CHARACTERIZATION AND UTILIZATION OF OIL SHALE ASH MIXED WITH GRANITIC AND MARBLE WASTES TO PRODUCE LIGHTWEIGHT BRICKS

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Abstract. This study aimed to investigate the possible utilization of different waste materials such as oil shale ash mixed with marble and granite sludge, to produce low-cost compressed strong lightweight masonry bricks and alike. Various mixtures of the three wastes were prepared with different proportions by weight. Characterization of the produced bricks was conducted by carrying out laboratory tests including but not limited to absorption, permeability, dry density, void ratio, thermal conductivity and compressive strength. On average, compressive strength values were 3.5 and 3.8 MPa at 28 days for ash-granite and ash-marble sludge, respectively, compared with the specified value of 3.5 MPa for cement bricks. The strength of ash-based samples is attributed to the alkali-pozzolanic reaction in the tested composites. On the other hand, the tested samples showed a very low permeability ranging from $3 \times 10^{-6}$ to $7.2 \times 10^{-6}$ cm/sec, in addition to the low dry density between 1.14 and 1.27 g/cm$^3$. Moreover, a low thermal conductivity of about 0.1 and 0.2 W/m K was measured for the produced bricks. Such results are encouraging to investigate further the properties and feasibility of production of such new bricks which would be used to build new low-income houses.

Keywords: oil shale ash, marble sludge, granite sludge, compressive strength, thermal conductivity, lightweight bricks.

1. Introduction

Huge resources of oil shale are located in many countries, e.g. USA, Morocco, Brazil, Russia and Jordan [1]. These resources are expected to be an alternative source of fuel in the near future, especially in Jordan [2].

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Estonia is considered as the largest shale oil producer and consumer in the world [3]. In China, about 5,000 tons of shale oil is produced on daily basis [4]. Large amounts of high-calcium oil shale ash waste are expected to be produced as a result of processing oil shale through retorting to yield shale oil or direct combustion to generate electrical power.

Recently, an agreement was signed to construct a direct combustion oil shale-fired power plant with an installed capacity of 470 (2 × 235) MW and a consortium led by the Estonian firm Eesti Energia using the fluidized bed boiler technology. This power station will be constructed within the next 2–3 years in the Attarat area, Jordan, about 100 km south-east of Amman. Ash disposal is considered as a major environmental problem. Leaching of potentially toxic substances into soils and groundwater, reductions in plant establishment and growth due to primarily adverse chemical characteristics of the ash were investigated thoroughly [5, 6].

Ash leachates are characterized by their high alkalinity (pH $>10$) and toxicity [7]. But the spent ash could be used as feedstock in different applications, including the cement industry, due to its cementitious characteristics.

Another type of considered solid wastes is sludge which is produced at marble and granite workshops through cutting and polishing of these rocks for construction purposes. The impacts of such waste on the environment are numerous: disturbance of natural landscape and air pollution resulting from fine particulates in addition to the possible pollution of ground water through infiltration and/or percolation.

Marble and granite sawing powder wastes represent one of the major worldwide environmental problems and, to alleviate these problems, these wastes are used in brick manufacturing [8].

The use of oil shale ash through construction aspects will help minimizing negative environmental and ecological issues. Oil shale ash is proved as a self-cementitious material composed of an alkali part represented by its high content of CaO, and a Pozzolanic part composed of SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$; it was used in stabilization of high-plasticity clay and marl [9]. It was also utilized for stabilization of phosphatic wastes as sub base material for road construction [10]. Oil shale ash was used as a complete replacement of ordinary Portland cement (OPC) to produce blinding concrete of compressive strength reaching 9.0 MPa at 28 days’ age under normal laboratory conditions [11]. The use of marble sludge wastes in building blocks production has proven to be safe for health and environmentally friendly [12]. Theoretically, any material composed of silica and aluminum can be alkali-activated [13].

The strength of clayey soil-lime and clayey soil fly ash mixtures was improved as a result of enhancing the alkali pozzolanic reaction in the mixtures [14, 15]. In the open literature, no research studies on the possible use of oil shale ash and marble/granite sludge for the production of safe construction materials, e.g. bricks, curbstone, and light sculpture stones for
decoration, have been reported. It was observed that building blocks prepared with an optimum quantity of lime along with cement led to a continuous build-up of strength even beyond two years [16].

Geopolymerization reactions take place between CaO in ash and SiO₂ and Al₂O₃ in granite and marble powder. These are alkali pozzolanic reactions. The durability of the product is increased by increasing the pozzolanic content in the mixture [17].

This research work is an attempt to discuss the possibilities of mixing oil shale ash with granite and marble sludge wastes to produce low-cost lightweight construction bricks to replace the traditional Portland cement bricks.

For convenience, these bricks are designated as (AG) and (AM) for ash-granite and ash-marble sludge mixtures, respectively. To characterize the physical and mechanical properties of various ash-granite and ash-marble sludge mixtures parameters such as dry density, absorption, permeability, void ratio and compressive strength were measured at 28 days.

In the current work, the expected results of mixing oil shale ash with granite and marble sludge can be as follows:

1) production of low-cost lightweight masonry bricks and decorative stones;
2) production of low-cost lightweight rib bricks in concrete slabs;
3) possible replacement of cement in non-bearing internal curtain walls.

2. Sample materials characterization

2.1. Physical and chemical properties of oil shale and spent shale ash

About 50 kg of fresh unweathered oil shale was collected from El-Lajjun area in central Jordan. The sample was crushed and then sieved passing 9 mm mesh. This size was used to determine the physical properties of oil shale. ASTM standards [18–20] were followed through the testing procedures. The results are presented in Table 1.

The concentrations of the major oxides were determined using the X-ray fluorescence (XRF) technique (XRF-Pioneer F4, manufactured by Broker at the laboratories of Natural Resources Authority (NRA), Amman). The results are given in Table 2.

High-calcium ash was prepared by crushing the oil shale sample using a jaw crusher. Passing the 3/8 inch sieve (9.51 mm mesh) the ash was

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Average result</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, g/cm³</td>
<td>1.95</td>
<td>ASTM C29 [18]</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.38</td>
<td>ASTM C127 [19]</td>
</tr>
<tr>
<td>Moisture content, %</td>
<td>0.85</td>
<td>ASTM D2216 [20]</td>
</tr>
<tr>
<td>Color</td>
<td>Dark grey-black</td>
<td>Laboratory results</td>
</tr>
<tr>
<td>Bitumen content</td>
<td>10%</td>
<td></td>
</tr>
</tbody>
</table>
collected and aerobically combusted at 950 °C for two hours. The prepared ash was ground utilizing the Los Angeles abrasion machine, instead of a ball mill. The drum and steel balls were cleaned. The ground ash was sieved; the fraction passing a 100-mesh sieve (0.149 mm) was collected and stored in dry condition. The major oxides as weight % were determined using XRF; the results are presented in Table 3.

The specific gravity of the ash sample was 2.49, following the procedure of ASTM C128 [21], while the bulk density was 1.14 g/cm³ [18].

Table 2. Chemical composition of bituminous limestone, wt%

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>L.O.I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil shale</td>
<td>12.6</td>
<td>2.7</td>
<td>1.5</td>
<td>27</td>
<td>0.47</td>
<td>0.46</td>
<td>2.59</td>
<td>51.98</td>
</tr>
</tbody>
</table>

Note: L.O.I. – loss on ignition.

Table 3. Chemical composition of oil shale ash

<table>
<thead>
<tr>
<th>Oxide</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>K₂O</th>
<th>MgO</th>
<th>P₂O₅</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>32</td>
<td>3.15</td>
<td>1.45</td>
<td>46.3</td>
<td>1.47</td>
<td>2.46</td>
<td>5.62</td>
<td>5.78</td>
</tr>
</tbody>
</table>

2.2. Physical and chemical properties of granite and marble wastes

Bulk saturated samples were collected from two stone workshops, one was involved in cutting and polishing granite and the other in cutting and polishing marble stones. Both samples were very fine. The samples passing the 200-mesh sieve (0.075 mm) were dried at room temperature. The marble sludge sample showed white color while the granite sludge sample revealed light grayish color as shown in Figure 1.

The physical properties were determined for the granite wastes sample designated with the letter (G) and the marble wastes sample designated with the letter (M). The specific gravity determined according to [21] and dry density of the wastes are given in Table 4.

(a)    (b)

Fig. 1. Dry granite (a) and marble (b) wastes samples.
The chemical composition of both granite and marble wastes samples were determined utilizing XRF at NRA in Amman. The major oxides contents of the wastes samples are presented in Table 5.

Table 4. Physical properties of granite and marble wastes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Sample</th>
<th>Dry density, g/cm³</th>
<th>Gs</th>
<th>Passing # 200 sieve, %</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Granite wastes</td>
<td>1.30</td>
<td>2.59</td>
<td>100</td>
<td>Light gray</td>
</tr>
<tr>
<td></td>
<td>Marble wastes</td>
<td>1.21</td>
<td>2.57</td>
<td>100</td>
<td>White</td>
</tr>
</tbody>
</table>

Table 5. Major oxides contents of granite and marble wastes, wt%

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sample</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Granite wastes</td>
<td>53.43</td>
<td>9.56</td>
<td>6.65</td>
<td>3.21</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Marble wastes</td>
<td>2.45</td>
<td>2.23</td>
<td>0.45</td>
<td>52.46</td>
<td>8.22</td>
</tr>
</tbody>
</table>

2.3. Ash-sludge mixtures

Several well-mixed homogeneous ash-marble and ash-granite waste mixtures were prepared. Ash was mixed with different proportions of granite and marble wastes separately. All mixtures were prepared using the same dry weight/water ratio, which was 0.5, regular cylindrical samples with a length/diameter (L/D) ratio of 2 were obtained from each mixture. A cylindrical stainless steel mold with an inner diameter of 25 mm and length of 50 mm provided with a piston with the same inner diameter of 50 mm was used to compress and extrude the samples.

In addition, a control mix of ash and water was prepared and designated by the letter (0). Another set of samples was prepared by mixing equal amounts of granite and marble wastes without any ash content. The mixtures were labeled as (GM50).

The ash-granite wastes samples with ash contents of 75, 50 and 25% by weight were abbreviated as (AG75), (AG50) and (AG25), respectively. The ash-marble wastes mixtures whose ash contents were similarly 75, 50 and 25% by weight were designated respectively as (AM75), (AM50) and (AM25). The samples were cured in laboratory conditions. Permeability and dry density were determined for ash-granite and ash-marble wastes mixtures. Compressive strength was determined for three samples of each mixture at 28 days under dry conditions and at 96-hour saturation directly before testing to investigate the effect of water on the strength of the cementing material.

The composition of the prepared mixtures of ash-granite and ash-marble sludge wastes with different proportions of ash by weight percentage is given in Table 6.

The thermal conductivity of the prepared samples (AG75 and AM75) was measured experimentally by establishing a steady-state linear flow of heat.
Table 6. Composition of the prepared mixtures, wt%

<table>
<thead>
<tr>
<th>Mixture</th>
<th>Ash</th>
<th>Granite sludge</th>
<th>Marble sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AG25</td>
<td>25</td>
<td>75</td>
<td>0</td>
</tr>
<tr>
<td>AG50</td>
<td>50</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>AG75</td>
<td>75</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>AM25</td>
<td>25</td>
<td>0</td>
<td>25</td>
</tr>
<tr>
<td>AM50</td>
<td>50</td>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>AM75</td>
<td>75</td>
<td>0</td>
<td>75</td>
</tr>
<tr>
<td>GM50</td>
<td>0</td>
<td>50</td>
<td>50</td>
</tr>
</tbody>
</table>

through the material and applying Fourier’s equation. A thin sample of about 5 mm was prepared and tested in different temperature ranges. In this research, the linear rod method was used employing two different testing units, the Hilton Heat Conduction Unit H940/06412 (UK) and a new axial conduction devise DIDATEC ZA DU PARC (France).

3. Results

3.1. Solid waste materials

The chemical composition of ash, marble and granite sludge was pozzolanic, with different weight percentages of SiO2, Al2O3 and Fe2O3. The marble waste showed a higher weight percentage of CaO at the expense of other oxides, mainly SiO2. Ash revealed a lower dry density, 1.14 g/cm3, compared to marble and granite sludge whose respective figures were 1.21 and 1.32 g/cm3. This was related to the specific gravity of the solid particles of the wastes used. All the results were obtained under normal laboratory conditions.

3.2. Compressive strength

The compressive strength test on the cylindrical samples was carried out employing a calibrated digital 50 kN testing machine. The average compressive strength values for three samples of each mixture are presented in Table 7. The table reveals that the compressive strength of the samples increased with increasing ash content in both AG and AM mixtures. The very slight differences in compressive strength between dry and saturated cured samples at 28 days were indicative of that non-soluble binding materials such as calcium silicate hydrate (CSH), calcium alumina silicate hydrate (CASH) and Portlandite (Ca(OH)2) were responsible for strength build-up as revealed by the scanning electron micrographs (SEM) of the tested samples (Fig. 3).

This is also indicative of the important role of ash as a self-cementitious material in compressive strength build-up and, as a source of alkali, its
potential reactivity towards granite and marble sludge as pozzolanic materials having a reasonable content of SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and Fe\textsubscript{2}O\textsubscript{3}. The reaction of ash alkali with the pozzolanic part of granite and marble sludge wastes takes place similarly to the hydration reaction in OPC. The resulting compounds, Ca\textsubscript{2}O\textsubscript{3}, CSH and CASH, are produced according to the following equations:

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2. \quad (1)
\]

\[
\text{Ca(OH)}_2 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{CaSiO}_2\cdot n\text{H}_2\text{O}. \quad (2)
\]

\[
\text{Ca(OH)}_2 + \text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{H}_2\text{O} \rightarrow \text{CaSiO}_2\cdot \text{Al}_2\text{O}_3\cdot n\text{H}_2\text{O}. \quad (3)
\]

Ettringite, C\textsubscript{3}A\textsubscript{3}S\textsubscript{3}H\textsubscript{3}2, was also produced as a result of the reaction of CASH with the sulphur inherited from the ash.

However, continuous strength build-up is expected to take place according to the following reactions in the presence of CO\textsubscript{2} in rain water or air:

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2. \quad (4)
\]

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3. \quad (5)
\]

Moreover, the test results showed the compressive strength values for the ash-marble sludge samples to be higher compared with the ash-granite sludge samples at the same ash content and curing age, for both dry and saturated samples as shown in Figure 2. The compressive strength difference between AG and AM mixtures at the same ash content was related to the content of SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, and CaO in both mixtures.

Scanning electron micrographs depicted in Figure 3 reveal the formation of fibrous CSH in the ash-granite sludge sample (a) and abundant portlandite in the ash-marble sludge sample (b). In fact, in the two types of mixtures there took place the formation of fibrous CSH minerals. However, the process was more intensive in the ash-granite sludge mixture, which could
Fig. 2. Compressive strength of ash-granite and ash-marble sludge mixtures.

be due to the higher silica and aluminum content of granite waste that increased the possibility of CSH formation. Compressive strength results for the tested AM samples were close to minimum compressive strength (4.2 MPa) requirements for non-load-bearing concrete masonry units as per [22] on-load-bearing concrete masonry block is classified as lightweight block if its density is more than 1.7 g/cm³ and compressive strength is not less than 2.5 MPa according to [23].

XRD established that in addition to CSH and CASH, ettringite was also a major product of hydrated ash (Fig. 4). Sulfate reacted with calcium aluminate hydrates of ash to form ettringite at the early age of the mixture. Ettringite may decrease the permeability and dimensional stability of the mixture and provide adequate strength when its content in the mixture is more than 70% [24].

Fig. 3. Scanning electron micrographs of samples AG75 (a) and AM75 (b).
3.3. Dry density

The dry density of the tested samples was low, ranging from 1.22 to 1.32 g/cm³, which enables the use of these materials for production of lightweight bricks for various construction purposes. The dry density of the ash-granite wastes mixtures decreased from 1.32 to 1.23 g/cm³ by increasing the ash content from 25 to 75%, whereas that of the ash-marble wastes mixtures decreased from 1.27 to 1.22 g/cm³ when the ash content was increased similarly from 25 to 75%. However, for all samples the dry density decreased with increasing ash content due to its low specific gravity. The ash-marble wastes samples showed lower densities compared with the ash-granite wastes samples at the same ash content, which was related to the lower specific gravity of marble sludge. The results are depicted in Figure 5.
3.4. Permeability

For permeability tests the samples were prepared with the same length, diameter and water content following the procedure of ASTM D5084 [25]. The obtained permeability values ranged from $3 \times 10^{-6}$ to $7.2 \times 10^{-6}$ cm/sec. The permeability of the ash-marble and ash-granite sludge mixtures decreased from $7 \times 10^{-6}$ to $4.5 \times 10^{-6}$ and from $6.5 \times 10^{-6}$ to $3 \times 10^{-6}$, respectively, when the ash content was increased from 25 to 75%. It was noticed that the permeability of the ash-marble sludge mixtures was lower than that of the ash-granite sludge mixtures at the same ash content, which could be explained by the higher rate of the reaction between ash pozzolanic materials in ash-marble sludge mixtures compared to ash-granite sludge mixtures. Permeability was decreased with increasing ash content in the tested samples, which was related to the increase of the cementing material in the matrix. The results are shown in Figure 6.

The permeability of the ash-marble sludge mixtures was lower than that of the ash-granite sludge mixtures with the same ash content. This was related to the higher content of cementitious Ca(OH)$_2$ and CSH in the matrix of the mixture.

![Fig. 6. Permeability test results for ash-granite and ash marble sludge mixtures.](image)

3.5. Absorption

The reported absorption of the tested samples varied between 35 and 45%. Absorption for the AG samples was higher compared with the AM samples with the same ash content. Absorption for both types of mixtures decreased with increasing ash content. Increasing the ash content from 25 to 75% decreased absorption for ash-granite sludge and ash-marble sludge mixtures from 42 to 39% and from 40 to 38%, respectively. At the same ash content the ash-marble sludge mixtures exhibited lower absorption compared with the ash-granite sludge samples, which was ascribed to the higher reactivity of the ash pozzolanic material in the AM mixtures compared with the AG
mixtures. The results revealed that absorption of the tested samples proved to be lower than that of hollow concrete blocks, which ranges from 45 to 50%. The results for the ash-marble and ash granite sludge mixtures are shown in Figure 7.

3.6. Void ratio

The void ratio (e) decreased from 4.82 to 4.79 and from 4.8 to 4.77 for ash-granite and ash-marble sludge mixtures, respectively, with ash content increasing from 25 to 50 wt%. This was associated with the partial filling of the voids in the matrix with extra cementing material as a result of ash hydration in the mixture. The results are illustrated in Figure 8.

3.7. Thermal conductivity

The calculated thermal conductivity (k) was 0.1 W/m K for sample AM75 as shown in Figure 9.

The thermal conductivity for sample AG75 was 0.2 W/m K as shown in Figure 10.
Fig. 9. Thermal conductivity of ash-marble sludge sample AM75.

Fig. 10. Thermal conductivity of ash-granite sludge sample AG75.

The values depicted in Figure 10 are lower than those for ordinary normal bricks made of concrete and gravel mix whose $K = 0.9–1.2$ W/m [26]. It is deemed that using ash and residuals to prepare low-cost building materials should provide a double effect, i.e. reduce the costs and enhance thermal comfort inside the building.

4. Conclusions

This research revealed that all compressed samples were of excellent cohesive regular cylindrical shape. Neither efflorescence nor cracking of the samples was observed after successive soaking and drying cycles during the curing period. However, the samples with zero ash content and an equal weight of marble and granite sludge (GM50) showed complete disintegration when soaked in water. This suggests that oil shale ash acted as a self-cementitious material and a good binding material if added to pozzolanic waste materials such as granite and marble sludge. Calcium silicate hydrate and calcium aluminum silicate hydrate were, to some extent, responsible for
strength gain in the tested samples. The said compounds were produced by alkali pozzolanic reactions, which were similar to the hydration reaction to give ordinary Portland cement. Ettringite was formed due to the reaction between sulphate and alumina in the tested samples. The low thermal conductivity of such bricks is encouraging from the viewpoint of their utilization in arid and semi-arid climates which desert dwellers live in. In addition to the stability of ash-marble and ash-granite sludge mixtures under fully saturated conditions, the said property is considered advantageous to produce low-cost lightweight bricks and similar construction items. The negative environmental impact of the three waste materials, i.e. ash, granite sludge and marble sludge, can be minimized through the production of low-cost suitable construction items.

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