Utilization of Gebel Attaqa Quarry Waste in the manufacture of Single Fast Firing Ceramic Wall Tiles
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ABSTRACT
Extensive and inexpensive quarrying operations have been done on a large scale in Gebel Attaqa area, Eastern Desert of Egypt, where the main source of dolomite deposits is located. The production line of the working crushers at Gebel Attaqa produces primary building and pavement aggregate types and fine quarry residues as a waste byproduct. These residues are in huge quantities that cannot meet the requirements of the safe disposal which does not exceed 25 % of the total accumulated amount forming a burden on the surrounding environment. So, it was suitable to try to utilize it as a ceramic tile raw material for both economical and environmental purposes, as well as sustainability, by keeping the natural resources for the coming generations.

A basic mixture with the same composition as that used in industry was prepared. The basic mixture raw materials and the waste were analyzed by XRF. The waste was investigated by DTA and TGA. Suggested mixtures were prepared, where the waste replaces limestone in the basic mixture as 3, 5, 7, 9% (total replacement) by weight. The tile specimens were prepared for each sample; as glazed and unglazed. Both molding and firing were required to be exactly as the industrial conditions. So, the tile samples were lab prepared then fired in the production line of the factory.

Physical and chemical properties of fired samples were tested according to ISO 13006 and harmonized ES 3168 – part 6. In addition, other vitrification parameters were measured as linear firing shrinkage, loss on ignition and hardness. Fired samples of the proposed mixtures were characterized by XRD and SEM techniques. The best results were obtained for the total replacement of limestone by this waste, which is recommended.

Keywords: Limestone, quarry waste, vitrification parameters, ceramic tiles, sustainability.

1. Introduction
Nowadays, industries of all kinds are looking for alternative, less expensive, raw material and have optimized their processes in order to reduce the amount of the produced waste and reduce the corresponding environmental impact. For a while, the ceramic industry has been the target for utilization of other wastes and industries rejects. Today, it is clear that some wastes are close in their composition to the natural materials required for the traditional ceramic industry. In addition, some wastes may contain materials that are not only compatible but also beneficial in the fabrication of ceramics (Acchar et al., 2006; Montero et al., 2009; Souza et al., 2010, a & b). Recently, wastes have been constructively applied to
resources in recycling research, and different authors have investigated the incorporation of different types of wastes and quarry residues in the manufacture of traditional ceramic materials (Toya et al., 2004; Kurama et al., 2006; Christogerou et al., 2008; Reinsoa et al., 2010). Ceramic wall tiles are a multi–component system primarily composed of clays, feldspar, quartz and a minor amount of additives. Each component within the body contributes differently to the microstructure and final properties. The mostly used additives can favor the formation of eutectic points at lower firing temperatures (Sanchez, 2003).

Egyptian researchers were also very interested in recycling quarry wastes in traditional ceramics, like dolomite (Youssef, 2003, a), limestone (Youssef, 2003, b) and granite–basalt fine quarry waste (Youssef et al., 2004) and as simultaneous replacement of calcite and dolomite fine quarry waste (Youssef, 2004) as wall and floor tile for both economical and environmental benefits.

In Egypt at Gebel Attaqa area, large numbers of carbonate quarries (more than 75) in a large scale are located. Gebel Attaqa stands as a prominent hill of 850 m above sea level at the northeast corner of the Eastern Desert of Egypt. The exposed sedimentary succession ranges in ages from Cenomanian to Recent (El–Akkad and Abdallah, 1971). The quarrying is executed extensively on the mountain foot by conventional heavy machines (wheel loaders). The field inspection clarifies that, the quarried natural deposits are made up of hard, grayish yellow sometimes reddish, semi–spherical carbonate rocks of variable sizes range from 2 mm to > 30 cm. These rock sizes are cemented together by weak cement materials of fine sands and calcareous matrix. It is worth mentioning that the dolomite deposits at Gebel Attaqa exhibit a compositional variation that ranges from Ca–rich through stoichiometry to Ca–poor dolomites (Wanas, 2002).

During the quarrying processes, considerable amounts of quarry waste in the form of powders are being generated as by–product of stone crushers. This fine quarry waste is being discarded and accumulated. Utilization of the waste is a big problem considering safe disposal, environmental pollution and health hazards. Nowadays, the quarries waste is often used in settling the quarries area after the final exploitation as well as in road works. It cannot meet the requirements of the safe disposal where getting rid of the waste by these means don't exceed 25 % of the total accumulated amount. It was found that the quarry waste used in this work, contains CaO, slightly less than the limestone, and richer in silica and in addition, it contains MgO too, while the loss on ignition (L.O.I.) was very close to that of limestone, when comparing the chemical analysis, as will be shown later. So, it was suitable to try to utilize it in the manufacture of ceramic wall tiles, replacing limestone as a ceramic tile raw material for both economical and environmental concerns, as well as sustainability, by keeping the natural resources for the coming generations.

2. Experimental Work

2.1 Assessment of the raw materials

A basic mixture, almost suitable composition and usually used in the ceramic industry for producing wall ceramic tiles. It is composed of plastic clay and ball clay from Aswan quarries, two types of potash feldspars from two different sources from the Eastern desert, limestone from El–Menia quarries, kaolin from Sinai, bentonite from the north coast of Egypt, and glass sand (quartz) from the Eastern desert. The basic mixture raw materials and the waste were analyzed by X–ray fluorescence technique (XRF) where the chemical analysis was carried out using Axios (PW4400) WD–XRF Sequential Spectrometer (Panalytical,
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Netherlands), using (Rubidium) Rb–kα radiation tube at 50 kV and 50 mA. The mineralogical composition of the studied components was determined by powder X–ray diffractometry analysis. The waste was investigated by differential and gravimetrical thermal analyses (DTA and TGA).

2.2 Suggested mixtures preparation

Suggested mixtures were prepared in weight percentage, where the waste replaces limestone partially or totally in the basic mixture as shown in table 1.

Mixing and grinding were carried out on dry basis, but for easy workability, the fine ground mixtures were moistened by spraying 5 wt. % water before molding. A screen analysis for the dry mixtures was carried out by using dry sieve analysis according to the American Standard (ASTM D422-2007).

Six tile specimens of rectangular shape of 110.4 × 55.4 mm², and a thickness of approximately 8mm were prepared for each mixture sample; three of them were unglazed, while the other three were glazed. They were molded by dry pressing under 24.5 MPa. Both molding and firing conditions were required to be exactly as the industrial conditions. So, the tile samples were lab prepared then fired in a production line of the factory. It is well known that wall ceramic tiles are almost glazed but unglazed wall tile samples were prepared for the investigation purposes.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Replacement of limestone wt. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM (Basic mixture)</td>
<td>9 % Limestone.</td>
</tr>
<tr>
<td>M1</td>
<td>3 % quarry waste + 6 % limestone.</td>
</tr>
<tr>
<td>M2</td>
<td>5 % quarry waste + 4 % limestone.</td>
</tr>
<tr>
<td>M3</td>
<td>7 % quarry waste + 2 % limestone.</td>
</tr>
<tr>
<td>M4</td>
<td>9 % quarry waste + 0 % limestone.</td>
</tr>
</tbody>
</table>

2.3 Experimental firing program

Five mixtures were fired through a fast single firing technique as follows:


Firing program of the factory for wall tiles is designed as shown in Figure 1. The required firing temperature was about 1145 °C for lower part of the industrial furnace that faced the tile’s body, and 1055 °C for upper part of the industrial furnace which faced the glaze layer and the total drying and firing time did not exceed 45 minutes.
2.4 Fired samples investigations

Physical and chemical properties of fired samples were tested according to ISO 13006 and ES 3168 – part 6. In addition, three vitrification parameters were measured: Linear firing shrinkage, loss on ignition and hardness.

Fired samples of the proposed mixtures were analyzed by the XRD apparatus and also were investigated using analytical techniques of a scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDAX) of a magnification power of up to 100000x. The operating modes are either high-vacuum mode (for conductive specimens), or low-vacuum mode (for non conductive specimens without coating). This last mode was used in investigating the samples of this work.

3. Results and Discussion

3.1 Characteristics of the raw materials

3.1.1 XRD results

The XRD diffraction results of the nine raw materials forming the basic mixture demonstrated the existence of the following minerals:

1. Aswan clay: Kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], and quartz [SiO$_2$].
2. Ball clay: Kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], and quartz low [SiO$_2$].
3. Kaolin: Kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], and quartz [SiO$_2$].
4. Coarse feldspar: Albite, ordered [NaAlSi$_3$O$_8$], quartz [SiO$_2$], and anorthoclase [(Na$_{0.667}$K$_{0.333}$) (AlSi$_3$O$_8$)].
5. Fine feldspar: Albite, ordered [NaAlSi$_3$O$_8$], microcline [K(Si$_{0.75}$Al$_{0.25}$)O$_8$]], and quartz [SiO$_2$].
6. Bentonite: Quartz [SiO$_2$], calcite [CaCO$_3$], montmorillonite–15A [Ca$_{0.2}$(Al,Mg)$_2$Si$_4$O$_{10}$(OH)$_2$.4 H$_2$O], kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], and gypsum [CaSO$_4$(H$_2$O)$_2$].

7. Glass sand: Quartz [SiO$_2$], kaolinite [Al$_2$Si$_2$O$_5$(OH)$_4$], albite low [NaAlSi$_3$O$_8$], calcite [Ca(CO$_3$)], and dolomite [CaMg(CO$_3$)$_2$] as impurity.

8. Albite: Albite high [NaAlSi$_3$O$_8$], calcite [CaCO$_3$], quartz [SiO$_2$], and biotite [KFeMg$_2$(AlSi$_3$O$_10$) (OH)$_2$].

9. Limestone: Calcite [CaCO$_3$], and quartz [SiO$_2$].

Figure 2 shows the XRD pattern of the quarry waste. The calcite [CaCO$_3$], dolomite [MgCa(CO$_3$)$_2$], quartz [SiO$_2$], and ankerite [CaMg$_{0.27}$Fe$_{0.73}$(CO$_3$)$_2$], were identified in this waste.

![XRD pattern of quarry waste](image)

**Figure 2:** The XRD pattern of the quarry waste.

### 3.1.2 Chemical composition

The chemical composition and loss on ignition of the raw materials used in this work are listed in table 2 (a & b). The analyzed raw materials, except the quarry waste, show the expected typical chemical composition. The waste is rich in calcium followed by less amounts of silica and magnesium and traces of the other element oxides matching with the type of existing phases. The waste material is accompanied by a noticeable magnesium oxide content (7.15 wt. %), which is responsible for the dark coloring of the natural waste.

Chemical analysis of the used raw materials is in good agreement with the XRD analysis. Small differences are attributed to the fact that raw materials are minerals that may contain water or liberated components which demonstrates the present volatilization of the analyzed materials during the firing process (L.O.I.).
The quarry waste was subjected to a DTA and TGA, in order to study the thermal effects. Figure 3 illustrates the pattern of the DTA–TGA of the quarry waste. It is clear that the gases will evolve before the required firing temperature is reached, ensuring no bubbles at the tile surface. Endothermic reaction curves in the DTA pattern matched well with the other detected phases by the XRD, such as the decomposition of carbonates (calcite and dolomite). Todor (1976) stated that calcite mineral will begin to decompose at about 675°C accompanied with evolution of CO$_2$ gas, and at 950°C its decomposition will be completed. Also, the marked curves at 791°C and 854°C in the DTA patterns are typical for the thermal behavior of dolomite transformations. The TGA pattern approves the observed high loss on ignition due to releasing of the CO$_2$ gas from the carbonates. This is confirmed as appeared clearly in table 2.
3.1.4 Screen analysis of mixtures

Figure (4) shows the cumulative screen analysis results of the mixtures before molding (McCabe and Smith, 2005).

Figure 3: DTA and TGA patterns of the quarry waste.

Figure 4: Cumulative fraction retained at different limestone replacements by quarry waste.
In order to obtain a sharper parameter of the effect of waste replacement on fineness of the prepared mixtures, volume – surface mean diameter ($D_s$) which is defined by Zhang (1998) and McCabe and Smith (2005) is shown in the following equation:

$$D_s = \frac{1}{\sum_{i=1}^{n} (x_i / D_{pi})}$$

Where $x_i$ = mass fraction in a given increment, and $D_{pi}$ = average diameter. The $D_s$ value was calculated and presented in Figure (5).

It is observed that the volume surface mean diameter decreases, and the fineness increases, as the replacement percentage increases, compared to the basic mixture. The decreasing trend can be clearly shown in Figure (5). This means that the addition of the waste affects the fineness of the mixture although all the mixture components are ground at once after mixing, but the odd behavior of the 7 % replacement sample is reflected over the coming successive results, as shown later.

**Figure 5:** Volume – Surface mean diameter at different limestone replacements by quarry waste.

### 3.2 Fired samples investigations

#### 3.2.1 Vitrification parameters

Linear firing shrinkage, loss on ignition, water absorption, breaking strength and modulus of rapture of fired samples were all measured and represented in the Figures (6 - 10), against the percentage replacement of quarry waste. Table (3) shows the physical properties, and Table (4) shows the chemical properties, all measured in accordance with both International and harmonized Egyptian Standards (ISO 13006, and ES 3168 – part 6).

As shown in Figure (6), the quarry waste replacement tends to reduce the firing shrinkage either for glazed or unglazed tiles, and the total replacement (9 %) showed the lowest firing shrinkage. On the other hand, the 5 % replacement had the same value of firing shrinkage.
Figure 6: Effect of percentage replacement of quarry waste on the linear firing shrinkage.

From Figure (7), the loss on ignition which is expected is referring to the chemical composition analysis and DTA–TGA, but, the full replacement (9 %) of the waste showed the best results. Referring to table (2), this result matches with L.O.I. of waste (39.16 %) and limestone (41.66 %). It was also observed that there is no difference at all between glazed or unglazed tiles.

From Figure (8), the basic mixture samples of the glazed tiles showed less water absorption than the unglazed tiles, which is an expected result. It can be concluded that the replacement of quarry waste, specially the total replacement (9 %), had better water absorption than the basic mixture itself, for both glazed and unglazed tiles.

From Figures (9 and 10), dealing with the mechanical strength, where the patterns did not differ much, the best results were obtained at the total replacement (9 %) of the quarry waste for the glazed tiles, although all the obtained results are within standards limits for wall tiles (breaking strength over 400 N).

Figure 7: Effect of percentage replacement of quarry waste on the loss on ignition.
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Figure 8: Effect of percentage replacement of quarry waste on the water absorption.

Figure 9: Effect of percentage replacement of quarry waste on the modulus of rupture.

Figure 10: Effect of percentage replacement of quarry waste on the breaking strength.
3.2.2 Physical and chemical properties

The results listed in Tables (3 and 4) clarify that all the prepared samples are in conformity with ES and ISO standards, and the hardness is not affected at all.

As long as the gloss measurement depends on the frit and glaze types, so, its change is apart from the waste addition. The results of the resistance to staining, and resistance to chemicals are also in conformity with the applied standards.

**Table 3: Physical properties of the fired samples.**

<table>
<thead>
<tr>
<th>Properties</th>
<th>BM</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>ES or ISO Limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Glossy (%)</td>
<td>54.5%</td>
<td>51.3%</td>
<td>49.3%</td>
<td>51%</td>
<td>52%</td>
<td>-----</td>
</tr>
<tr>
<td>Hardness (Moh)</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
<td>-----</td>
</tr>
<tr>
<td>Thermal shock resistance</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
<tr>
<td>Craze resistance</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
<td>Pass</td>
</tr>
</tbody>
</table>

- Not mentioned in Reapproved ES or ISO Standards.

**Table 4: Chemical properties of the fired samples.**

<table>
<thead>
<tr>
<th>Properties Mixture</th>
<th>Tiles type</th>
<th>Resistance to staining</th>
<th>Resistance to chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glazed Tiles</td>
<td>Grade (5)</td>
<td>GLA (V)</td>
<td>GA (V)</td>
</tr>
<tr>
<td>BM</td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>ULB</td>
</tr>
<tr>
<td>Glazed Tiles</td>
<td>Grade (5)</td>
<td>GLA (V)</td>
<td>GA (V)</td>
</tr>
<tr>
<td>M1</td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>UA</td>
</tr>
<tr>
<td>Glazed Tiles</td>
<td>Grade (5)</td>
<td>GLA (V)</td>
<td>GA (V)</td>
</tr>
<tr>
<td>M2</td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>UA</td>
</tr>
<tr>
<td>Glazed Tiles</td>
<td>Grade (5)</td>
<td>GLA (V)</td>
<td>GA (V)</td>
</tr>
<tr>
<td>M3</td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>UA</td>
</tr>
<tr>
<td>Glazed Tiles</td>
<td>Grade (5)</td>
<td>GLA (V)</td>
<td>GA (V)</td>
</tr>
<tr>
<td>M4</td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>UA</td>
</tr>
<tr>
<td>ES or ISO Limit</td>
<td>Glazed Tiles</td>
<td>Min.Grade (3)</td>
<td>GLB (V)</td>
</tr>
<tr>
<td></td>
<td>Un–Glazed Tile</td>
<td>-----</td>
<td>UB</td>
</tr>
</tbody>
</table>

**3.3 XRD investigation of the fired samples**

Results of the XRD investigation are recorded in Table 5. The detected phase in the different fired tile samples are quartz as a major component and albite as a minor phase in the all tested fired samples but only the kyanite phase (Al₂SiO₅) in the sample of mix M4 (full replacement of limestone by the quarry waste) is identified as a minor newly formed phase.
However, the fired samples are composed of the same crystalline phases of quartz and albite, except for the fired sample containing total replacement by the quarry waste. It is characterized by presence of kyanite mineral as additional phase. Regarding that the mixture includes both glassy and crystalline phases, these phases are result of interactions, at high temperatures, between the basic components (clay, feldspar, and quartz) themselves and with any present additive materials (either limestone or quarry waste). The kyanite is a metamorphosed mineral that represents a refractory material and has a high melting point, low thermal conductance, and maintains its strength up to about 1100 °C. Its appearance in the 9 % replacement fired sample may be due to the excess of silica as detected in the chemical analysis of the waste (8.87wt.%) compared with the limestone (2.51 wt. %).

Table 5: Detected phases in the fired powdered tile samples.

<table>
<thead>
<tr>
<th>Mix</th>
<th>Phases</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>BM</td>
<td>Quartz</td>
<td>Albite</td>
</tr>
<tr>
<td>M2</td>
<td>Quartz</td>
<td>Albite</td>
</tr>
<tr>
<td>M4</td>
<td>Quartz</td>
<td>Albite, kyanite</td>
</tr>
</tbody>
</table>

3.4 SEM and EDAX investigations

Figures (11-13) show the SEM micrographs of the fracture surfaces of the fired samples of basic mixture, 5 %, and 9 % replacement with the quarry waste, respectively. It can be observed that, all the SEM micrographs depict a good interlocked microstructure and a general glassy matrix in which different crystal phases are present.

All micrographs with their corresponding EDAX results manifest the following characteristic features:

1. Well appeared agglomerated and isolated particles corresponded to the quartz and feldspars phases.
2. Clear occurrence of the vitreous phase in the full replacement sample (9 % waste), probably increased in comparison with the basic mixture and 5 % replacement with the quarry waste. The rest of the feldspars usually appeared in the fired samples when initial feldspars agglomerate forming large enough crystals (Reinosa et al. 2010).
3. It is identified that at the full replacement by the quarry waste (Figure 13) more particles are bonded, the liquid phase with a strong interface is increased and the figure shows a structure with fewer pores. The sign of good vitrification is in agreement with the results of vitrification parameters previously tested.

4. Basic mixture: EDAX was spotting on three crystals, the big crystal to the left side; the main oxides were Si, Al, with minor Na, K, and Ca. It is a big crystal of silica surrounded by small crystals of albite as discovered by XRD. The same major oxides were observed by EDAX spotting on the smaller crystal on the opposite side (right hand), but with more Ca, and Fe. The 3rd EDAX spot at the bottom crystal, distinguished by its dark color with few white small crystals on its surface, with much high Si, Al, and existence of K, Na, could be a big silica crystal with few albite and very few feldspars.

5. 5% replacement: EDAX was spotting on two crystals, not far from each others on the middle right hand side; the one above had high Si, Al, and little Ca, Fe, and Na. This is due to its whiter color, could be albite scattered over a silica crystal, while the lower one is only silica crystal.
6. 9 % replacement (total replacement): EDAX was spotting on the white crystal up the photo; it showed high Al relative to Si and minor Fe, Ca, and Na. It agrees with XRD as silica, albite, kyanite, but the darker borders could be iron compound small crystals which did not show in XRD pattern.

As these replacements showed the best physical and mechanical properties, it can be noticed that it does not contain the big crystals as shown in the basic mixture and 5 % replacement, which approves the grain growth of crystals that might leave larger voids around it.

4. Conclusions

The quarry waste resulting from the extraction of aggregate quarries of G. Attaqa can be utilized by adding it as a partial or total replacement of the raw limestone extracted from El–Menia quarries, to the basic mixture used for manufacture of ceramic wall glazed tiles from Egyptian raw materials. It is recommended to add this waste in a maximum replacement of 9 wt. % which achieved better properties than the basic mixture, as it conform to both International and harmonized Egyptian standards of ceramic wall tiles. This addition will be beneficial both environmentally and economically, and it also helps sustainability.

Acknowledgments

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5. References


5. ES 3168 – part 6 (2005), "Dry pressed ceramic tiles with water absorption > 10% group BIII", Egyptian Organization for Standardization and Quality (EOS), Cairo, Egypt, pp 1–19.


