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Reuse of the Product Obtained on Grinding Kiln Rollers in the Manufacture of Ceramic Wall Tiles

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Reuse of the Product Obtained on Grinding Kiln Rollers in the Manufacture of Ceramic Wall Tiles

M H Roushdy, ShK Amin, M M Ahmed and
M F Abadir research the
possible reuse of a hazardous waste

THE PRODUCTION OF CERAMIC TILES AND TO A LESSER EXTENT FLAT DINNER WARE AND POTTERY IS INCREASingly being done by firing in roller kilns. These kilns offer several advantages over conventional tunnel kilns: lower fuel consumption, computer controlled firing curves, low maintenance due to lack of kiln cars, rapid firing cycles of less than one hour and the possibility of shutting down the kiln on short notice.[1]

One recurrent problem in the operation of such kilns is the periodic need to grind the kiln rollers. These are usually fabricated from high alumina clays and are continuously contaminated by depositions of alkali salts by condensation from the vapour phase. These latter salts, in turn, arise from some additions made on the original ceramic body recipe to impart some specific properties.

In an average plant using one or two such kilns, the monthly product of grinding will consist of several tons of fine powder that usually accumulates within the plant premises as stock piles. This represents an extremely high ecological hazard as such powder, if inhaled for long periods, can lead to serious lung problems such as silicosis.[2]

RAW MATERIALS: The raw materials used are the product of the grinding of ceramic rollers used in kilns for the production of tiles and standard wall tiles raw mix both obtained from PRIMA factory at Sadat City (90 km North of Cairo). The chemical analysis of such materials was performed by XRF using and x-ray fluorescence Philips type PW spectrometer. Phase identification was performed using Philips type PW 1373 x-ray diffractometer.

Sieve analysis of the as-received material was effected using a set of standard sieves of 100 mesh (0.147 mm) down to 375 mesh (0.039 mm).

SAMPLE PREPARATION: The as-received powder was dry pressed in a uniaxial hydraulic press under a pressure of 27 MPa in 110.4 × 55.4 × 8 mm^3 moulds. The dry pressed samples were then fired for periods reaching 15 minutes in a muffle kiln at temperatures ranging from 1050 to 1150°C to simulate conditions in the firing zone of roller kilns. Three specimens were tested each time and the average value of results calculated each time.

STANDARD TESTS: The following tests were performed on the fired specimens according to the International standard ISO 13006/2012:[3]
- Bulk density, water absorption and apparent porosity were determined using the hot test piece boiling water method, according to ASTM C 373/1988 (reapproved 2006).[4]
- Linear firing shrinkage was measured according to ASTM C 326/2009.[5]
- True density was determined using the density flask method, according to Egyptian standard ES 1859–2/2006.[6]
- The modulus of rupture was determined by the three point bending test, according to British–International standard BS EN ISO 10545–4/2012.[7]

CHEMICAL ANALYSIS OF RAW MATERIALS: Table 1 shows the results obtained using XRF technique. As can be seen from this table the main oxides present in the powder are SiO_2 and Al_2O_3, with the latter being in majority.

Table 2 on the other hand shows the chemical analysis of a standard wall tile mix. The loss on ignition is mainly due to loss of the chemical water of clays and carbon dioxide from limestone.

As can be seen from this table, silica, alumina, calcium oxide and iron oxide constitute more

than 96 percent of the mix (on loss on ignition – free basis).

The loss on ignition is due to calcination of limestone and loss of chemical water from clay.

MINERALOGICAL ANALYSIS: Although not shown in the figure, the XRD pattern of the ground powder showed that it mainly consists of corundum (Al_2O_3) and mullite ($3Al_2O_3.2SiO_2$) with two minor phases present: magnesium aluminium oxide spinel ($MgO.Al_2O_3$) and cordierite (($Mg,Fe)_2Al_3Si_5AlO_{18}$). As for the raw mix, its XRD pattern has been studied by Amin et al.[8] They found that the mix is mainly composed of the following phases: quartz, albite, calcite and kaolinite.

SIEVE ANALYSIS: Figure 1 describes the particle size distribution of both waste powder and wall mix. It can be seen that the powder is finer than the mix. This was confirmed by calculating the mean particle size following McCabe et al.[9] The mean surface to volume particle size was found to be 0.2 mm for waste powder and 0.25 mm for raw wall mix powder.

DENSITY OF RAW MATERIALS: The density of dry raw mix has been determined using the density bottle method repeating the procedure three times to take the mean value. This gave the following result for raw mix true density: 2.63 (± 0.02) g/cm³

On the other hand, the high alumina waste had its density previously determined by Ibrahim[10] who found it to equal 2.94 g/cm³. These results mean that adding waste powder to the raw mix will have for effect to increase its true density. Simple volume balance calculations show that a 10 percent addition will increase the density from 2.63 to about 2.67g/cm³.

EFFECT OF WASTE ADDITION ON PLASTICITY OF MIXTURES: Wall tiles are formed using the dry pressing technique using as much as seven percent water to impart plasticity to the raw mix. Adding the non-plastic waste is expected to have for effect to reduce plasticity.

Constituents (wt. %)	Waste
SiO_2	23.55
Al_2O_3	63.86
Fe_2O_3	1.16
TiO_2	0.33
ZrO_2	3.45
CuO	0.22
ZnO	0.22
MgO	1.96
CaO	3.51
Na_2O	0.8
K_2O	0.48
HfO_2	0.18
P_2O_5	0.17
Total	99.89

Above: Table 1: Chemical analysis of powder.

Below: Table 2: Chemical analysis of wall mix.

	25 % Aswan Clay	35 % Ball Clay	2 % Bentonite	14 % Coarse Feldspar	15 % Glass Sand	9 % Limestone	Mixture
SiO_2	14.8	19.53	1.05	11.41	13.23	0.23	60.25
Al_2O_3	4.91	8.61	0.21	1.49	0.44	0.03	15.69
Fe_2O_3	1.54	1.68	0.17	0.15	0.04	0.01	3.59
CaO	0.11	0.07	0.21	0.2	0.35	4.95	5.89
MgO	0.12	0.11	0.02	0.06	0.25	0.02	0.58
Na_2O	0.14	0.11	0.02	0.21	0.04	0.014	0.53
K_2O	0.44	0.16	0.04	0.02	0.01	0.001	0.67
SO_3	0.01	0.02	0.002	0.001	0.002	0.002	0.04
TiO_2	0.58	0.79	0.02	0.001	0.002	0.002	1.4
P_2O_5	0.03	0.07	0.01	0.003	0.01	0.004	0.13
L.O.I.	2.29	3.82	0.24	0.46	0.62	3.75	11.18
Total	24.97	34.97	1.992	14.005	14.994	9.013	99.95

This has been confirmed by determining the Pfefferkorn plasticity number for mixes containing from zero percent to 10 percent addition. Figure 2 shows this relation. It is clear that adding as little as two percent waste powder has had for effect to decrease the plasticity number from 0.39 to 0.28. Adding more powder did not affect the plasticity in any appreciable way, its value reaching 0.255 at 10 percent addition.
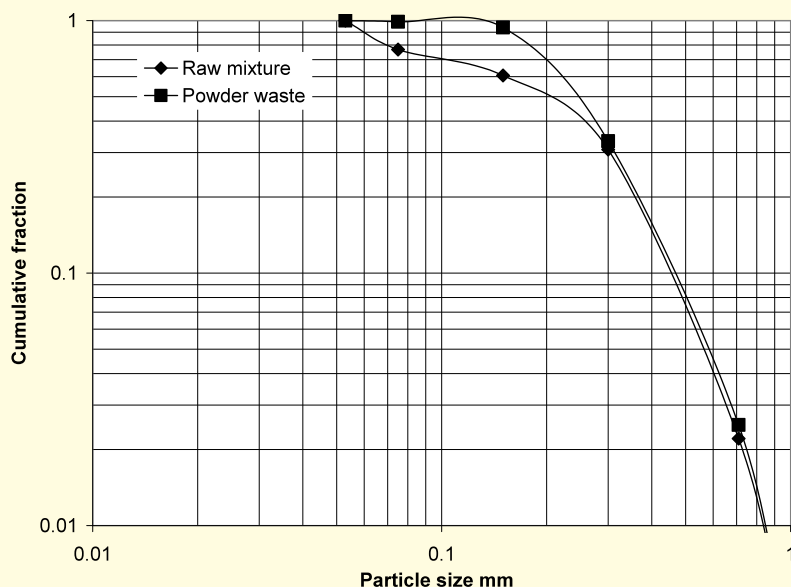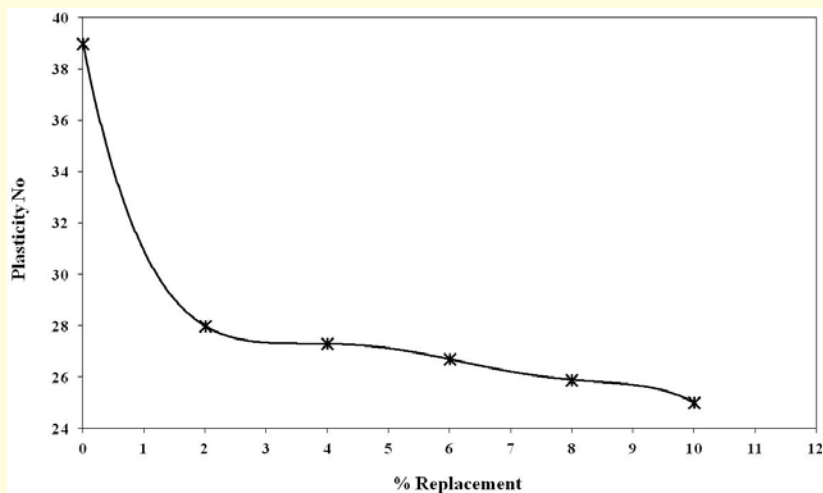
Above: **Fig 1**: *Particle size distribution of wall raw mix and waste.*
Below: **Fig 2**: *Effect of percent waste addition on plasticity number.*

This result means that adding any small percentage of waste must be accompanied by regulating the pressing cycle to account for reduced plasticity, or eventually adding a suitable plasticising agent.

EFFECT OF WASTE ADDITION ON THE SINTERING PROPERTIES OF THE MIX:

a) Linear firing shrinkage: The linear firing shrinkage was followed as a function of three parameters: percent waste added, firing temperature and soaking time. Figure 3a shows the results obtained at 15 minutes soaking time.

The main conclusion that can be drawn from such curve is that any increase in the amount of waste added has for effect to decrease the firing shrinkage reaching a zero level at all soaking times at four percent addition at low sintering temperatures.

It is believed that the addition of the high alumina refractory waste had for effect to limit or even suppress the formation of a liquid phase. This would explain the drop in firing shrinkage observed on adding such waste. This point will be elucidated in view of XRD and SEM results in a coming section.

b) Percent water absorption: The percent water absorption was investigated as a function of the three aforementioned variables. The effect of the percent waste added on water absorption is shown in Figure 3b for 15 minutes soaking time. Curves obtained for other soaking periods were not shown for lack of space. These curves show that the percent water absorption behaviour is in harmony with that of linear firing shrinkage. As the percent waste increases in the mix, more pores are created owing to the refractory character of the addition which suppresses liquid phase formation. For example, on soaking for five minutes at 1150°C, the percent water absorption

increases from 14.2 percent to 15.5 percent as the percent addition increases to 10 percent.

c) Apparent porosity: The relation between apparent porosity and the three investigated firing parameters for 15 minutes soaking time is shown in Figure 3c. This figure shows the same general trend observed in water absorption. That is, an increase in porosity with increased waste addition and a decrease in porosity following an increase in either soaking time or firing temperature.

d) Bulk density: The bulk density of fired bodies will depend primarily on their total porosity and to a lesser extent on the true particle density. This is since this latter is only slightly affected by the degree of waste addition (up to 10 percent). That is why the pattern of change of bulk density with waste addition is not regular. Figure 3d depicting the effect of waste addition on bulk density shows that behaviour.

Upon adding the refractory waste, an increase in bulk density is generally observed owing to the slight increase in true density of the mix. After a certain addition level, the effect of increased porosity overshadows that of density and the bulk density tends to stabilise or slightly decrease. Here also the effect of soaking time was negligible.

A more detailed interpretation of bulk density results can be deduced by considering the closed porosity of different samples.

e) Closed porosity: The previously reported data for porosity were only concerned with apparent porosity (ε). In trying to understand the behaviour of different samples upon firing, closed porosity has been calculated from the following equations requiring knowledge of bulk density and true density. This latter was calculated by simple volume balance between the raw mix and added waste.

$$\varepsilon_c = \varepsilon_{total} - \varepsilon = \left(1 - \frac{\rho_b}{\rho_t}\right) \times 100 - \varepsilon$$

From corresponding data of bulk density and open porosity, it was possible to plot the percent closed porosity as a function of both percent waste addition and firing temperature at the three selected soaking times. As for previously studied variables the effect of soaking time was negligible and only the results at 15 minutes are reported in Figure 3e.

For all soaking times, the closed porosity is highest for the raw mix samples particularly at 1150 °C firing temperature indicating the possible existence of a glassy liquid phase. On adding the waste this phase disappears and more open pores are available. In all cases (except on firing at 1150°C for 15 minutes) closed porosity practically disappears on about six percent addition. This has been confirmed by XRD and SEM examination as will be shown later.

f) Modulus of rupture of fired bodies: The variation of the modulus of rupture for different specimens with the three aforementioned parameters was investigated and the results obtained for 15 minutes soaking time shown in Figure 3f.

The pattern of change was similar for all soaking times with minute differences. This is characterised by a rise in MOR for two percent addition, followed by a sharp drop at four percent addition then a subsequent rise at six percent addition to practically stabilise at higher levels of addition.

It is to be noticed that at all soaking times and firing temperatures, the values of MOR at two percent addition generally exceed the minimum value required by standards (15 MPa). This suggests that waste free samples and possibly up to two percent addition contained some glassy phase that disappears at four percent addition. The formation of primary mullite at doses above four percent may be responsible for the increase in strength observed thereby.[11] This will be assessed in the next sections.

XRD AND SEM RESULTS OF FIRED BODIES: Although not shown in figures, the XRD results obtained for some typical samples were as follows:
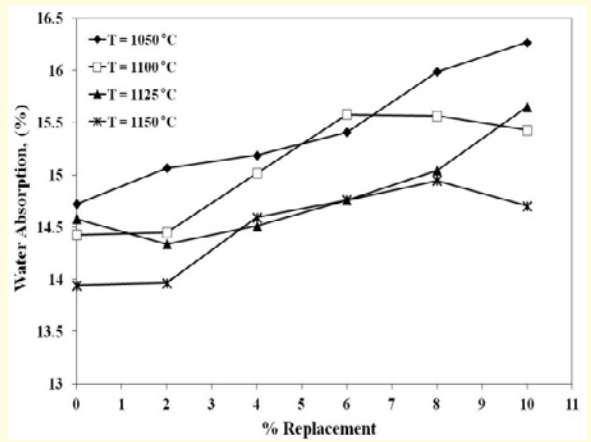
a) Sample of pure wall tile mix fired at 1100 °C for 10 minutes:

The pattern consisted of diffuse peaks with sharp quartz peaks and small albite and mullite peaks proper to low crystallinity and probable presence of a glassy phase.
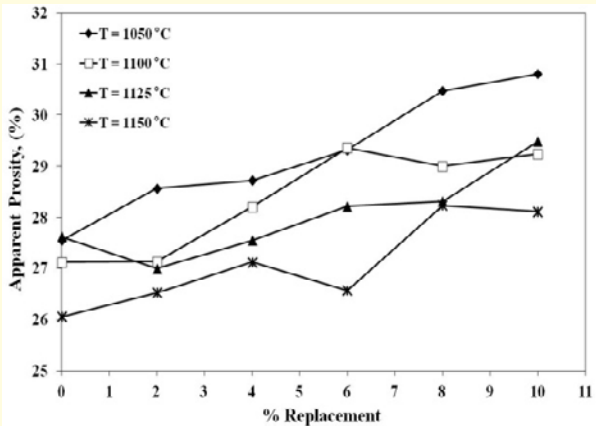
Fig. 3: Effect of percent waste addition on the sintering properties of the mix.
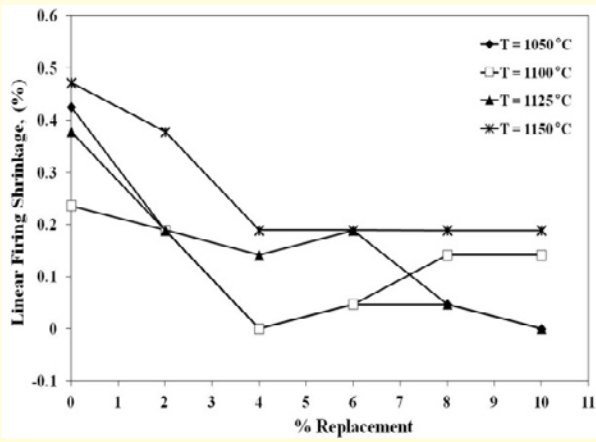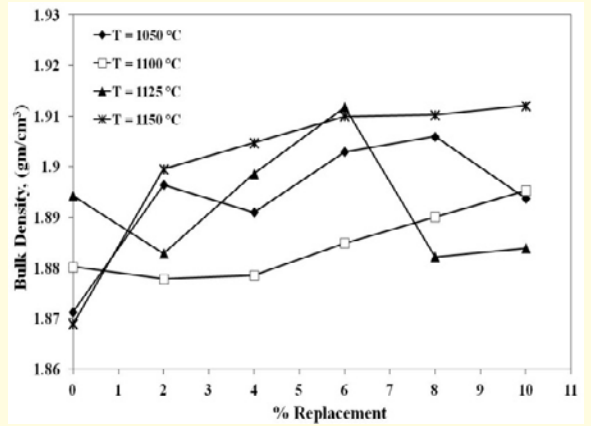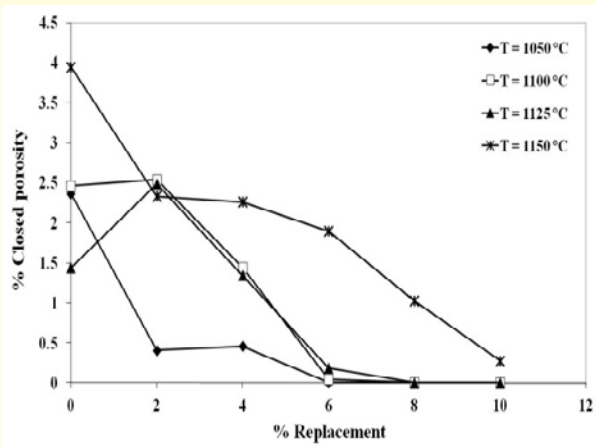
a) Linear firing shrinkage.
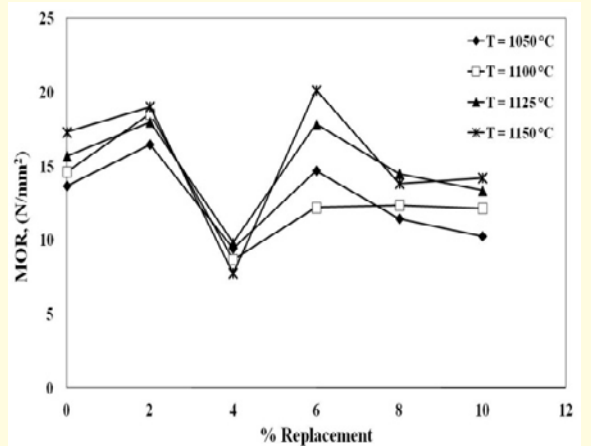

b) Percent water absorption.

c) Percent apparent porosity.

d) Bulk density.

e) Percent closed porosity.

f) Modulus of rupture (MOR).

(Soaking time = 15 min.)

This was verified by subjecting a specimen to SEM analysis. An SEM micrograph for a pure raw mix specimen fired at 1100°C for 10 minutes is shown in Figure 4a. This micrograph shows the presence of a liquid phase besides clear quartz crystals and scattered smaller albite crystals. The circular craters associated with the liquid phase region are due to the evolution of carbon dioxide from calcite present in a small quantity in the raw mix. This gas is liberated at temperatures above 900°C and will easily diffuse in the formed liquid phase. This would also
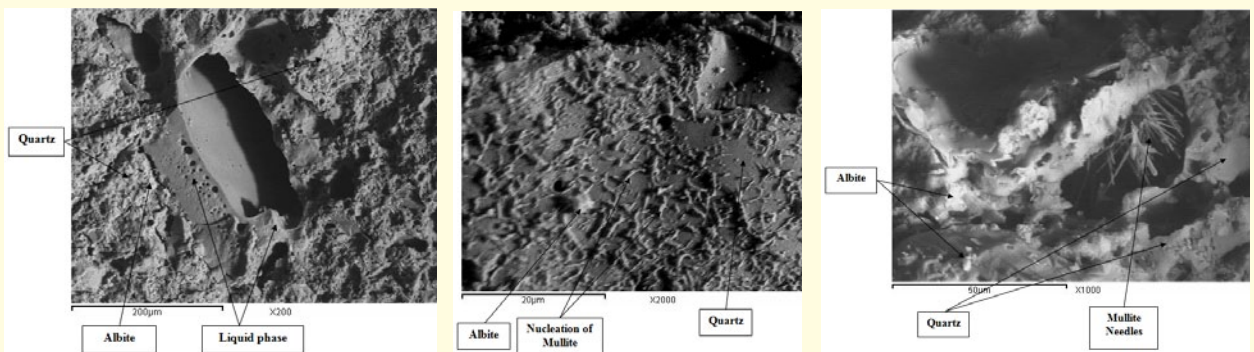
account for the high values of closed porosity and the relative high values of strength observed.

b) Sample of raw wall mix plus four percent waste specimen fired at 1100°C for 10 minutes: On adding four percent waste, the peaks of both quartz and albite became sharper and more mullite peaks are revealed. The SEM micrograph is shown in Figure 4b and reveals the absence of glassy phase and the presence of small mullite crystals that have barely crystallised.

In this micrograph there is no trace of liquid phase. It is believed that the addition of a refractory material has suppressed the formation of liquid phase. This is in accordance with the XRD findings. This could also explain the sharp drop in firing shrinkage, in closed porosity and in strength observed on adding four percent waste. This micrograph also reveals the beginning of nucleation of primary elongated mullite crystals of sizes hardly exceeding five μm. This means that under such conditions no appreciable crystal growth has occurred.

c) Sample of raw wall mix plus 10 percent addition fired at 1150°C for 10 minutes: The XRD pattern of such sample showed sharp mullite and quartz peaks with smaller albite peaks. No glassy phase was detected. Well crystallised primary mullite needles can be observed in Figure 4c exhibiting the corresponding SEM micrograph. The presence of mullite explains the increase in mechanical strength observed for samples containing higher amounts of waste. The absence of a glassy phase accounts for the annihilation of closed pores.

a) Pure raw mix specimen fired at 1100°C for 10 minutes (x200).

b) Raw mix plus four percent waste specimen fired at 1100°C for 10 minutes (x2000).

c) Raw mix plus 10 percent waste specimen fired at 1150°C for 10 minutes. (×1000).

Fig. 4: SEM micrographs.

CONCLUSION: In a typical production line, the quantity of produced waste is in the order of a few hundred tons per year where as that of wall tiles exceeds 50,000 tons per year. This means that in the event of recycling the waste powder to be used as a body addition, a maximum of two percent such addition is possible.

That is why; the possibility of such reuse in the light of the results has been obtained for one and two percent waste addition, firing temperature of 1150°C (which is in the normal industrial range) and 10 to 15 minutes soaking, corresponding to the retention time of tiles in the hot zone of the kiln.

The following table shows the results obtained as compared to standard requirements for wall tiles of thickness < 7.5 mm.[3] Waste free mix results were also included for comparison.

This table shows that the results obtained on adding two percent waste as well as those deduced for one percent addition comply with standard requirements.

	% Waste	Firing Temperature (°C)	Soaking Time (min)	Water Absorption (%)	Breaking Strength (N)	MOR (MPa)
Mix 1	0	1150	10	13.8	440	11
Mix 2	0	1150	15	13.9	430	16
Mix 3	1	1150	10	13.75	490	16
Mix 4	1	1150	15	13.9	460	18
Mix 5	2	1150	10	13.7	520	21
Mix 6	2	1150	15	13.9	490	19
ISO Limits				> 10	> 200	> 15

Table 3: Compliance with ISO 13006/2012

ENDNOTES

1. Smothers W, Heimsoth D A. "Operating experiences with roller kilns", A Collection of Papers Presented at the 1980 Fall Meeting and 83rd Annual Meeting of the Materials & Equipment and White wares Divisions, the American Ceramic Society: *Ceramic Engineering and Science Proceedings*, Volume 2, No. 9/10.

2. Gulati M, Cullen M R. "Occupational lung diseases", *International Encyclopedia of Public Health*, (2008), p 157.

3. ISO 13006/2012, "Ceramic tiles: definitions, classification, characteristics and marking", (Annex L), International Organization for Standardization, Geneva, (2012), pp 41–43.

4. ASTM C 373/1988 (Reapproved 2006), "Standard test method for water absorption, bulk density, apparent porosity and apparent specific gravity of fired white ware products", *Annual book of American Society for Testing of Material* (ASTM), US, 15 (2), (April 2012).

5. ASTM C 326/2009, "Standard test method for drying and firing shrinkages of ceramic white ware clays", *Annual book of American Society for Testing of Material* (ASTM), US, 15 (2), (April 2012).

6. ES 1859 – 2/2006, "Testing of physical properties for dense shaped refractory products, Part (2): determination of true density", Egyptian Organization for Standardization and Quality, Cairo, Egypt, (2006).

7. BS EN ISO 10545 – 4/2012, "Ceramic tiles – Part 4: Determination of modulus of rupture and breaking strength", the British Standards Institution (BSI), London, (2012).

8. Amin Sh K, Youssef N F, Abadir M F. "The use of magnesite waste as feldspar replacement in the production of ceramic wall tiles", *The Journal of Ceramic Forum International* (CFI), (February 2012), 89 (2), pp E39–E45.

9. Mc Cabe W, Smith J C, Harriott P. *Unit Operations of Chemical Engineering*, 7th Edition, Mc Graw-Hill, (2005), p 970.

10. Ibrahim O A. "The use of the product obtained on grinding kiln rollers in the production of refractory bodies", 24th International Conference on Solid Waste Management., Philadelphia, US, (March 2009).

11. Richerson D W. *Modern Ceramic Engineering*, 3rd Edition, Taylor & Francis, (2006), p 535.

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