Mineralogy and Microstructures of Sintered Sewage Sludge Ash as Lightweight Aggregates

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Abstract: In this study, we investigated the sintering characteristics of incinerator residues that were obtained from sewage sludge by heating the residues from 1000 to 1100 °C for 30 min. The bulk density of the sintered monoliths, ranging from 0.6 to 1.0, decreased significantly when the sintering temperature increased from 1050 to 1100 °C. The major crystalline phases identified in the raw ash were quartz (SiO₂), hematite (Fe₂O₃), Al₂O₃, and AlPO₄; small amounts of Na₂O and K₂O were also detected. Higher sintering temperatures, 1050 and 1100 °C, resulted in porosities of 33 and 43 %, respectively, but variations were profound, because both the pore volume and the pellet volume increased concurrently. The amount of quartz decreased on sintering, with the intensity of the major peak decreasing further as the sintering temperature increased. SEM images confirmed the presence of SSA aggregates treated at 1100 °C; spaces existed between the sintered SSA particles, due to the formation of larger pores by excessive bloating. Moreover, the targeted heavy metal leaching concentrations in the sludge ash samples all met the current regulatory thresholds of the Taiwan Environmental Protection Agency.

Keywords: lightweight aggregates, speciation variation, weight loss, 24-h absorption

Introduction

Urbanization, economic growth, and an increase in the portion of the population served by sewer systems have contributed to the constantly increasing generation of sewage sludge. The use of sewage sludge in landfills and in farming as a use and treatment technique has long been practiced. However, limited landfill space, increasing disposal costs, and a need for sustainable waste management strategies that produce zero emissions have all hastened efforts to recycle sewage sludge into usable materials. Incinerated sewage sludge ash (SSA), which contains inorganic components, has been used in mortars, and cement mixtures [1], as a fine aggregate in mortars, asphalt paving mixes [2], and to make aggregates, particularly lightweight aggregates, for construction purposes. A renewed interest in developing such useful materials would also effectively assist in the disposal of the ash [3].

However, for artificial lightweight aggregates to be produced from sewage sludge ash, bloating of the material (sludge ash) is essential. This phenomenon occurs only at high temperatures when two essential conditions take place and overlap for a sufficient length of time, i.e., the development of a glassy phase and the evolution of gases from the dissociation of the mineral components. This process allows the pyroplastic mass to trap gaseous bubbles, which then form a cellular structure in the mass [4]. Typical bloating materials, such as clay [5], shale, and slate, and, to some extent, treated coal shales, are known to contain natural-gas-producing components, which generate gases at different temperature levels. This bloating mechanism is sensitive to variations in the ash components and the operational temperatures. Therefore, the major components in sludge ash, such as Al₂O₃, SiO₂, and flux (i.e., Fe₂O₃, FeO, CaO, MgO, Na₂O, and K₂O), as well as the typical gas-producing components, such as carbonates, oxides, hydrates, and sulfates [6], if present, will profoundly affect the bloating behavior of sewage ash during the heat-treatment process [7].

This paper describes the preparation of artificial aggregates from SSA by the firing of sludge ash pelletized at
high temperatures. The critical bloating temperatures for the sludge were determined and the physical properties of the sintered products were characterized with respect to their potential use as lightweight aggregates. The products were characterized by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Mercury Intrusion Porosimetry (MIP; to determine the pore volume), chemical composition characterization, Toxicity Characteristic Leaching Procedure (TCLP test; for testing the hazardous materials), X-ray diffraction (XRD; for crystal mineralogy determination), and scanning electron microscopy (SEM; for microstructural observation). In addition, the effect of the sintering temperature on the characterization, including weight loss, 24-h absorption, specific gravity, bulk density, and aggregate crushing strength, was also investigated.

Materials and Methods

Preparation of the Sludge Ash
A dewatered sludge cake sample was fired in a brick-firing kiln at a temperature of 900 °C for 1 h. The ash was then pulverized with a ballmill and passed through a 150-µm sieve. This dried and homogenized ash was then stored in a desiccator until required for testing.

Preparation of Compacted Sintered Sludge Ash at Different Sintering Temperatures
The tested ash was compacted at 3.5 MPa to form cylindrical specimens (1.2 cm diameter; 1.3 cm height) and then desiccated before being tested. To characterize the bloating temperature of the SSA during the sintering process, experiments were conducted at a given constant temperature in an electrically heated furnace, which is a different operating process than that conducted under an ambient temperature. A constant temperature (from 1000 to 1100 °C), was maintained for each batch; it was increased in increments of 100 °C and held for 30 min. The SSA sample, after being sintered at a given temperature for a given duration, was taken out of the furnace, cooled rapidly to room temperature, and then stored in a desiccator prior to analysis of its physical properties and for leachability testing.

Analyses
The following chemical and physical analyses of the SSA pellets and sintered products were conducted:

- Weight loss: NIEA R204.00T.
- Absorption testing: ASTM C556
- Chemical composition: The chemical composition was determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Samples (2 g) were digested with ultrapure-grade reagents using a three-step procedure. Firstly, a concentrated hydrofluoric/nitric acid (5 mL/5 mL) mixture was added to the sample; after evaporation, a 3 mL/9 mL mixture of concentrated nitric/hydrochloric acid was added; after another evaporation, the samples were dissolved in 5 % nitric acid solution.
- Aggregate crushing strength: An estimate of the mechanical quality of the aggregates was obtained from the crushing strength test [8]. An oven-dried sample of the aggregates was placed in a steel cylinder having an internal diameter of 57 mm and a height of 87 mm. The aggregates were filled up to an upper incision mark in the cylinder and afterwards covered with a steel puncheon that was pressed down until the upper level of the aggregate was reduced to a prescribed distance. The value of the crushing strength was calculated, in stress units, as the ratio between the load and the cross-sectional area of the cylinder.
- Toxicity Characteristic Leaching Procedure (TCLP) for heavy metal: SW846-1311
- Mercury Intrusion Porosimetry: A Quantachrome Autoscan MIP was used with intrusion pressures up to 60,000 psi. By using the Washburn equation, $p = -2\gamma\cos\theta/V$, the pore volume (V) and the corresponding radius (γ) could be plotted synchronously by an X-T plotter; the wetting angle of mercury was assumed to be θ=140°. In this equation, p, γ, r, and θ, represent the applied pressure, surface tension, pore radius, and wetting angle, respectively.
- X-ray diffraction: The XRD analyses were performed using a Siemens D-5000X-ray diffractometer with CuKα radiation and 2θ scanning ranging between 5 and 70°. The XRD scans were run at 0.05° steps, with a 1 sec counting time.

Results and Discussion

Characterization of the Sewage Sludge Ash
The chemical composition and heavy metal concentration of the sludge ash are shown in Table 1. SiO₂, Al₂O₃, Fe₂O₃, and P₂O₅ are the major components in the ash. According to ICP-AES analysis, the major components observed in the sewage sludge ash were SiO₂ (46.27 %), Al₂O₃ (14.12 %), and P₂O₅ (17.75 %). The next most abundant components were Fe₂O₃ (7.46 %), CaO (4.80 %), MgO (2.01 %), and K₂O (1.46 %). Figure 1 shows the speciation in the SSA, as identified by the XRD techniques; the major components were quartz (SiO₂), P₂O₅, and Fe₂O₃. The TCLP leaching concentrations for the target metals met the EPA’s current
Table 1. Chemical Composition and Heavy Metals within the Sewage Sludge Ash

<table>
<thead>
<tr>
<th>Composition</th>
<th>Sludge ash (wt%)</th>
<th>Heavy metal Total conc. (mg/kg)</th>
<th>Heavy metal TCLP conc. (mg/L)</th>
<th>Regulation threshold</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>46.27±3.21</td>
<td>Pb 199.4±4.3</td>
<td>Pb ND</td>
<td>5</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.12±1.29</td>
<td>Cd 8.9±0.1</td>
<td>Cd 0.03±0.01</td>
<td>1</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>7.46±0.51</td>
<td>Cr 75.7±3.3</td>
<td>Cr ND</td>
<td>5</td>
</tr>
<tr>
<td>CaO</td>
<td>4.80±0.11</td>
<td>Cu 432.6±3.3</td>
<td>Cu 0.51±0.03</td>
<td>15</td>
</tr>
<tr>
<td>MgO</td>
<td>2.01±0.19</td>
<td>Zn 2236.8±16.5</td>
<td>Zn 7.04±0.04</td>
<td>---</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.42±0.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>0.01±0.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.46±0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* expressed as oxides
** Mean Deviation (n = 6)

regulatory thresholds, and are presented in Table 1.

Effect of Sintering Temperature on the Physical Properties of Sintered Sewage Sludge Ash

The weight loss of the SSA pellets after sintering could be attributable to (a) the release of gases via the conversion of organic residues, (b) mineral decomposition, or (c) the vaporization of volatile metals in the SSA during the sintering process. The quantity and the time of the release can affect the microstructure of the sintered SSA pellets, and, thus, the strength of the resultant product. The weight loss of the sintered SSA at various sintering temperatures is shown in Table 2. The weight loss increased from less than 1.4 to 3.4 %, when the sintering temperature increased from 1000 to 1100 °C. The former change was probably due to the oxidation of organic residues in the SSA.

The water absorption of SSA aggregates was determined by measuring the apparent weight increase of a dried sample that had been immersed in water for 24 h (defined as the 24-h absorption). When the sintering temperature was 1000 °C, the absorption rate (as low as 3 %) decreased significantly. We believe that this phenomenon was due to the decreasing pore volume and the effects of densification. When the sintering temperature was between 1050 and 1100 °C, the occurrence of bloating resulted in dramatic swelling and the formation of open surface pores, meaning that the 24-h absorption of SSA pellets (SSA aggregates) increased. However, the 24-h adsorption weight for SSA pellets sintered at 1100 °C showed that the pore structure had become closer; the pores, although abundant, were isolated and less permeable.

The bulk density of the sintered monoliths, ranging from 0.6 to 2.3, decreased significantly when the sintering temperature was increased from 1050 to 1100 °C. Table 2 indicates the recommended bulk densities for ordinary (<2.9 g/cm$^3$) and lightweight aggregates (<1.6 g/cm$^3$). The sintering of SSA is useful for the production of lightweight aggregates that can be used as construction materials.

In general, the strength of SSA aggregates is affected by interrelated factors, such as the porosity, the pore size and distribution, the mineral species present in the SSA, speciation variation during heating, densification effects due to sintering, SSA bloating, and even pellet surface cracking or fracturing due to the thermo-stress. The strengths of the SSA aggregates at different sintering temperatures and times are shown in Table 2. For sintering times longer than 1000 °C, the sintering process tended to intensify the liquid-phase sintering, forcing it to become viscous-flow sintering. This phenomenon possibly resulted in the formation of a cellular structure in the matrix, thus decreasing the aggregate’s strength. It is interesting to note that there was a clear gap in the strength between the samples prepared at 1000 °C and 1050—100 °C for the 30-min sintering time. A sharp decrease in strength, governed by sintering temperature variations within 50 °C, indicated that the SSA bloated at ca. 1050—100 °C to form a cellular structure in the matrix that reduced the strength of the SSA aggregates. Moreover, at a higher temperature (1100 °C), the SSA aggregates could also decrease in strength because of excessive bloating and a longer heating time (>15 min).

The porosity varied with the heating temperature, which indicates that increasing the sintering temperature would
Table 2. Effect of Sintering Temperature on the Physical Properties of Sintered Sewage Sludge Ash

<table>
<thead>
<tr>
<th>Physical property</th>
<th>Sintering temperature (°C)</th>
<th>Specifications*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000</td>
<td>1050</td>
</tr>
<tr>
<td>Weight Loss (%)</td>
<td>1.44±0.05**</td>
<td>1.64±0.11</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>2.30±0.11</td>
<td>1.07±0.03</td>
</tr>
<tr>
<td>Absorption (wt%)</td>
<td>3.21±3.02</td>
<td>6.06±1.91</td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>199.6±0.32</td>
<td>16.34±0.15</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>7.68±0.24</td>
<td>32.72±0.35</td>
</tr>
</tbody>
</table>

* CNS 382.R2 (National Standards of the R.O.C.)
** Mean ± deviation (n = 5)

Figure 2. Scanning electron micrograph images of (a) Raw sludge ash and sewage sludge ash sintered at (b) 1000, (c) 1050, and (d) 1100 °C for 30 min.

result in the formation of a viscous flow, which in turn reduced the pore volume, thereby decreasing the porosity of the pellets. The lowest porosity occurred at 1000 °C, where the pellets were well densified. Higher sintering temperatures, 1050 and 1100 °C, resulted in porosities of 33 and 43 %, respectively, but variations were profound, because both the pore volume and the pellet volume increased concurrently. The inner pores were filled by the viscous flow, resulting in low porosity and densification, as evidenced by less differential intrusion at 1000 °C. A significant shift in pore size was also noted when the sintering temperature was between 1050 and 1100 °C. This result might be due to the rapid release of gases that formed at the higher temperature (1100 °C), which could significantly affect the pore size distribution.

SEM Observation

Figures 2(a)–(d) show the microstructures of sintered ash examined by applying the SEM technique. The pore structures became more compact upon increasing the sintering temperature. The images clearly showed the particulate nature of the sintered SSA particles in the untreated aggregates [Figure 2(a)], whereas in the sintered aggregates they become more fused. On other hand, Figure 2(b) indicates clear neck growth between

XRD Patterns for the Sintered Sewage Sludge Ash

The XRD patterns for the sewage sludge ash samples sintered at different temperatures are shown in Figure 1. The major crystalline phases identified in the raw ash were quartz (SiO₂), hematite (Fe₂O₃), Al₂O₃, and AlPO₄; small amounts of Na₂O and K₂O were also detected. The major crystalline phases identified in the sintered sewage sludge ash samples were quartz, hematite, and AlPO₄. Na₂O and K₂O originally in the sewage sludge ash were not detected in the sintered samples. The amount of quartz decreased upon sintering, with the intensity of the major peak decreasing further as the sintering temperature was increased.
the particles, although the particle size is much greater than that of the original untreated ash, suggesting the occurrence of defect neck growth. Figure 2(c) shows a more uniform distribution of larger pores in the aggregate treated at higher temperature (1050 °C). The reduction in density and sample expansion that occurs when firing at 1050 °C is clearly associated with the formation of a significant volume of approximately spherical pores, which can be seen in Figure 2(c). Similar pyroplastic effects have been observed in other materials, where gas generation is reported to be due to decomposition of alkaline metal salts [9]. Figure 2(d) reveals that in the SSA aggregates treated at 1100 °C, there are spaces between the sintered SSA particles; they arose as a result of the formation of larger pores by excessive bloating.

Conclusions

1) The major crystalline phases identified in the raw ash were quartz (SiO$_2$), hematite (Fe$_2$O$_3$), Al$_2$O$_3$, and AlPO$_4$; small amounts of Na$_2$O and K$_2$O were also detected.

2) The bulk density of the sintered monoliths, ranging from 0.6 to 2.3, decreased significantly with the increase of sintering temperature from 1050 to 1100 °C.

3) Higher sintering temperatures, 1050 and 1100 °C, resulted in porosities of 33 and 43 %, respectively, but variations were profound, because both the pore volume and the pellet volume increased concurrently.

4) The amount of quartz decreased upon sintering, while the intensity of the major peak decreased further as the sintering temperature increased.

5) SEM images confirm the structures of the SSA aggregates treated at 1100 °C; spaces existed between the sintered SSA particles because of the formation of larger pores by excessive bloating.

References