Improved concrete via upgraded oil shale ash

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Abstract

Oil shale combustion produces large amounts of bottom ash residue that currently adds a storage problem due to a lack of efficient utilization modes. Oil shale is an abundant potential energy source, but its low calorific value and high ash content have limited its large-scale economic utilization as a fossil fuel. In Israel, there is only one industrial user which utilizes oil shale as fuel for process heat (steam production), producing so far more than a million tons of useless oil shale bottom ash (OSBA) in large piles under atmospheric conditions, raising environmental concerns. Previous studies show that OSBA can be a good substitute for cement due to its good pozzolanic reaction, in concrete without reducing strength, but its cementitious properties are limited. This study explores several chemical treatment methods to upgrade OSBA so that it can be used as a partial substitute for cement or aggregates in concrete. The study proved that the chemical-treated OSBA has improved reactivity and suitability as a concrete ingredient. Thus, upgrading OSBA could provide a productive use for the ash while reducing the need for cement production which is a polluting process. It could also cut off the environmental risks of long-term storage of large ash piles. The results may demonstrate a way for fruitful economic environmentally safe utilization of oil shale combustion as a fossil fuel. This also has the benefit of producing useful building materials without the need for large quarries while harnessing an abundant energy source with less waste.

Keywords: Oil Shales; Concrete; Hydration; Phosphoric Acid; Cement; Sustainability

1. Introduction

One of the main economic problems facing the world today is the increased demand for energy and on the other hand the fact that the major fuels used: fossil fuels, are the main source of the greenhouse effect. Mainly, due to carbon dioxide emissions as a product of the combustion process and also by methane leaks via the cycle of natural gas as a cleaner source for power production. Moreover, the process of fossil fuel combustion results in the production of large ash quantities as waste residues, thus creating a secondary environmental problem that might contaminate the land and the underground aquifers due to the leaching of trace elements. Though green energy is the present target of the world, in the next decades, fossil fuels will still serve as a major energy source worldwide in the next decades. Coal and oil shale are two types of solid fossil fuels that produce large amounts of ash residues. Oil shale combustion releases much higher amounts of ashes compared to coal per mass unit and has an appreciable lower calorific value. However, oil shale is a much more abundant potential fossil fuel worldwide. Oil shales (calculated based on the oil shale produced in situ) served as an alternative energy source, producing about 400 billion tons of oil worldwide, which is larger than any traditional crude oil source (estimated at more than 300 billion tons). As already mentioned, Oil shale combustion results in appreciably higher emission of pollutants compared to other fossil fuels, including relatively large amounts of ash as a residue, and thus, the utilization of oil shale as a source of energy worldwide is relatively small.

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Currently, oil shale is potentially the largest local energy source of fossil fuels in the State of Israel, even more than the large natural gas deposits in the Mediterranean sea. The oil shale deposits are spread in different areas spanning from the Negev desert in the south, to the Zebulun Valley in the north. As a source of fossil fuel energy, oil shale appears in the form of porous stones rich in organic matter. Most of the organic matter is in the form of kerogen and has a high molecular weight. Oil shales can be used via direct combustion for steam and energy (electricity) production. The disadvantages (beyond being fossil fuels whose usage increases the greenhouse effect) lie in its relatively low calorific value, due to the high percentage of inorganic material that are the source of formation of large amounts of ash-shaped mineral waste post-combustion, which must be treated for safe storage. Owing to the high costs required for mining and oil shale extraction, compared with crude oil, few of the oil shale deposits are used for direct combustion; thus, in situ treatment to produce oil and combustible gases via fracking is more commonly used.

In Israel, much-applied R&D research has been devoted to checking the possibility of using local oil shale as a fossil fuel. However, it was concluded that the combustion of local oil shale cannot compete economically with coal or natural gas as fossil fuels and therefore, in Israel no utilization of oil shale as a fossil fuel has taken place. In Israel, the only industrial company that uses direct combustion of oil shale is Rotem Amfert Negev Ltd., which produces phosphate-based products; located in the Negev desert in Southern Israel, where both oil shale deposits and phosphate rocks are present. The company uses sulfuric acid to dissolve the mined phosphate rock and extract from the slurry the phosphoric acid, which is used to produce several phosphate-based materials. Rotem Amfert Negev Ltd. must strip the upper layers, which cover the phosphate rock deposits; these layers mainly consist of oil shales. Thus, there is no extra cost to produce oil shale as a fuel. The company uses a 30MW drop tube boiler to produce steam from the heat produced in the boiler and the steam is used as a commodity in the plant. Two types of ashes are formed in the combustion process: Oil shale fly ash-OSFA (~10w%) and Oil shale bottom ash-OSBA (~90w%). The fly ash is utilized in Israel as a substrate for lining barns and in products that absorb animal excrement. At present, there is no utilization method for the bottom ash, which is the primary waste residue produced. Thus, large piles of bottom ash are stored under open air near the plant (at present the estimate is for ~8 million tons of OSBA) and this fact causes these OSBA piles to be of an environmental concern.

Cement is a binding material used in construction that hardens, sets, and adheres to other materials to bind them together. It is typically produced from a mixture of limestone, clay, and other minerals that are heated in a kiln at high temperatures to form a hard substance. Cement is commonly used in the production of concrete, mortar, and stucco, and is an essential component in the construction of buildings, bridges, roads, and other infrastructure. The production process of cement is an environmental concern of environmental problems.

OSBA possesses a limited cementitious value, and its contribution to mortar or concrete comes through its involvement in the pozzolanic reactions; the mineralogy of the ash affects the hardening and leaching dynamics of the concrete. The hardening of OSBA binders, when used as supplementary cementitious materials, tends to be much slower compared with typical Portland cement because of the slower rate of the pozzolanic reaction. In addition, the OSBA is not a pure material with high CaO content (in Israel up to 40%) and other impurities that have to be treated in order to use the OSBA as one of the components in the concrete mixture. time-consuming (up to several weeks).

In this study, several potential chemical treatments of OSBA were tested as partial replacements of cement or aggregate in concrete mixture. The main goal of this study is to evaluate the potential solution to the above-mentioned problem of safe storage of the OSBA and will upgrade it into a useful commodity that needs no storage.

2. Material and method

2.1. Materials

The oil shale bottom ash (denoted as OSBA) as well as the phosphoric acid (see below) was supplied by Rotem Amfert Negev Ltd.

Green Phosphoric Acid- Solutions of green phosphoric acid (which is one of the products of Rotem Amfert Negev Ltd.) are used in the agricultural industry. Green phosphoric acid contains high concentrations of phosphoric acid and some trace elements (which give it the green color which stems from formation of metal phosphate complexes). The chemical composition of the Green Phosphoric Acid is presented in Table 1.
Table 1 Chemical composition of the Green Phosphoric Acid used

<table>
<thead>
<tr>
<th>The component</th>
<th>Green acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>P₂O₅ (%)</td>
<td>27.2</td>
</tr>
<tr>
<td>TOC (ppm)</td>
<td>1,868</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>0.328</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>4.86</td>
</tr>
<tr>
<td>B (ppm)</td>
<td>24.7</td>
</tr>
<tr>
<td>Ba (ppm)</td>
<td>&lt;0.10</td>
</tr>
<tr>
<td>Cd (ppm)</td>
<td>17.02</td>
</tr>
<tr>
<td>Cr (ppm)</td>
<td>61.24</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>10.04</td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>266</td>
</tr>
<tr>
<td>F (%)</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>0.116</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>0.68</td>
</tr>
<tr>
<td>Mo (ppm)</td>
<td>14.3</td>
</tr>
<tr>
<td>Na (ppm)</td>
<td>1,290</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>76.9</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>0.43</td>
</tr>
<tr>
<td>SO₄ (ppm)</td>
<td>14,800</td>
</tr>
<tr>
<td>SiO₂ (ppm)</td>
<td>11,900</td>
</tr>
<tr>
<td>Sr (ppm)</td>
<td>30.6</td>
</tr>
<tr>
<td>Ti (ppm)</td>
<td>16.2</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>42.8</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>333</td>
</tr>
<tr>
<td>CaO (ppm)</td>
<td>2,240</td>
</tr>
</tbody>
</table>

All water used throughout this study was non-mineral water produced with a resistance of 2 MΩ·cm.

All other chemicals used were of AR grade and supplied by Sigma-Aldrich Co.

2.2. Analysis and Methods

- XRD analysis- The ash samples were analyzed in an X’pert Pro X-ray diffractometer by PANalytical Company at the Surface laboratory of Ariel University.
- BET analysis- The ash samples were analyzed to determine the surface area of the oil shale ash at Ilza Katz Nanotechnology Ctr., Ben-Gurion U. of the Negev.

The acidity was measured using pH sticks or using a glass electrode with a CyberScan Bench pH 510 pH meter.
3. Results and Discussion

3.1. Untreated OSBA

The oil shale bottom ash consists of gray particles in the size range of 20-50 mm, which are further formed via the aggregation of small 1,500-2,000 μm smaller particles. A photograph of a of the untreated OSBA is presented in Figure 1. In addition, the mineral composition of its constituents was determined via XRD analysis, Table 2.

![Untreated OSBA](image)

**Figure 1** Untreated OSBA a- A pile of large particles. b. Aggregation of small 1500-2000 μm particles (Taken from Nov et al.22)

<table>
<thead>
<tr>
<th>The component</th>
<th>Untreated OSBA W%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium Silicate Oxide- Ca$_3$(SiO$_4$)O</td>
<td>40</td>
</tr>
<tr>
<td>Ettringite- Ca$_6$Al$_2$(SO$_4$)$<em>3$(OH)$</em>{12}$·26H$_2$O</td>
<td>12</td>
</tr>
<tr>
<td>Calcite - CaCO$_3$</td>
<td>32</td>
</tr>
<tr>
<td>Anhydrite- CaSO$_4$</td>
<td>9</td>
</tr>
<tr>
<td>Potassium nitrate(III)- KNO$_3$</td>
<td>4</td>
</tr>
<tr>
<td>Hydrotalcite- Mg$_6$Al$_2$CO$<em>3$(OH)$</em>{16}$·4H$_2$O</td>
<td>2</td>
</tr>
<tr>
<td>Magnetite- Fe$_3$O$_4$</td>
<td>1</td>
</tr>
</tbody>
</table>

As can be seen, the main mineral constituents of OSBA are Calcite (CaCO$_3$), and Tricalcium Silicate Oxide (Ca$_3$(SiO$_4$)O) minerals. The presence of calcite could result from carbon dioxide absorption (from air) during the long-term storage of the OSBA under open air before its analysis.

3.2. Treatment of OSBA

To test the suitability of ash as a partial replacement for cement and aggregates in concrete, multiple concrete mixtures were prepared using varying ratios of OSBA and green acid. The OSBA and acid were combined into a slurry, mixed for 15-20 minutes, filtered, and dried at room temperature overnight. Then we checked the pH in the different slurries, following the procedure detailed in a previous publication.22

![Untreated OSBA](image)

The dry-treated OSBA samples were analyzed in the BET to determine the surface area of selected samples. In addition, the BET test was also performed for untreated OSBA as shown in Table 3. Two samples having a significant pH value were tested compared to untreated sample to evaluate the effect of the treatment on the surface area of the oil shale ash.
Table 3 Surface area of selected samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated OSBA</td>
<td>13.60</td>
</tr>
<tr>
<td>Treated OSBA pH 3.2</td>
<td>58.90</td>
</tr>
<tr>
<td>Treated OSBA pH 6.4</td>
<td>26.96</td>
</tr>
</tbody>
</table>

As can be seen from Table 3, the surface area of the sample has increased appreciably post-treatment with the green acid. The Treated OSBA at pH 3.2 contains the largest surface area. Thus, it can be concluded that the porosity of the treated samples is higher than that of the untreated OSBA, and thus this process might has improved them so that these treated ashes are suitable for use as a partial substitute for cement, aggregates, or sand, in concrete mixtures.

In addition, the dry-treated OSBA samples were analyzed in the XRD to determine their composition post-treatment; the data are presented in Table 4.

Table 4 The composition of treated OSBA; the OSBA/Green Acid Ratio (Taken from Nov et al.22)

<table>
<thead>
<tr>
<th>pH+ OSBA/Green Acid Ratio / the component in weight percentage (%wt.)</th>
<th>1.pH 6.4 1/0.45</th>
<th>2.pH4.3 1/0.57</th>
<th>3.pH 3.6 1/0.73</th>
<th>4.pH 3.2 1/0.89</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite - 3CaO·SiO₂</td>
<td>52.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcite - CaCO₃</td>
<td>21.2</td>
<td>17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gypsum- CaSO₄·2H₂O</td>
<td>8.1</td>
<td>13</td>
<td>-</td>
<td>17.8</td>
</tr>
<tr>
<td>Anhydrite- CaSO₄</td>
<td>8.1</td>
<td>10</td>
<td>11</td>
<td>8.9</td>
</tr>
<tr>
<td>Hydrogen peroxide- H₂O</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcium silicide- CaSi</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Brushite- CaHPO₄·2H₂O</td>
<td>-</td>
<td>22</td>
<td>21</td>
<td>14.9</td>
</tr>
<tr>
<td>Silicon oxide- SiO₂</td>
<td>-</td>
<td>11</td>
<td>15</td>
<td>13.9</td>
</tr>
<tr>
<td>Vanadium sulfide- V₃</td>
<td>-</td>
<td>3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hexahydroborite- CaB₂O₄·6H₂O</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Coesite- polymorph of SiO₂</td>
<td>-</td>
<td>24</td>
<td>22</td>
<td>25.7</td>
</tr>
<tr>
<td>Killalaite- Ca₆Si₆O₇·H₂O</td>
<td>-</td>
<td>-</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>Phosphorus (V) oxide- P₂O₅</td>
<td>4</td>
<td>-</td>
<td>15</td>
<td>16.8</td>
</tr>
</tbody>
</table>

The results, Table 4, indicate that in all the samples of treated OSBA the amount of gypsum-anhydrate, CaSO₄, formed in the treated OSBA is reduced compared to the untreated OSBA, in the range 8-10w%. In addition, in all the samples there is phosphorous either as Brushite- CaHPO₄·2H₂O 15-22w% or as Phosphorus (V) oxide, P₂O₅ 4-15w%. In treated OSBA that was produced by using excess acid and resulted in an acidic slurry (pH 3.2 or 3.6), no calcite (CaCO₃), was observed.

3.3. Concrete Mixtures

The fresh and hardened concrete performances were tested with a partial addition of treated OSBA with green phosphoric acid, compared to untreated OSBA, as described above. The properties were tested according to Israeli standards to evaluate the ability to use the ash in industrial concrete mixtures. Partial replacement of the coarse aggregate, fine aggregate, and natural sand was carried out also with the OSBA. Table 5 presents the mix design of the concrete mixture studied compared to a reference sample without OSBA.
Table 5 Mix design of the concrete without and with treated or not treated OSBA

<table>
<thead>
<tr>
<th>Concrete with oil shale ash</th>
<th>Concrete without oil shale ash</th>
<th>unit</th>
<th>component</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>270</td>
<td>Kg m$^{-3}$</td>
<td>CEM I 52.5 R</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>Kg m$^{-3}$</td>
<td>Oil Shale Ash</td>
</tr>
<tr>
<td>860</td>
<td>860</td>
<td>Kg m$^{-3}$</td>
<td>Coarse aggregate</td>
</tr>
<tr>
<td>510</td>
<td>580</td>
<td>Kg m$^{-3}$</td>
<td>Coarse aggregate</td>
</tr>
<tr>
<td>420</td>
<td>450</td>
<td>Kg m$^{-3}$</td>
<td>Sand</td>
</tr>
<tr>
<td>160</td>
<td>160</td>
<td>Kg m$^{-3}$</td>
<td>Water</td>
</tr>
<tr>
<td>4.3</td>
<td>4.3</td>
<td>Kg m$^{-3}$</td>
<td>Chemical Admixture</td>
</tr>
</tbody>
</table>

The properties of concrete having a not-treatment OSBA were compared to the properties of the concrete without OSBA. The slump of the concrete was tested according to SI 26/2.1. Fig. 2 compares the slump received of the concrete mixture without oil shale ash and the slump of the concrete with nontreated OSBA. As can be seen, the slump was reduced significantly from 155 mm to 40 mm. To increase the reduced slump of the concrete containing OSBA, adding extra water will increase the water-to-cement ratio and therefore reduce the performance of the concrete compressive strength. The suggested reasons for the decreased slump of the concrete having oil shale ash are the high water absorption by the oil shale ash, which was found to be 35% wt. and the high content of CaO and CaCO$_3$ which increase the water absorption and the occurrence of the reaction of CaO with water to form Ca(OH)$_2$.\textsuperscript{23}

The oil shale ash is considered a pozzolanic material. Therefore, extra calcium silicate hydrates (C-S-H) which are the main products of the hydration of Portland cement, is formed by the reaction of the silica oxide in the oil shale ash with the Ca(OH)$_2$ in the hardened concrete.

caused the observed increased strengths. Fig. 3 presents the compared Ca(OH)$_2$ content tested in XRD. As can be seen higher content of Ca(OH)$_2$ was found in concrete mixtures having oil shale ash. Therefore it can be concluded that the pozzolanic reaction in the concrete mixture reduced the Ca(OH)$_2$ content and caused the increased strength, (see below Fig. 5).
The acid treatment of OSBA was described above. As can be seen in Fig. 4 a similar slump was obtained of the concrete with and without treated OSBA. It was also found that by using higher amounts of acid for the treatment (the reduced pH), a lower amount of water was needed to obtain a constant slump. Therefore, it can be concluded that treatment of the OSBA with higher amounts of green phosphoric acid decrease the water needed to acquire the required slump. The reason of the decreased water needs with the decreased pH is due to the reduced amount of CaO and CaCO$_3$ occurring in the treated OSBA.

**Figure 3** XRD pattern of concrete after 28 days from casting with untreated OSBA (orange) and with treated OSBA (blue)

**Figure 4** The measured slump of the concrete without and with treated OSBA

**Figure 5** The measured water needed to reach constant slump of the concrete with treated OSBA at various pH compared to regular concrete (no OSBA added)
The compressive strengths of the concrete having the treated OSBA were determined compared to the concrete without the addition of OSBA. The cement amount in the concrete without oil shale ash was 270 kg m\(^{-3}\) and the cement amount in the concrete having oil shale ash was 230 kg m\(^{-3}\) and 150 kg m\(^{-3}\) of oil shale respectively (non-treated and treated OSBA). The OSBA treatment involved mixing with green phosphoric acid (approximately 10 minutes) until the pH reached a value in the range of 6.5 to 3.0. In Fig. 6 the final compressive strengths of the concrete mixture without OSBA and compared to concrete having untreated and treated OSBA. As can be seen in Fig. 6, similar final compressive strength after 28 days was obtained for concrete without oil shale and concrete with non-treated OSBA, although the reduction amount of cement in the concrete having treated OSBA. The reason for the similar compressive strength, although the reduction of the cement content in the concrete with OSBA stems from the pozzolanic reaction of the oil shale ash with the Ca(OH)\(_2\) in the concrete to form an additional volume of CSH. However, it can be seen that higher compressive strength was obtained in the concrete having treated OSBA. The increased compressive strength of the concrete containing treated OSBA stems from the pozzolanic reaction and the decreased water needed to reach a constant slump. In addition, as can be seen from Fig. 7 a lower water penetration was obtained in the concrete containing treated OSBA compared to concrete without oil shale ash and compared to concrete with non-treated OSBA, due to the same reasons for the increased compressive strength of the concrete treated OSBA oil shale ash.

**Figure 6** Compressive final strengths of the concrete without and with treated and untreated OSBA

**Figure 7** The measured water penetration of the concrete without and with treated and untreated OSBA

4. Conclusions

Treating oil shale bottom ash, OSBA with green phosphoric acid improved its quality as a good substitute to cement and aggregates in concrete mixtures due to the increased surface area and porosity compared to untreated OSBA and reduced the lime-CaO and calcite-CaCO\(_3\) content. The mineral analysis confirmed the formation of cementitious compounds like gypsum, anhydrite, and phosphates in the treated ash. This indicates that the chemical treatment upgrades the reactivity of OSBA to serve as a supplementary cementitious material.
Concrete containing acid treated OSBA showed improved workability compared to concrete with untreated OSBA, enabled by reducing the water content while maintaining the slump. The 28-day compressive strengths and water penetration resistance were also superior for concretes incorporating treated OSBA versus untreated OSBA or plain concrete without OSBA.

Chemically enhancing waste OSBA to replace a portion of aggregates and cement in concrete demonstrates a promising route for productive utilization of the abundant ash piles currently stored near the oil shale combustion plant. Using treated OSBA as a concrete ingredient promotes more sustainable oil shale utilization as a fossil fuel by offsetting ash disposal needs adding a new cement and aggregate substitute and reducing the concrete construction industry's demands for cement.

The potential utilization of oil shale ashes as a cement substitute will reduce the number of cement plants which are air-polluting centers and greenhouse sources and will reduce the price of building materials.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest to be disclosed.

References


