The Influence of sintering temperature on sludge ceramsite

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Abstract: In order to investigate the effect of sintering temperature on the characteristics of sludge ceramsite made with dried sewage sludge as an additive, clay, water glass and dried sewage sludge were mixed at ratios of sludge/clay of 33% and water glass/clay of 15%, and fired the mixture at different temperature to produce a range of ceramsite, analysed thermal behaviours of raw material by DTA-TGA and crystalline phases of ceramsite by XRD, and conducted SEM-EDS analyses to examine the morphological structures of ceramsite. DTA-TGA results indicate the differences in thermal behaviours are caused by the compositional and structural variations of the material. SEM-EDS analyses indicate the ceramsite sintered at 1000°C have more uniformly distributed finer pores (0.5 < pore size < 10.0 nm), interconnected with crystals, and the ceramsite sintered at other temperatures have less pores and rougher surfaces. XRD patterns show the main crystalline phases of ceramsite are quartz and kyanite below 1000°C, and kyanite become the major crystalline phases at 1000°C and 1100°C, and most of the crystalline phases are mullite at 1200°C. It is concluded that ceramsite with fine characteristics can be obtained at well-selected sintering temperature (about 1000°C).

Keywords: Crystalline phase; sintering temperature; sludge ceramsite; thermal behaviour

INTRODUCTION

Due to rapid urbanization and implementation of higher effluent criteria in recent years, sewage sludge is now being generated in an ever increasing amount. Conventional disposal options include landfill, application to farmland and forestry, incineration and sea dumping (Chena et al., 2002; Otero et al., 2003a). However, the high concentration of organic substances in sewage sludge creates much concern about leachate contamination. In addition, these organic matters lead to excessive propagation of microorganisms such as red tides in the ocean (Endo et al., 1997; Kikuchi, 1998, Otero et al., 2003b).

The ultimate disposal of excess sludge has been and continues to be one of the most expensive problems encountered by wastewater utilities, e.g. the treatment of excess sludge may account for 25% up to 65% of the total plant operation cost (Zhao and Kugel, 1997). So far, production and disposal of sludge are entering a period of dramatic change, driven mainly by stringent environmental legislation (Liu, 2003). Sewage sludge could be directly used in agriculture as fertilizer a few years ago, but this is now hampered by the legal criteria for its high content of heavy metal (Veeken and Hamelers, 1999). Another usually used way is thermal (Qiao and Ho, 1996; Cenni et al., 1998; Krebs et al., 2001; Obrador et al., 2001; Wanga et al., 2001), which involves incineration, gasification, and pyrolysis.

Many researchers have recognized sewage sludge as a resource with much potential for beneficial use other than direct disposal. Almost any carbonaceous material could be used as precursor for preparation of activated carbons, sewage sludge, which is of this nature and rich in volatile components, have the potential to be used for producing activated carbon if it can be pyrolyzed under controlled conditions and/ or through chemical treatment. Recently, several investigations have been made to show the feasibility of this conversion (Jeyaseelan and Lu, 1996; Martín et al., 1996; Calvo et al., 2001).

Solidification/ stabilization (S/ S) technologies are processes designed to improve waste-handling, decrease the surface area across which pollutants can be not transfer or leach, limit the solubility of contaminant compounds and detoxify hazardous constituents (Andrés et al., 1998; Obrador et al., 2001), and they are widely used for treating both inorganic and organic waste materials. Much work has been done on the characteristics of glass-ceramics...
made of sewage sludge ashes (Endo et al., 1997; Young et al., 2003). Sewage sludge ash has been compacted and fired at different temperatures to produce a range of sintered ceramic materials (Khalili et al., 2002; Cheeseman et al., 2003). In addition to the silicon and aluminum-rich characteristics, dried sludge also exhibits a significant specific surface area and cation-exchange capacity. Therefore the use of dried sludge to produce lightweight aggregate is a new effective approach for disposal of sludge. All these observations above can be used as guidelines for the use of dried sewage sludge as an additive in the clay mixtures to produce ceramsite (Xu et al., 2006).

The aim of the present work is to obtain valuable information about the influence of different sintering temperatures (850°C, 900°C, 950°C, 1000°C, 1100°C and 1200°C) on characteristics of ceramsite.

**METHODS**

The ceramsite under study was made with the following: (1) Clay with components as shown in Table 1; (2) Water glass with modulus of 3.2; (3) Dried sewage sludge made of wet sewage sludge dried at 105°C until invariable mass and then manually crushed, which consists of 35% of inorganic matter in form of metal, non-metal oxidation and salt, and 60% of organic matter in form of death bio-solid, and 5% of water content.

**Table 1 General characteristics of clay**

<table>
<thead>
<tr>
<th>Chemical composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>CaO</th>
<th>MgO</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight (%)</td>
<td>≥65.0</td>
<td>≥25.0</td>
<td>≤2.5</td>
<td>≤1.2</td>
<td>≤1.2</td>
<td>&lt;0.4</td>
<td>&lt;0.5</td>
<td>&lt;0.5</td>
<td>&lt;10.0</td>
</tr>
<tr>
<td>Physical properties</td>
<td>Particle size (µm)</td>
<td>Plastic index</td>
<td>Linear shrinkage</td>
<td>Moisture</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>&gt;5</td>
<td>4.0</td>
<td>8.5% - 12.0%</td>
<td>≤15.0%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Powder XRD patterns of ceramsite were recorded on a D /max-y-β X-ray diffractometer with 50mA and 40Kv, Cu K radiation. Major elements of ceramsite were analyzed using a Philips PW 4400 XR spectrometer (XRF). SEM-EDS analyses were conducted using an S-570 scanning electron microscope and TN-5502 X-ray energy dispersive spectrum. The thermal behaviours of samples were examined by DTA-TGA using a ZRY-2P simultaneous DTA-TGA analyser while the samples was heated at a rate of 8°C/min from 20 to 1150°C with nitrogen blown at 100 ml/min. Samples ranged from 4 to 10 mg in mass, and they were compacted into a Pt-Rh crucible with 20 taps. All curves were evaluated using the TA-instruments software, and Two-point rotations were carried out for all DTA curves. The second derivative differential thermal curve was used for determination of peak temperature.

**RESULTS AND DISCUSSION**

**Thermal behaviour analyses**

Thermal behaviours of clay, sludge, and a mixture made at a ratio of sludge /clay of 33 wt%, and a mixture made at ratios of sludge /clay of 33 wt% and water glass /clay of 15 wt%.
It can be seen from Figure 1 that the trend of DTA curves does not change from 20°C to 463.2°C and an endothermic reaction occurs from 463.2°C to 544°C. Silicate hydrates are known to dehydrate gradually and differently over a wide temperature range up to 800°C (Danielle et al., 1998). So, it can be seen that the mass loss is overlapped due to silicate hydrates dehydrates gradually at a temperature between 492.2°C and 537.2°C.

The observed exothermic peaks, endothermic peaks and corresponding mass losses in Figure 2 are ascribed to: Exothermic reaction: 87°C -327.7°C, presence of silicate hydrates; Endothermic reaction: 327.7°C -399.8°C, reaction of carbonaceous materials; Exothermic reaction: 399.8°C -482°C, release of CO₂; Endothermic reaction: 482°C -1100°C, formation of crystalline phases.

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![Figure 3 DT and TG analyses of mixture of clay and sludge (sludge/clay of 33%)](image1)

![Figure 4 DT and TG analyses of mixture of clay, sludge and water glass (sludge/clay of 33% and water glass/clay of 15%)](image2)

It can be seen from Figure 3 that there is an obvious relationship between thermogravimetric (TG) and differential thermal (DT) plots of clay and sludge. DT diagrams for mixture of clay and sludge show an endothermic peak at 215°C, due to evaporation of adsorbed water. Exothermic peak signals at 315.3°C correspond to H₂O loss from the mixture of clay and sludge. The deep peak at 601°C, corresponding to the decomposition of carbonaceous materials, is associated with 20.1% weight loss in TG analysis.

The thermal analysis of the mixture of clay, sewage sludge and water glass indicates there is a substantial weight loss at 530°C represented by a definite endothermic peak, which suggests the decomposition of carbonaceous materials as shown in Figure 4. Heat absorption is observed from 286.3°C to 1100°C, which attributes to the crystallization of mullite, quartz, kyanite etc. The formation of crystals is accompanied by relatively abundant glassy phases at a temperature above 950°C (Young et al., 2003), which prompts us to select 950°C- 1100°C as the range of sintering temperatures for ceramsite production and approves it is proper to select 1000°C as the best sintering temperature for using dried sewage sludge as an additive in the clay mixtures to produce ceramsite (Xu et al., 2006).

The differences in (Figures 1-4) thermal behaviours of the 4 mixtures are due to changes in compositions and structures of the mixtures (Danielle et al., 1998). It can be concluded from the results above that the thermal behaviour of the mixture of clay, sludge and water glass is more stable than those of the other 3 mixtures.

**Morphological structures analyses**

The selected ceramsite are gilt with porous Pt and its surface morphology is examined by SEM-EDS.
Table 2 Elementary analysis on surface of ceramsite (wt%)

<table>
<thead>
<tr>
<th>Sintering temperature</th>
<th>Al</th>
<th>Si</th>
<th>K</th>
<th>Ca</th>
<th>Ti</th>
<th>Fe</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>850°C</td>
<td>12.21</td>
<td>65.05</td>
<td>3.39</td>
<td>1.11</td>
<td>4.23</td>
<td>14.00</td>
<td>---</td>
</tr>
<tr>
<td>900°C</td>
<td>14.15</td>
<td>62.92</td>
<td>3.75</td>
<td>2.27</td>
<td>2.84</td>
<td>14.07</td>
<td>---</td>
</tr>
<tr>
<td>950°C</td>
<td>11.84</td>
<td>62.23</td>
<td>3.46</td>
<td>2.28</td>
<td>2.61</td>
<td>16.05</td>
<td>1.51</td>
</tr>
<tr>
<td>1000°C</td>
<td>11.78</td>
<td>44.99</td>
<td>4.68</td>
<td>6.97</td>
<td>4.08</td>
<td>25.78</td>
<td>1.71</td>
</tr>
<tr>
<td>1100°C</td>
<td>11.34</td>
<td>46.24</td>
<td>4.22</td>
<td>6.87</td>
<td>3.54</td>
<td>26.00</td>
<td>1.79</td>
</tr>
<tr>
<td>1200°C</td>
<td>12.18</td>
<td>50.59</td>
<td>4.10</td>
<td>5.97</td>
<td>4.18</td>
<td>21.36</td>
<td>1.61</td>
</tr>
</tbody>
</table>

As shown in Table 2 Na, Al, Si, K, Ca, Ti and Fe are all detectable on the surface of ceramsite. There are some differences in the contents of detectable elements on the surface of ceramsite sintered at different temperatures, which indicate sintering temperature has a significant effect on the distribution of elements in ceramsite. The contents of Si and Al are higher at a temperature below 1000°C, and that of Fe, Ca, Ti, K and Na are higher at a temperature above 950°C, which suggests that the kinetics of reaction of glassy phases may be higher near the quartz or kyanite grains, and its viscosity may be lower in comparison with the glass embedded in the mullite rich zone.

EDS analyses made on surface of ceramsite show that quartz content decreases in the range of sintering temperature (850°C-1200°C) as other crystals form at the periphery of ceramsite and quartz species go further into ceramsite which indicates that sintering temperature has a significant effect on crystalline phase of ceramsite.

Figure 5 Scanning photomicrographs of ceramsite surface at 850°C, 900°C, 950°C, 1000°C, 1100°C and 1200°C.

It can be seen from Figure 5(a) that the enrichment of quartz (SiO₂) on surface of ceramsite is accompanied by rough surfaces and big pores. Figure 5(b) shows a large number of quartz crystals on surface of ceramsite and kyanite crystals in a subsurface region of ceramsite and an intermediate region with less albite between quartz and kyanite crystals, and that is where an incomplete-glassy phase is embedded.

It can be seen from Figure 5(c) that the surface structure of ceramsite is very rough and has tiny pores, and the microstructure of ceramsite consists of a network of quartz crystals embedded in an incomplete-glassy phase. The formations of a bubbled microstructure due to the softening of the glassy phase together with evolution of gases generated by the decomposition of inorganic phases appear within the material (Cheeseman et al., 2003). The coarsening of quartz crystals as sintering temperature increases is one of the detectable characteristics of ceramsite, and totally different microstructures of ceramsite can be observed at a sintering temperature above 950°C.

It can be clearly seen from Figure 5(d) that there is a matrix containing a large number of isolated, approximately spherical pores, typically 0.5-10µm in diameter. The microstructure of ceramsite have more uniformly distributed small pores (0.5µm<pore size<10.0µm), interconnected with quartz and other crystals. The pores form as the residual glassy phase viscosity falls to a level when gas-forming inorganic decomposition reactions can produce the observed pores (Ducman et al., 2002).
It can be seen from Figure 5(e) that the well densified microstructures in ceramsite are due to the formation of glassy phases at 1100°C. The decrease in the viscosity of glassy phase in the region enhances the diffusion of kyanite species from the subsurface region to the upper surface region.

Irregular crystals form at 1100°C as shown in Figure 5(e) while relatively regular crystals of glassy structures crystallize at 1200°C as shown in Figure 5(f). The relative low-density ceramsite produced by firing at 1200°C appears to be hard and has a glassy surface. However, it is still an open question why this crystallisation process of mullite occurs in the surface of ceramsite. It seems to be reasonable to assume that most of volatile components (alkaline oxides) of glassy phases tend to evaporate from the surface of ceramsite, therefore, originate a concentration gradient of crystals that may be favourable to the nucleation of mullite in this region.

**Crystalline phase and chemical composition analyses**

The crystalline phases of ceramsite sintered at different sintering temperature (850°C, 900°C, 950°C, 1000°C, 1100°C and 1200°C) are as shown in Figure 6, although the analysis was conducted using an XRD pattern data base (International Centre for Diffraction Data, ICDD), no other crystalline phases matched sufficient peaks to be positively identified.

![XRD patterns of ceramsite](image)

**Figure 6** XRD patterns of ceramsite at 850°C, 900°C, 950°C, 1000°C, 1100°C and 1200°C.

The changes in crystallization temperature do not have any effect on the formation of crystals and the major crystalline phases remain almost unchanged as shown in Figure 6(a) – Figure 6(c). It also can be seen from Figure 6 that no major crystalline transformation and/or crystalline phase occur at a sintering temperature below 1000°C, and Quartz (SiO₂) and Kyanite (Al₂SiO₅) are the main crystals.

The amount of mullite increases until it becomes a major crystalline phase as sintering temperature increases as shown in Figure 6(d) - Figure 6(f). Kyanite crystals are major crystalline phases when the crystallization temperatures are 1000°C and 1100°C, and similarly, a major portion of crystals is occupied by mullite crystals at 1200°C. The microstructures of ceramsite sintered at 1200°C also confirm the formation of several indistinct crystalline phases in ceramsite as shown in Figure 5(f).

Mullite has already been formed at 950°C, as one of minor crystalline phases, and co-existed with quartz and a small amount of kyanite. As the sintering temperature increases, the intensity of XRD peaks of mullite increases while other crystalline phases tend to decrease. As the total amount of quartz decreases, albite and mullite derived from kyanite dissolution either remain in glassy phase or be used to nucleate other crystals in ceramsite at a sintering temperature above 950°C. Accordingly, although these crystalline phases (mullite, quartz and kyanite) appear at 1200°C, there is still the residual of albite in ceramsite as shown in Figure 6(f).
Table 3: Chemical composition of ceramsite sintered at 1000°C (wt%)

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Na₂O</th>
<th>Fe₂O₃</th>
<th>P₂O₅</th>
<th>CaO</th>
<th>TiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>K₂O</td>
<td>64.46</td>
<td>19.52</td>
<td>6.98</td>
<td>2.41</td>
<td>2.23</td>
<td>1.23</td>
<td>1.14</td>
</tr>
<tr>
<td>MgO</td>
<td>1.03</td>
<td>0.59</td>
<td>0.09</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

Chemical composition of ceramsite sintered at 1000°C are analysed by XRF and tabulated in Table 3 above.

CONCLUSIONS

DTA-TGA results indicate that the thermal behaviours of the 4 types of mixtures are different from each other due to the differences in the silicate contents and structures of the mixtures, and the mixture of clay, dried sewage sludge and water glass has the perfect physical and chemical properties to be used to produce ceramsite. The ceramsite sintered at 1000°C has uniformly distributed small pores, and the ceramsite sintered at other temperatures have rougher surface and less pores. The main crystalline phases of ceramsite sintered at a temperature below 1000°C are quartz and kyanite, and kyanite crystals and/or mullite crystals is one of major crystalline phases at a temperature above 1000°C (≤1200°C). Glassy and liquid phases occur due to the transformation of fine quartz particles and presence of alkaline silicates in ceramsite above 900°C, which enhance the reaction kinetics and increases chemical communication during sintering reaction stage of ceramsite.

It can therefore be concluded from the results and discussion above that sintering temperature is a major factor having a significant effect on the characteristics of sludge ceramsite.

REFERENCES


