Optimization of Alkali Activated Grog/Ceramic Wastes Geopolymer Bricks

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ABSTRACT: In recent years there has been a great deal of interest and support worldwide in using construction and demolition waste as ceramic as well as clay brick wastes (grog) for production of aggregate material which can then be reused for road base courses or construction backfill materials, and other engineering applications. However, they can also be employed as supplementary cementitious materials or even as raw material for alkali-activated binder for producing more value binders that can be applied in various building applications. Geopolymer bricks prepared by partial binder substitution of ceramic by clay brick wastes in the ratio from 0 up to 100%, while the used fine sand was in the ratio of 15% from the total weight, also sodium hydroxide activator was used in the ratio of 8% of the total eight. The properties of the produced geopolymer bricks have been studied through measurement of compressive strength, water absorption, FTIR, XRD and SEM imaging. Results demonstrate the possibility of using alkali activated ceramic and grog materials in producing heavy duty building with compressive strength values more than 35 MPa up to 20% grog increase, however further increase results in lowering strength values as a result of increase of crystalline content and sufficiency of the used activator to dissolve all the crystalline fractures.

KEYWORDS: GEOPOLYMER, SUSTAINABILITY, ACTIVATION, CLAY BRICKS, CERAMIC WASTES.

I. INTRODUCTION

Carbon dioxide emission from the concrete production is directly proportional to the cement content used in the concrete mix; the cement industry is responsible for about 6% of all CO₂ emissions, because the production of one ton of Portland cement emits approximately one ton of CO₂ into the atmosphere. The geopolymer technology which offers other possible cementing materials could reduce the CO₂ emission to the atmosphere caused by cement industries by about 80% [1].

Recycling of building waste can reduce the need for energy and natural resources and can also reduce both the need for land area for extracting resources and the need for land area for landfill. The benefits of recycling depend on the materials and the form of recycling [2]. The Ceramic World Review survey [3] reported a world tile production of 9515 million square meters in 2010, of which 96.0% (9170 Mill m²) implied the 50 major manufacturing countries.

Despite the vast majority of the ceramic wastes being used in landfills with a low added value, prior research has observed not only a slight increase in water absorption and permeability when replacing traditional coarse aggregates with ceramic wastes, but also superior durability when traditional sand was replaced. Furthermore, several studies have confirmed the potential of ceramic wastes to produce pozzolanic cements [6-9]. Among them, Puertas et al. [7] not only successfully used up to 35.0% of certain types of ceramic wastes as pozzolan admixtures, but also proved their suitability as raw materials for Portland cement clinker production.

Although ceramic materials can be used as cement admixtures and concrete aggregates, in these applications only a portion of cement is replaced (usually 10-35%) so, it is interesting to develop binders that are made entirely, or almost entirely, from waste materials [10]. The success of converting waste materials into useful products following this process has been extensively proved in materials such as silicoaluminous fly ash, metakaolin or blast furnace slag [12-
and its suitability has also been confirmed for other waste materials, such as hydrated-carbonated cement [15], glass [16] or ceramic materials [17-19].

In the study by Puertas et al. [17], six different ceramic wastes were mixed with NaOH and sodium silicate solution to give a maximum compressive strength of 13 MPa for pastes cured for 8 days at 40°C. Mortars with similar compressive strengths (14 MPa) were obtained by Reig et al. [18, 19] by mixing red hollow bricks with a NaOH solution and by curing samples for 7 days at 65°C.

According to Baronio and Binda [20], powder from bricks is expected to present pozzolanic activity as the crystalline network is destroyed when the structural hydroxyl groups of clay minerals (phyllosilicates or sheet silicates) are lost (600 °C -900 °C). Zanelli et al. [21], which analyzed 93 porcelain stoneware samples, porcelain tiles are also presumed to react. Their mineralogy is composed of some crystalline phases, such as quartz, mullite or feldspars, which are dispersed throughout a main vitreous phase whose proportion varies from 40% to 80% depending on the sample. According to Vieira et al., [22] grog waste could be used to improve the mechanical properties, workability, and chemical resistance of conventional ceramic brick. The recycling of grog waste in ceramic bricks shows highly positive results in terms of environmental protection, waste management practices, and saving of raw materials [23].

This paper aimed to develop new geopolymer binders by the alkali activation of (grog and ceramic waste), elucidate the optimum ratio from both materials and to analyze the influence of the alkali activator concentration on the mechanical strength, water absorption, bulk density and microstructure of the binders formed.

II. EXPERIMENTAL PROCEDURES

II. 1. MATERIALS

Materials used in this investigation are Ceramic wastes and clay brick wastes (grog) brought from 6th October landfills, Egypt. Sodium hydroxide (NaOH) with purity 99 % in the form of pellets used as alkali activators, obtained from SHIDO Co., Egypt, The used sand dunes for mortar preparation are sourced from fine sand (<1 mm) from Oases (Wahat)-Road, Egypt.

The chemical compositions of the starting raw materials are given in Table (1). Mineralogical characterization of the raw materials was done using X-ray diffraction analysis in powder form as represented in (Fig. 1).

Clay brick wastes composed of high percentage of silica and alumina, and low percentage of calcium, magnesium and alkalis, which are considered the main component in the geopolymer formation; this confirmed also by XRD pattern where quartz, albite, are predominant in addition to lesser amounts of hematite (Fe₂O₃). However, ceramic wastes composed of nearly the same constituent as clay bricks but with alkalis about 2.15 %. The mineralogical data illustrate that it is composed of quartz and anorthite (calcium sodium aluminium silicate).

<table>
<thead>
<tr>
<th>Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>MnO₂</th>
<th>Fe₂O₃</th>
<th>P₂O₅</th>
<th>Cl</th>
<th>L.O.L</th>
<th>SrO</th>
<th>BaO</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic Wastes</td>
<td>63.50</td>
<td>18.00</td>
<td>4.84</td>
<td>4.69</td>
<td>0.42</td>
<td>0.22</td>
<td>1.93</td>
<td>1.74</td>
<td>0.33</td>
<td>0.09</td>
<td>0.43</td>
<td>0.06</td>
<td>1.02</td>
<td>-</td>
<td>-</td>
<td>99.83</td>
<td></td>
</tr>
<tr>
<td>Clay Bricks Waste (Grog)</td>
<td>60.00</td>
<td>14.00</td>
<td>8.06</td>
<td>5.76</td>
<td>1.44</td>
<td>2.74</td>
<td>1.24</td>
<td>1.42</td>
<td>1.05</td>
<td>0.04</td>
<td>0.16</td>
<td>0.05</td>
<td>3.72</td>
<td>-</td>
<td>-</td>
<td>99.77</td>
<td></td>
</tr>
<tr>
<td>Fine Sand (Sand dunes)</td>
<td>89.91</td>
<td>2.00</td>
<td>1.45</td>
<td>1.56</td>
<td>1.91</td>
<td>0.87</td>
<td>0.37</td>
<td>0.06</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.12</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
<td>99.98</td>
<td></td>
</tr>
</tbody>
</table>
II. GEOPOLYMERIZATION AND CURING

Geopolymer mixes were made by hand-mixing raw materials of each mixture passing a sieve of 90 μm with the alkaline activator (8% NaOH of the total weight) for 10 min and a further 5 min with an electronic mixer as represented in Table 2 and then with. The water-binder ratio (w/b) was 0.288: 0.339 by mass. The paste mixture was cast into 25×25×25 mm cubic-shaped moulds, vibrated for compaction and sealed with plastic sheet to minimize any loss of evaporable water. The mix design of the materials used in this section was tabulated in details in Table (2); where the water content increases with the increase of grog content as the increased silica content in grog absorbs water. The table also illustrate the oxide ratios of the reacting raw materials, where the silica/alumina increases with grog content from 3.62:4.29, while the total alkali to silica is in the range of 0.178 to 0.179 and will be compared with respect to the optimum range of oxide molar ratios [24, 25]: 0.2<M₂O/SiO₂<0.48, 3.3<SiO₂/Al₂O₃<4.5 resulting in three dimensional networks with a more branched structure and so homogeneous and compact structure formed and M₂O/Al₂O₃, 0.8 to 1.6 [26].

Table (2): Composition of the geopolymer mixes. (Mass, %)

<table>
<thead>
<tr>
<th>Mix no.</th>
<th>Ceramic waste (CW)</th>
<th>Grog</th>
<th>Sand (&lt;1mm)</th>
<th>NaOH</th>
<th>Water/ binder</th>
<th>T.M₂O/Al₂O₃</th>
<th>SiO₂/Al₂O₃</th>
<th>T.M₂O/ SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>A'</td>
<td>100</td>
<td>-</td>
<td>15</td>
<td>8</td>
<td>0.288</td>
<td>1.01</td>
<td>3.62</td>
<td>0.164</td>
</tr>
<tr>
<td>B'</td>
<td>80</td>
<td>20</td>
<td>15</td>
<td>8</td>
<td>0.313</td>
<td>1.04</td>
<td>3.73</td>
<td>0.164</td>
</tr>
<tr>
<td>C'</td>
<td>60</td>
<td>40</td>
<td>15</td>
<td>8</td>
<td>0.318</td>
<td>1.08</td>
<td>3.85</td>
<td>0.164</td>
</tr>
<tr>
<td>D'</td>
<td>40</td>
<td>60</td>
<td>15</td>
<td>8</td>
<td>0.319</td>
<td>1.12</td>
<td>3.98</td>
<td>0.165</td>
</tr>
<tr>
<td>E'</td>
<td>20</td>
<td>80</td>
<td>15</td>
<td>8</td>
<td>0.329</td>
<td>1.16</td>
<td>4.12</td>
<td>0.165</td>
</tr>
<tr>
<td>F'</td>
<td>-</td>
<td>100</td>
<td>15</td>
<td>8</td>
<td>0.339</td>
<td>1.21</td>
<td>4.29</td>
<td>0.165</td>
</tr>
</tbody>
</table>

All mixes were left to cure undisturbed at ambient temperature for 24 hours, and then cured at a temperature of 40 °C and 100 % relative humidity. At the end of the curing regime, the specimens were subjected to the compressive...
strength measurements and then the resulted specimens were subjected for stopping of the hydration process by drying the crushed specimens for 24 hrs at 105 °C [27] and then preserved in a well tight container until the time of testing.

II.3. METHODS OF INVESTIGATION

Chemical analysis was carried out using Axios, Wave Length Dispersion X-ray Fluorescence (WD-XRF) Sequential Spectrometer (Panalytical, Netherland, 2009). The X-ray diffraction -XRD analysis was carried out using a Philips PW3050/60 Diffractometer. The data were identified according to the XRD software. Perkin Elmer FTIR Spectrum RX1 Spectrometer (Fourier Transformation Infra-Red) was used to evaluate the functional groups in the sample. Small amount of potassium bromide (KBr) and geopolymer powder were mixed and placed in the sample holder then the mix was pressed at 295 MPa for 2 minutes to produce specimen for examination, The wave number was ranging from 400 to 4000 cm⁻¹ [28,29].

Water absorption measurements of the bricks were carried out according to ASTM C140 [30]. The percentage absorption was calculated using the equation:

\[
\text{Absorption (\%)} = \frac{[(W2 – W1)/ W1] \times 100}{100}
\]

where W1 = weight of specimen after complete drying at 105°C, W2 = final weight of surface dry sample after immersion in water for at least 24 hours.

Compressive strength tests were carried out using five tones German Brüf pressing machine with a loading rate of 100 Mpa/s determined according to ASTM-C109 [31]. The microstructure of the hardened specimens was studied using Scanning Electron Microscopy- SEM Inspect S (FEI Company, Netherland) equipped with an energy dispersive X-ray analyzer (EDX). Removing of the free water was accomplished by using drying of the crushed specimens for 24 hours at 105°C [27].

III. RESULTS AND DISCUSSION

III.1. FOURIER TRANSFORM INFRARED FTIR SPECTROSCOPY

Figure (2) showed the IR spectra of geopolymer products cured at 28 days synthesized using 8% NaOH solution as activator. The FTIR bands are as follows: stretchy vibrations of OH bond at about 3500 cm⁻¹, 1650 cm⁻¹ related to O-H bending modes of molecular water, asymmetric stretching vibration (Si-O-Si) at 1100 cm⁻¹ for non-solubilized silica, asymmetric stretching vibration (T-O-Si) at 980 cm⁻¹ where T= Si or Al, symmetric stretching vibration (Al-O-Si \text{ ) in the region} 778 cm⁻¹, symmetric stretching vibration (Si-O-Si \text{ ) in the region} 688 cm⁻¹ and bending vibration (Si–O–Si) and O-Si-O in the region 450 cm⁻¹. All the tested samples contain carbonate species pointed out by the presence of the large absorption band near 1450 cm⁻¹, related to asymmetric stretching and out of plane bending modes of CO₃²⁻ ions [32].

The pattern indicates an increased growth of the main asymmetric band at about 980 cm⁻¹ along with the decreased intensity of asymmetric vibration band (Si-O-Si) at about 1100 cm⁻¹ for non-solubilized particles coming from the crystalline clay brick waste (grog) increase. Also the main asymmetric band at 980 cm⁻¹ turned to be wider with the increase of the added grog up to 20% reflecting the increase of the geopolymerization. Further increase in the grog (40%) leads to decrease in the symmetrical band of T-O-Si with the shifting towards high wave number reflecting the decrease in the vitreous component in the geopolymer network this is in conjunction with the increased intensity of the shoulder at about 1100 cm⁻¹ for crystalline unreacted materials which emphasize the decrease in the reactivity with increased grog content, also, using 40% grog leads to increase in the carbonate band at about 1470 cm⁻¹, resulting from carbonation of free alkalis within the matrix as the alkalis used are not capable of broking all the crystalline chains of grog material and so will be susceptible for carbonation.
Figure (2): FTIR spectra of 28 days cured (40 °C and 100% R.H.) geopolymer specimens having various grog content as a partial replacement of ceramic waste. 1: Stretching vibration of O-H bond, 2: Bending vibrations of (HOH), 3: Stretching vibration of CO3-4, 4: Asymmetric stretching vibration (Si-O-Si), 5: Asymmetric stretching vibration (T-O-Si), 6: Symmetric stretching vibration (Al-O-Si), 7: Symmetric stretching vibration (Si-O-Si), 8: Bending vibration (Si-O-Si and O-Si-O).

Figure (3) showed the effect of curing on mix 20/80 grog/ceramic waste at 7, 28, 60, 90 days. A comparison of the wave numbers shows that Si-O stretching band shifts progressively towards lower wave numbers from mix B’ 7 days to mix B’ 90 days reflecting the increase of the amorphous geopolymer network. Also, the main asymmetric band at about 1027 cm⁻¹ for N-A-S-H as well as C-A-S-H which represent the amorphous geopolymer structure as well as calcium aluminate phases that seems to be in a maximum intensity with curing time increase.

Figure (3): FTIR spectra of geopolymer specimens having various 40 % slag as a partial replacement of grog. 1: Stretching vibration of O-H bond, 2: Bending vibrations of (HOH), 3: Stretching vibration of CO3-4, 4: Asymmetric stretching vibration (Si-O-Si), 5: Asymmetric stretching vibration (T-O-Si), 6: Symmetric stretching vibration (Al-O-Si), 7: Symmetric stretching vibration (Si-O-Si), 8: Bending vibration (Si-O-Si and O-Si-O).

III.2. X-RAY DIFFRACTION ANALYSIS

The XRD result of 28 days mixes A’, B’, and C’ with various grog content are shown in Fig. (4). The chart indicates that the reaction of grog and ceramic waste with NaOH results mainly in new alkaline sodium aluminosilicate (these phases are zeolitic minerals) and calcium silicate hydrate phases, partial dissolution of the alumina-silica constituents into fully polycondensed amorphous phase as confirmed by the presence of the dominant amorphous hump from 2 theta =17°: 35° in the XRD pattern.

It can be noticed an increased in the Anorthite peak as feldspar phase results from increased grog ratio as well as increased zeolite phase formation as a results of increased Si/Al ratio with grog increase as shown in details in table 2, these phases results in low contact between amorphous geopolymer networks and so leads to decrease in the intensity of the formed geopolymer structure. Quartz occurs as a major phase in the specimen due to the added sand as a filler and hematite from the raw material. Also, an increased water content with increased grog ratios favored the formation of zeolite as indicated which has lower reactivity against formation of three dimensional network., this in accordance
with the increased hematite content with grog which has precipitate as iron hydroxide with time and so decrease medium alkalinity and so zeolite formed in a greater extent [11].

However, B’ achieved the lower zeolite content in addition to the increased CSH phases that will act as nucleation sites for geopolymer formation and accumulation and so form a more dense and compact structure as will be shown later in SEM section formation beside formation of calcium silicate hydrate (CSH). Also, it can be noticed an increased broadness of band in the region of 6-10° 2Ө for aluminosilicate gel as compared with other mixes.

Figure (5) showed the effect of curing time on mix 20/80 grog/ceramic waste (B’) at 7, 28, 60, 90 days which is the optimum mix elucidated from the previous figure. It is noticed that the amount of amorphous phases slightly increased with curing time. Also, the crystallinity of crystalline minerals as quartz and anorthite decreased with curing time because of increasing geopolymerization.

An increase in the CSH content is also noticed with the increase of curing time as indicated from the increased broadness at 29.4° that results from the interaction of freely dissolved silica with Ca species in the matrix forming CSH, which accumulate in the open pores and transformed into crystalline form at the later curing ages [33]. Also, increase broadness of band in the region of 6-10° 2Ө for aluminosilicate gel.
III.3. SCANNING ELECTRON MICROSCOPY (SEM)

The scanning electron micrograph of hardened ceramic waste/grog geopolymer mortar specimens activated by using 8% NaOH solution are shown in (Fig. 6). Alkaline activation of ceramic waste lead to the dissolution of the alumino-silicate materials forming tetrahedral polymer that linked together forming three dimensional chains spread over surface (Fig. 6-A).

Geopolymer specimens formed of 20/80 grog/ceramic waste (B') results in an enhancement in the morphological structure of the resulting geopolymer illustrated as from the massive geopolymer plats that fill most of the matrix in addition to CSH binder phases that spread within the structure and bound most of the formed oligomer by forming nucleation sites for the accumulation of the geopolymer[34].Van Deventer and co-workers suggested that presence of calcium in solid waste materials will provide extra nucleation sites for precipitation of dissolved species and cause rapid hardening [11]. Adding the grog up to 20% as represented in Fig. (6-B) resulting in the formation of massive crystalline structure, where resulting in additional CSH and CSAH that will strengthen the microstructure and form a more dense and compacted structure.

Further increase in the grog 40% grog[C'] (Fig. 6-C), the micrograph turns to a less dense structure with the increased bright spots on the surface related to iron compounds as illustrated before in XRD, the zeolite structure with high Si/Al ratio spread in the specimens and so inhibit the progress in the three dimensional network and so negatively the morphological structure as illustrated clearly in Figure (4-C); also the hetroegnity of the structure is a peredominant feature of this micrograph.
Results of compressive strength of the hardened geopolymer mortar specimens cured up to 90 days are shown in (Fig. 7). It is clear that the compressive strength of activated ceramic waste/grog increases with time for all activated mortar specimens, which attributed to the continuous pozzolanic reaction of ceramic waste and grog binder materials. The geopolymeric mortars containing 20: 80% from grog and ceramic waste, respectively, exhibited the highest compressive strength for all curing time up to 90 days. The compressive strength values are both higher in specimens with high Si/Al ratio and a high alkali concentration. Decreasing the alumina content reduces the amount of alkali required for the activation of the solid amorphous aluminosilicate. The ceramic waste material has a pozzolanic material and it has a very good contain of reactive silica which is responsible for higher strength [35].

According to the results obtained by Kourtis et al. [16], ceramic waste particles are expected to influence the mechanical properties of the matrix more positively, as they are stronger and better bonded to the matrix than clay brick particles. The data of compressive strength confirmed and emphasized by XRD and FTIR as and increased zeolite content with increased crystalline grog content in addition to shifting of the main asymmetric band of Al-O-Si to a lower wave number reflecting the increased vitreous content for the 20% replacement by grog, also the increased CSH
emphasized at about 3500 cm\(^{-1}\) in FTIR and at about 29.4 ° (2Θ) in XRD which is coherent with the increased homogeneity and compaction for the aforementioned mix.

III.5. WATER ABSORPTION

The water absorption of the cured geopolymer specimens are represented in Fig. (8), indicate the decrease of water absorption with the increase of curing time as a result of progressive hydration with the formation of CSH and geopolymer, leading to a denser structure [34]. The results indicate also, the reverse trend of water absorption as compared with compressive strength, where the water absorption decrease up to 20% grog and increase in all specimens up to 100% grog. The decreasing in water absorption due to formed CSH and increased geopolymer formation, while the increase in absorption with grog confirm the increased zeolite formation as it acquire higher water content within its structure.

IV. CONCLUSION

The main conclusions derived from this work can be summarized as follows:
1. Alkaline activation of aluminosilicate wastes in the presence of ceramic wastes and clay brick wastes (grog) results in the formation of sustainable building materials with efficient features up to 20 % grog replacement
2. Increasing the grog replacement results in an increase in the crystalline content with low potential for increasing the structure homogeneity.
3. Compressive strength of 20 % grog achieved 445 and 490 at 28 and 90 days which can be used in the formation of heavy duty bricks [36]and in severe aggressive medium as reported by ASTM C-62 [37].
4. Ceramic waste particles are expected to influence the mechanical properties of the matrix more positively, as they are stronger and better bonded to the matrix than clay brick waste (grog) particles.
5. Possibility of waste ceramic and clay brick waste as recycled material used in geopolymer mortar production increases and may beneficial to decreases further CO\(_2\) burden to the environment and helpful for conserve natural resources.
6. Water absorption of mostly all the produced geopolymer bricks are in the range 13 to 16% which is lower than required for the severe weathering clay bricks according to ASTM-C62 [37].

ACKNOWLEDGMENTS

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VI. REFERENCES