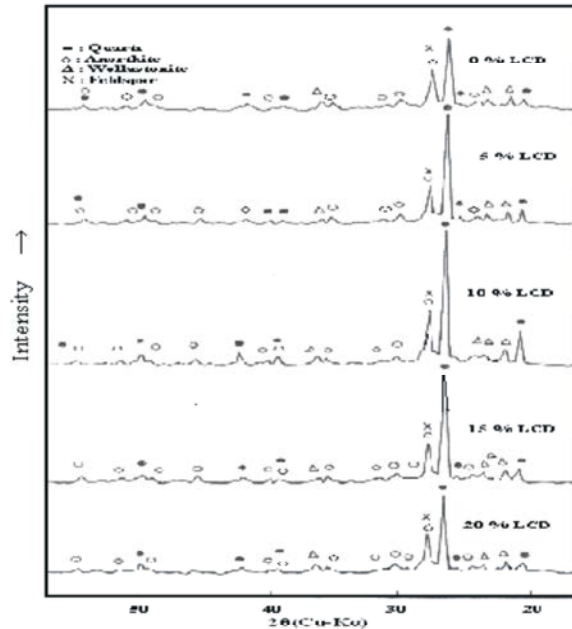


Fig. 10: The XRD patterns of the ceramic products containing 0 - 20 wt. % LCD waste

(CAS₂), quartz and may be traces of unreacted feldspar, in addition to minor phases as cyclo-wollastonite. The intensity of the peaks increased with LCD content only up to 10 wt. % and then gradually decreased. Consequently, the XRD analysis is in a good agreement with those of the densification and mechanical properties and confirmed them.

Accordingly, the prepared samples fired at 1050-1100°C are characterized by a higher porosity evident by water absorption (>15 %) and a very low firing shrinkage (< 2 %) which indicated a high dimensional stability as required for wall tiles, whilst those fired at 1150 °C with a lower porosity evident by water absorption (<15 %) are much suitable for floor tiles.

CONCLUSIONS

- The densification parameters in terms of water absorption, apparent porosity and bulk density as well as mechanical properties in terms of flexural (or bending) and crushing strengths are improved and enhanced with firing temperature up to 1150°C and also with the partial substitution with the leached cement kiln dust waste (LCD) up to 10 wt. % and then adversely affected.
- The dry shrinkage is unchanged, while the firing shrinkage slightly increased with LCD content and firing temperature.

- The prepared ceramic products with 10 wt. % LCD recorded the best results at all firing temperatures compared with the others, particularly at 1150°C.
- The optimum amount of LCD substitution is 10 wt. % and the optimum firing temperature is 1150°C.
- The XRD analyses showed that the detected final phases are Ca-rich silicate phases as anorthite (CAS₂) and cyclo-wollastonite as well as quartz and traces of hematite.
- These phases, which could be formed during firing, are contributed to the clear improvements of physical and mechanical properties of the prepared ceramic articles containing LCD and H.
- This clearly points out that the ceramic products fired at lower temperatures (1050°C) are suitable for porous wall tiles, while those fired at high temperatures (1150°C) are much suitable for floor tiles, where the dimensional stability (very low firing shrinkage) are the most requirements for tiles.

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