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Characterisation of glass ceramics made from incinerator fly ash

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Abstract

The feasibility of recycling the incinerator fly ash from domestic waste incineration by developing a process to produce glass and glass-ceramic materials has been investigated. Quenched glass was obtained by high temperature molten technology. A one-step sintering and heat treatment at various temperatures (i.e. 850, 900, 950, 1000 and 1050 °C) was used to obtain glass-ceramics after pressing the quenched glass powder. A porous glass-ceramic material was formed with gehlenite ($Ca_2Al_2SiO_7$) as the main crystal phase.

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1. Introduction

The problem of waste disposal and the corresponding issue of resource conservation have been given wide attention by the developed and developing countries because of increasing population density. Incineration has become a significant solution for municipal solid waste (MSW) treatment, due to the rising difficulty in finding suitable sites for traditional sanitary landfill. In Taiwan, incinerators have been rapidly planned and built for several major metropolitan areas since 1990 [1]. There will be 36 MSW incinerators on this island, including 21 supported by the Environmental Protection Administration (EPA) and another 15 adopting build–operate–own (BOO) or build–operate–transfer (BOT) strategies [2]. It is estimated that over two million tonnes of incineration ash will be generated each year after 2003, while 21 metro-waste incinerators are put into operation. However, with growing public concerns and rigorous regulatory requirements, hazardous waste disposal practices being used to date offer challenges. One of the main difficulties is the requirement of proper disposal of incinerator fly ash.

The incinerator residuals have approximately one fifth the weight of the raw refuse, while heavy metals and dioxins are condensed into incinerator ashes causing more potential harm to the environment. Hence, the ash residues need further treatment in order to immobilize the harmful materials into a stable state. In Taiwan, for air pollution control, incinerators are equipped with different types of device. Generally, incinerators are equipped with cyclones, a dry lime scrubbing system with fabric filters, or an electrostatic precipitator followed by wet scrubbers for removing air contaminants from flue gas streams. However, due to its simplicity of engineering and high efficiency, activated carbon injection has become a popular retrofit technology for reducing dioxin emissions in newly built incinerators. For treating incinerator fly ash, the cement-based solidification or chelant addition on solidification technology is used. These disposal methods are costly and mainly still lead to environmental contamination. Therefore, a viable competing immobilization technology is required. This technology should maximize safety factors and reliability to transfer the fly ashes into a stable form. Prior studies on treating toxic waste [3–6] have shown that melt processing is a satisfactory route. In melt vitrification, the heat generated from a induction furnace or plasma is used to treat hazardous waste containing metals and/or organics at temperatures range 1300–1500 °C. Metal-bearing wastes are melted and organic contaminants are thermally decomposed. The thermal molten vitrification yields a glass-like, large volume/weight reductions and leach-resistant monolith

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slag, which is environmentally safe for landfill disposal and/or can be reused as a glass-ceramic in construction materials, such as interior, exterior wall cladding or ordinary floor tile applications. Although melt technology is costly, if the melter is built near the incinerator, the electricity for melting the fly ash can be supplied by the incinerator itself. On the other hand, reuse of the products may also cover this high energy cost. According to the evaluation report from the Institute of Nuclear Energy Research of Taiwan [7], treating incinerator fly ash (25 ton/day capacity) cost approximately US$289 (not including the slag products value) per tonne using the plasma molten method, and US$237 (includes landfill cost) per tonne for cement-based solidification. However, when treatment capacity is more than 100 tonnes/day, thermal plasma molten technology is competitive.

This research is concerned with the reuse of wastes from incinerators. Incinerator fly ash containing large amounts of CaO, SiO_2, and Al_2O_3 may be a suitable raw material for glass-ceramic production. Controlling the initial composition so that by suitable heat treatment desired crystalline phases are obtained so that control over the properties of the glass-ceramic is achieved. Using melt technology and crystallization processing to recycle various waste materials has been reported elsewhere [3,5–14].

The objective of this study was to characterise the heat treatment of as-quenched fly ash slag generated from melting technology, to establish a better understanding of the feasibility of treating the incinerator fly ash to produce glass-ceramic materials for construction usage. The products were characterized by a Toxicity Characteristic Leaching Procedure (TCLP) for testing the hazardous materials, X-ray diffractometry (XRD) for crystal structure determination, scanning electron microscopy (SEM) for microstructure/morphology observation, and energy dispersive spectroscopy (EDS) for X-ray chemical microanalysis. In addition, other properties, such as compressive strength, four-point bending strength, porosity, water absorption rate and volumetric density were also investigated.

2. Experimental procedures

The incinerated fly ash from a municipal solid waste incinerator in Taipei was used in this investigation. Fig. 1 shows that the incinerator fly ash has a wide particle size range from 0.2 to 500 μm with D_{50} of 28.4 μm. This incinerated fly ash was analyzed by inductively coupled plasmas–atomic emission spectrometry (ICP-AES) and had the following chemical composition (wt.%): 19.7% CaO; 19.4% SiO_2; 10.1% Al_2O_3; 1.8% Fe_2O_3; 2.8% MgO; 1.9% TiO_2; 8.9% Na_2O; 8.1% K_2O. A high frequency induction furnace was used as the heat source. About 3.5 kg of fly ash samples were placed in a graphite crucible and melted for 20 min at 1400 °C, before quenching into water. Differential thermal analysis (DTA) scans of the quenched glass was carried out by a Perkin Elmer Thermal Analyzer and by heating 100 mg glass powder (−149 μm) in a Pt-crucible and using Al_2O_3 as the reference material in the temperature range between 25 and 1200 °C at a heating rate of 10 °C/min. The quenched glass was then ground to minus

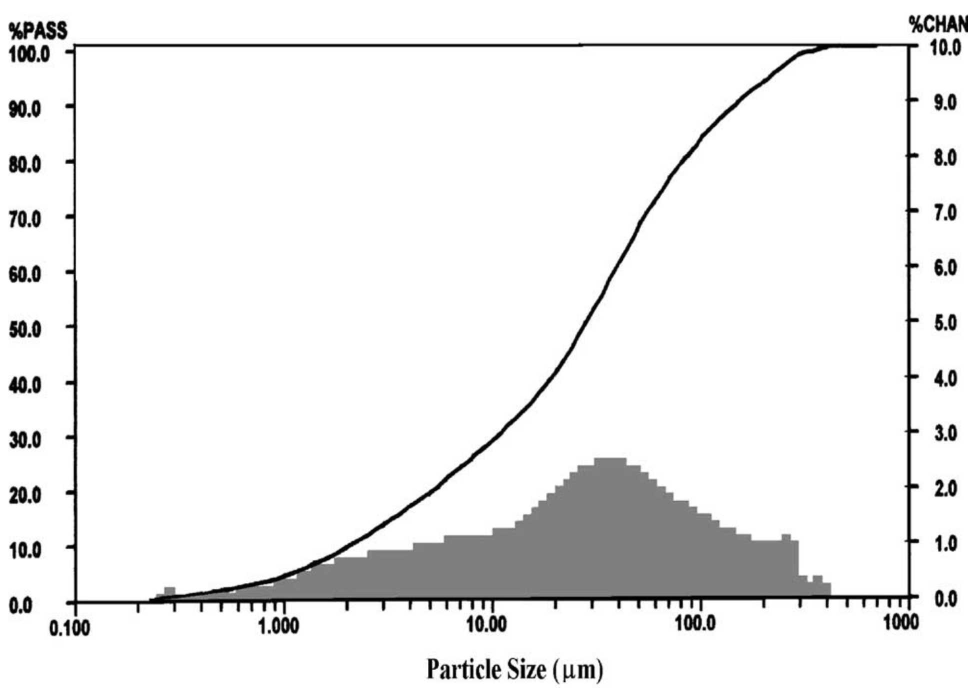

Fig. 1. Particle size distribution for incinerator fly ash.

149 μm, followed by pressing the powder into a 4×1.5×0.7 cm stainless mold under 11.8 MPa pressure. The formed green bodies were sintered and heat treated for 2 h at temperatures of 850, 900, 950, 1000 and 1050 °C, respectively, and then cooled to room temperature. For SEM and EDS examination, a Hitachi S-4100 scanning electron microscope with an energy dispersive (EDS Noran Vantage 1.2) attachment was used to examine the glass-ceramics. XRD was done using a Rigaku D/MAX-VB diffractometer with CuK_α radiation in the 2θ range from 5 to 80°. The crystallized phases were identified by comparing the peak intensities and positions with those in the Joint Committee on Powder Diffraction Standards (JCPDS) data files. The testing methods and formulae for physical property tests such as water absorption rate and volumetric density were evaluated according to Archimedes method. A Testometric 220D bending test machine carried out four-point bending test and compressive strength test, and at least three samples were tested in each experiment.

Table 1
TCLP results for incinerator fly ash and quenched glass

Elements	Incinerator fly ash (mg/l)	Quenched glass leached (mg/l)
Zn	25.6	6.9
Cd	16.9	0.2
Pb	2.5	ND
Cu	0.4	ND
Cr	20.3	ND

ND indicates not detected.

3. Results and discussion

3.1. Toxicity characteristic leaching procedure (TCLP) results

Toxicity Characteristic Leaching Procedure (TCLP) results of the incinerator fly ash and quenched glass obtained in this study is given in Table 1. Each sample analyzed has insignificant leachability characteristics for the Zn, Cr, Pb, Cu, and Cd. It is clear that the vitrification in the form of quenched glass significantly improves the chemical resistance. The extracted amounts of heavy metals are lower than the limits required by the EPA of Taiwan (Cd <1.0 ppm, Cr <5.0 ppm, Pb <5.0 ppm). In the case of low leachability characteristics for the Cr, Pb, and Cu are due to the heavy metal ions replacing other ions and hold in the framework of glass. It should be noted here, the total elemental mass balances were not considered in this study due to the volatile metals, such as Cd, may be lost to the atmosphere during molten stage. Therefore, when using thermal molten technology to treat incinerator fly ashes, a secondary air pollution control system should be designed and further research on this topic is needed.

3.2. Differential thermal analysis investigation

To evaluate the crystallization properties of the glass and determine the characteristic glass transition, crystallization and melting temperatures, differential thermal analysis was carried out. Fig. 2 shows the DTA thermogram of the powder sample (−149 μm) from quenched

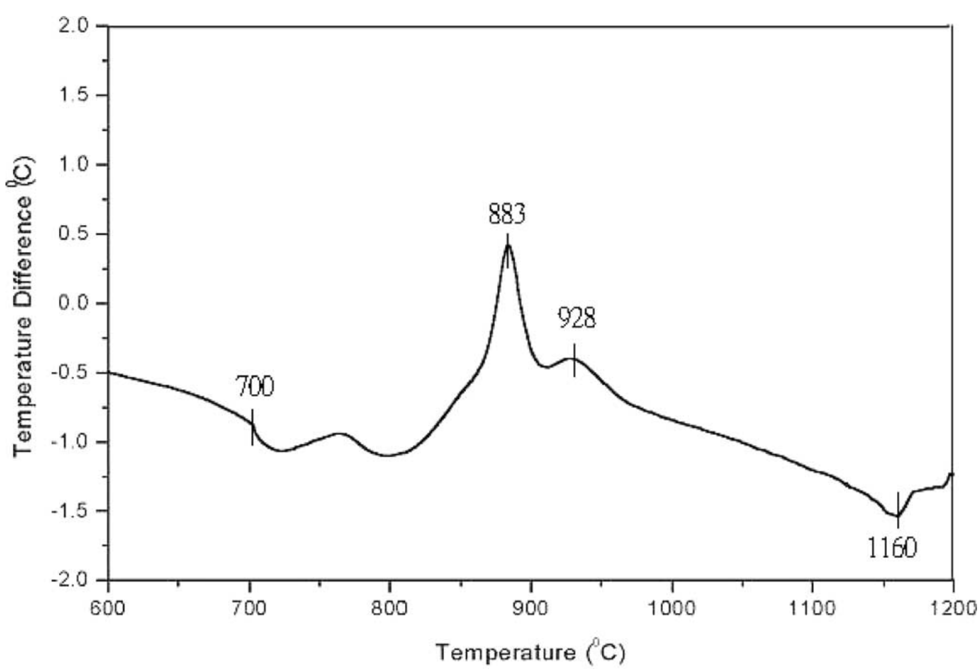

Fig. 2. DTA curve for quenched glass, crystallizing with increasing temperature 10 °C/min.

glass scanned between 25 and 1200 °C. It exhibits the shallow endothermic peak starting at the onset of 700 °C and shows glass transition temperature which is 50 °C lower than seen previously [4], followed by two exothermic crystallization peaks at the temperatures 883 and 928 °C, respectively. Finally, an endothermic reaction at 1160 °C indicating of formation of a liquid phase was observed. Generally, the nucleation temperature is 50–100 °C above the dilatometric softening point, therefore, the temperature range for heat treating the quenched glass was chosen to be 850–1050 °C.

3.3. Glass-ceramics microstructure characterization

To identify the crystallizing phases, X-ray diffractometry (XRD) scans were carried out on bulk glass-ceramic samples which had been heat treated for 2 h at various temperatures and the results are shown in Figs. 3 and 4. To eliminate segregation effects, the bulk

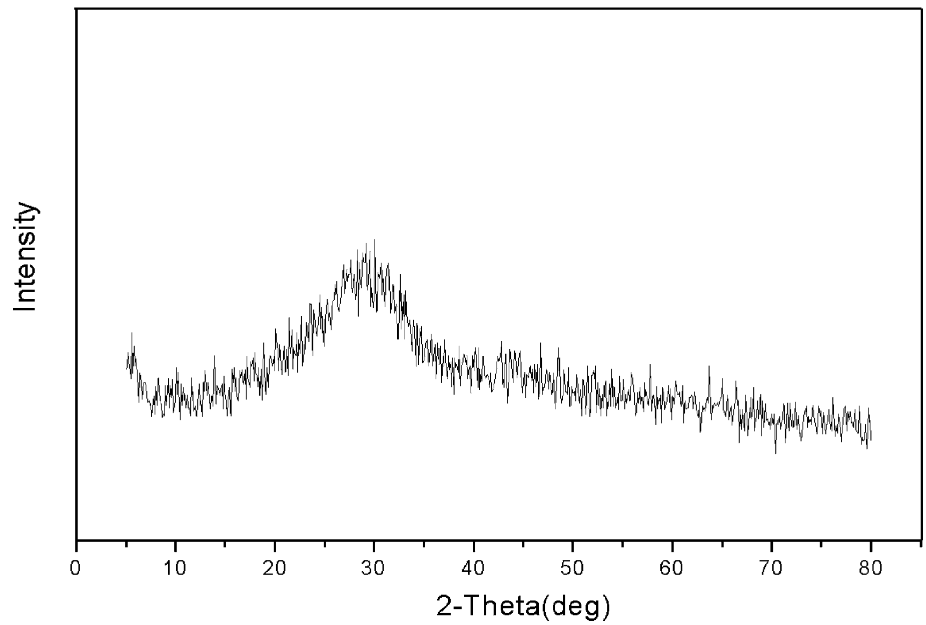

Fig. 3. XRD pattern of quenched glass, revealing an amorphous structure.

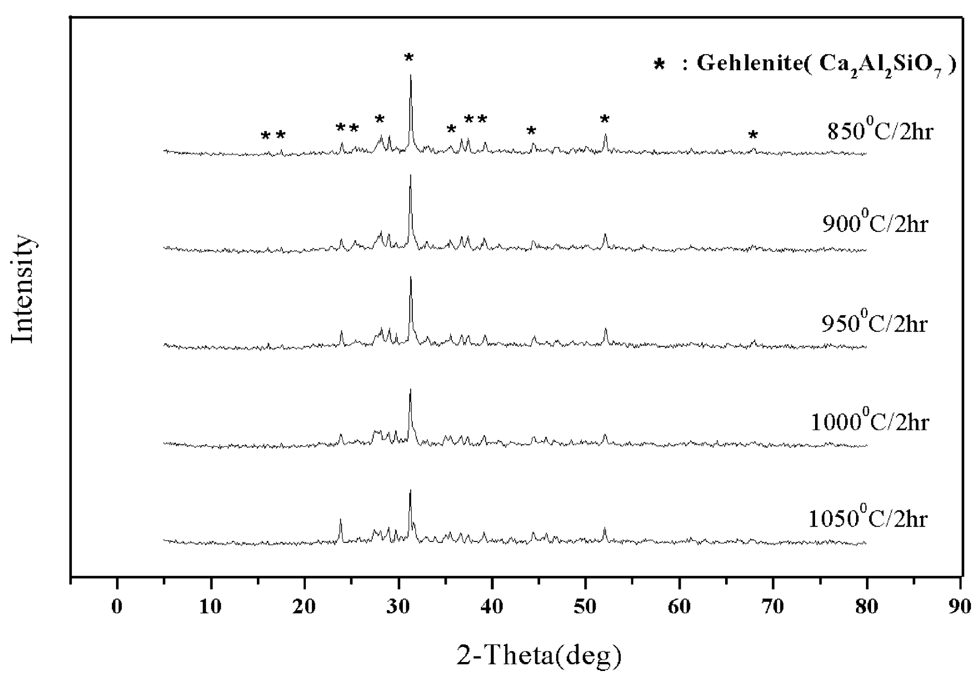

Fig. 4. XRD after 2 h at different heat treatment temperatures.

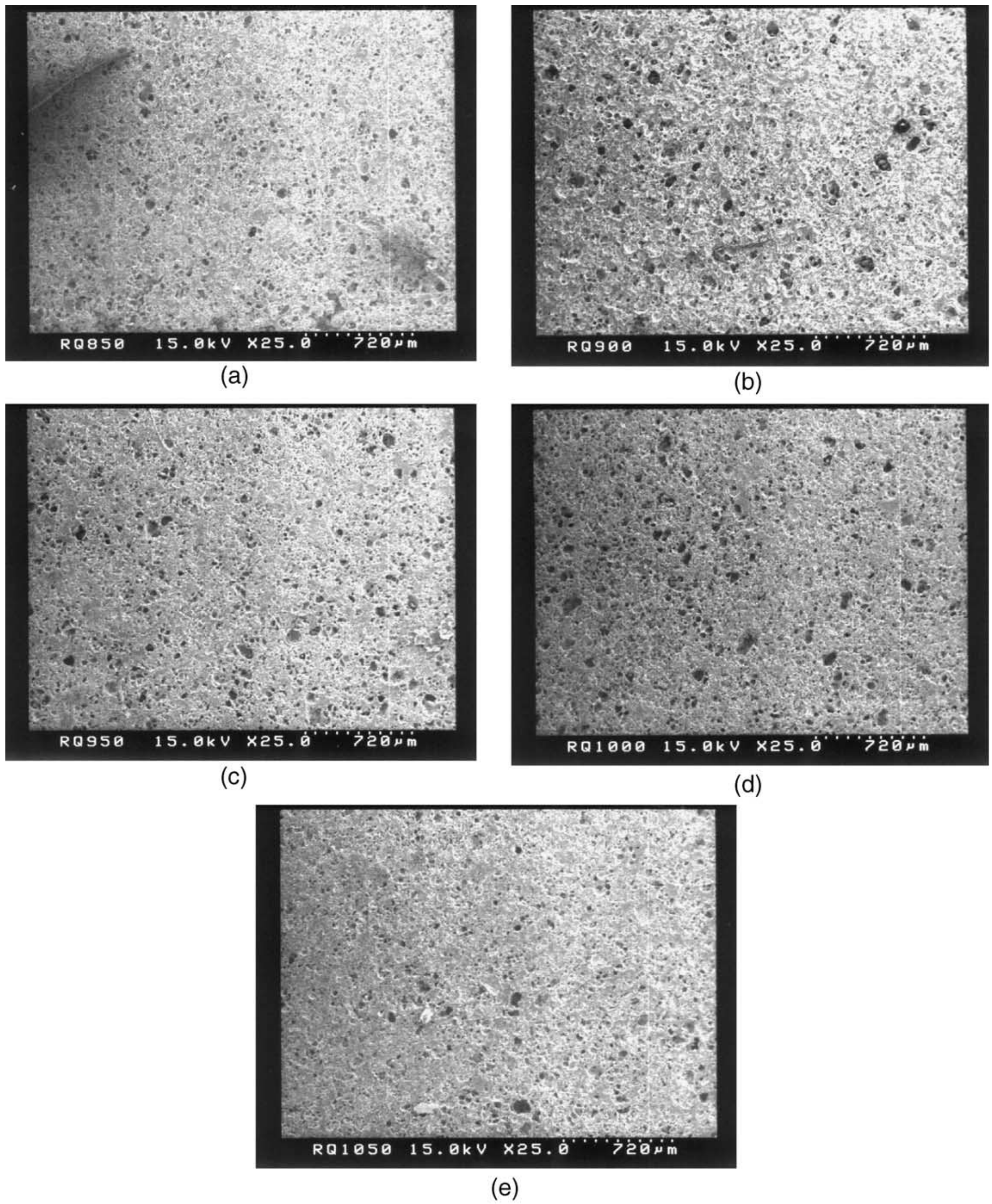

Fig. 5. SEM micrograph of samples heat-treated for 2 h at various temperatures (1) 850 °C, (2) 900 °C, (3) 950 °C, (4) 1000 °C, (5) 1050 °C.

glass sample was pulverized prior to the XRD analysis. It can be seen from Fig. 3 that the quenched glass examined in this study was amorphous. After heat treatment at 850, 900, 950, 1000 and 1050 °C, respectively, the glass has a crystallises phase (Fig. 4). It should be noted here that a cellular material containing extensive porosity was formed. The major phase of the glass-ceramics is gehlenite ($Ca_2Al_2SiO_7$) that belongs to the melilite group. Similar results were also found for a slag-based glass-ceramic in Turkey [12] and mixed with incinerator bottom ash in Italy [15]. The peak intensities decreased with increasing the heat treatment temperature. After the heat treatment at 850–900 °C, the amount of nuclei, nucleation rate and crystal growth rate increased substantially (see Fig. 2, DTA result), and thus produced a better crystalline. However, with heat treatment temperature increased to higher temperatures, the nucleation rate and crystal growth rate were decreased, therefore the peak intensities decreased.

Scanning electron microscope images of samples heat treated at different temperatures are shown in Fig. 5. Honeycomb structure glass-ceramics were formed and

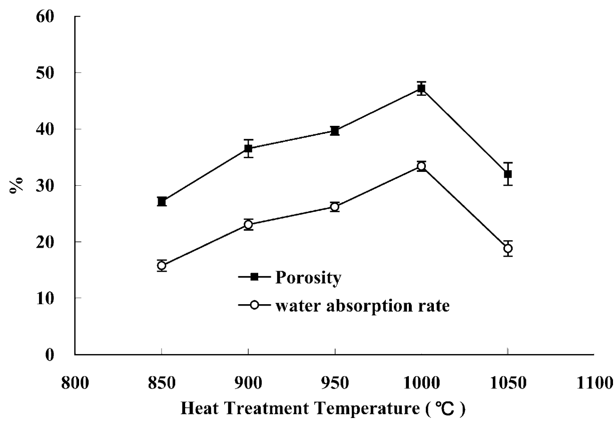

Fig. 6. Porosity and water absorption after heat treatment at various temperatures.

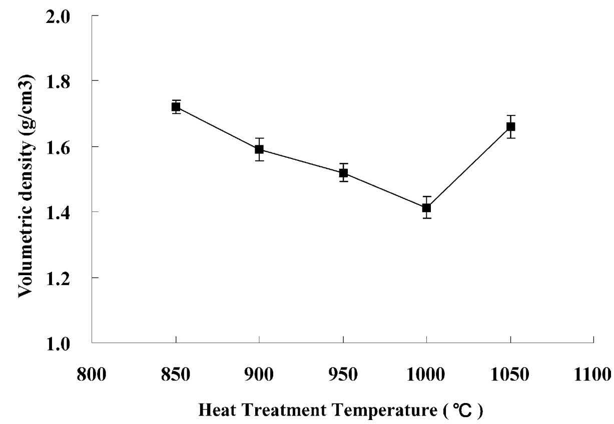

Fig. 7. Volumetric density after heat treatment at different temperatures.

Table 2
EDS results on the surface and in the hole of the porous glass-ceramics at heat treatment temperature 850 and 950 °C

Element wt.%	O	Ca	Si	Al	Na	Mg	Ti	S
850 °C	31.2	26.2	23.8	11.3	2.8	2.5	1.1	ND
950 °C	43.5	24.0	15.3	6.9	3.6	1.5	1.9	3.2

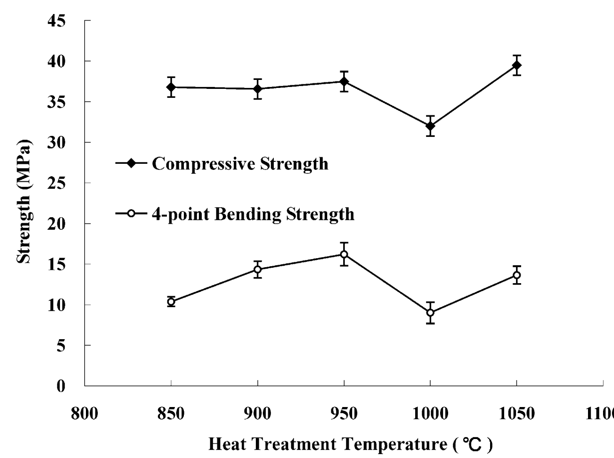

Fig. 8. Four-point bending strength after heat treatment at different temperatures.

the pore size was around the range 20–80 μm. Pore sizes increased with increased heat treatment temperature. After reaching the maximum size (about 80 μm) after heating at 1000 °C, the pore sizes decreased abruptly after heating at 1050 °C. Porosity and water absorption rate tests (Fig. 6) show similar behaviour confirming this behaviour. Table 2 also gives the chemical composition of the glass-ceramics analysed by EDS. The major components were CaO, Al_2O_3 and SiO_2 which agree with the gehlenite phase in the phase diagram of the $CaO–Al_2O_3–SiO_2$ system [16].

3.4. Physical and mechanical properties of the glass-ceramic materials

According to the physical property analysis, both porosity and water absorption rate curves, illustrated in Fig. 6, increased gradually as the heat treatment temperature increased, subsequently reaching a maximum porosity of 47.2% and water absorption rate 33.4% at 1000 °C. However, with a heat treatment above 1000 °C, porosity and water absorption rate decreased sharply. On the other hand, as shown in Fig. 7, a trend of decreasing volumetric density was observed from 1.7 g/cm^3 at 850 °C down to the minimum about 1.4 g/cm^3 at 1000 °C by increasing the heat treatment temperature. After increasing the heat treatment temperature to 1050 °C, the volumetric density of the glass-ceramic material again increased rapidly.

Fig. 8 shows that the compressive strength and four-point bending strength of glass ceramics is a function of heat treatment temperature. Both curves show a trend of increasing strength as heat treatment temperature increasing. After the strength reached 15.9 MPa for four-point bending test and 36.1 MPa for compressive test at 950 °C, the strength decreased at 1000 °C because of the high porosity at this temperature, and subsequently increased again at 1050 °C.

Changes in the density, porosity and water absorption with heat-treatment temperature between 850 and 1000 °C, arise from the softening of the glassy phase in the system, together with concurrent gas generation due to decomposition of alkaline metal salts [17] or reduction of Fe^{3+} to Fe^{2+} involving O_2 release [18]. However, above 1000 °C, the crystalline phase transformation is nearly complete, and simultaneously, shrinkage occurred making porosity/water absorption rate decrease and volumetric density increase. These results indicate that the best behaviour and characteristic of the glass-ceramics can be produced at 950 °C.

4. Conclusions

The investigated incinerated fly ash has a good vitrification and devitrification characteristic by using melt technology and a heat treatment process. It is possible to treat incinerator fly ash as a raw material to produce glass-ceramic products. On the basis of the results reported in the present investigation, the crystallization of incinerator fly ash-based glasses takes place at temperatures above 700 °C with formation of one of the melilite group minerals—gehlenite ($Ca_2Al_2SiO_7$). Honeycomb structure glass-ceramics form with pore sizes around 20–80 μm. The incinerator fly ash-based glass-ceramic material with optimum physical and mechanical properties in this investigation is the one sintered and heat treated at 950 °C for 2 h. This material has good potential to manufacture light-weight aggregates or bricks for engineering applications.

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