

## CHARACTERIZATION OF GLASS-CERAMICS PRODUCED FROM VITRIFICATION OF CLASS F MALAYSIAN COAL FLY ASH

M. Convery<sup>a</sup>, L. Downing<sup>a</sup>, C.Y. Yin<sup>b</sup>, B.M. Goh<sup>c</sup> and A.S.A.K. Sharifah<sup>b</sup>

<sup>a</sup>Department of Chemical & Biomolecular Engineering, Melbourne School of Engineering, Building 173, Grattan Street, The University of Melbourne, VIC 3010 Australia.

<sup>b</sup>Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, Malaysia.

<sup>c</sup>Faculty of Applied Sciences, Universiti Teknologi MARA Perlis, 02600, Arau, Perlis, Malaysia  
Email: yinyang@salam.uitm.edu.my

### ABSTRACT

A glass-ceramic material was produced from class F Malaysian coal fly ash by using vitrification method. Determination of physico-chemical properties of formed samples was conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), Rockwell hardness and toxicity characteristic leaching procedure (TCLP). XRD analysis showed an amorphous annealed material followed by the strong crystal growth of quartz and mullite phases over the heat treatment stage. Growth of crystalline phase was also observed. The TCLP results showed that the glass-ceramic was non-hazardous. Results showed that it was technically possible to use vitrification to produce glass-ceramics from Malaysian coal fly ash.

**Keywords:** Glass-ceramics; Class F coal fly ash; Characterization; Vitrification; Metal leachability

### 1. INTRODUCTION

The Malaysia relies heavily on industrialisation for economic growth. This has often produced high volumes of waste, for example ashes from combustion of coal or other waste material. This is often seen, however, as an unsustainable practice and is detrimental to the immediate environment since ashes commonly contain toxic substances such as heavy metals which may leach into the soil matrix and groundwater. In addition, it can also alter the elemental composition of vegetations growing in the vicinity as well as potential accumulation of toxic elements in the ecological food chain (Carlson & Adriano, 1993). Increased realization of serious harm being caused to the environment by industrialization has served as an impetus for research into the reuse of industrial-based waste ashes around the world. These ashes are well-suited as precursors to glass-ceramics since they contain large quantities of CaO, SiO<sub>2</sub>, and Al<sub>2</sub>O<sub>3</sub> (Cheng, 2004). Glass ceramics can be produced by vitrification of fly ash in either pure form or with additives. This technique can reduce the volume of fly ash by up to 97% (Jantzen & Brown, 1993). Conveniently, glass ceramics display a wide range of chemical and mechanical

properties which can be used in a variety of applications (Barbieri *et al.*, 2008). These properties and the success of the vitrification depend upon process conditions and the type of ash used. Coal fly ash is categorized into two classes; class C and class F (Safiuddin *et al.*, 2009). Differentiation between these classes is made from the composition of the ash and from the coal from which it was formed (Vassilev & Vassileva, 2005). Typically, class C ash has higher calcium concentrations, formed from lignites or subbituminous coals and exhibit cementitious properties without the need for additives (Kutchko & Kim, 2006; Biernacki *et al.*, 2008; Kim & Prezzi, 2008). Class F ash, on the other hand, is formed from burning bituminous or anthracite coals, contains smaller concentrations of calcium and does not exhibit cementitious property unless combined with additives (Kim & Kim, 2005). There were many previous studies on reuse of fly ashes as precursors for production of glass-ceramics. Studies had focused on using both standalone fly ash (Cioffi *et al.*, 1993; Erol *et al.*, 2003), as well as compositions modified with additives such as fluxing agents (Leroy *et al.*, 2001), nucleating agents (Kim & Kim, 2005) and glass cullet. To the authors' knowledge, there is no known utilization of class F Malaysian coal fly ash for production of glass-ceramics.

The objectives of this study were to produce glass-ceramics from class F Malaysian coal fly ash via vitrification and characterize the resultant products to determine their morphology, surface microstructure, hardness and toxicity. Characterization was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), Rockwell hardness and toxicity characteristic leaching procedure (TCLP).

### 2. METHODOLOGY/ANALYSIS/EXPERIMENTAL SET-UP

The Class F coal fly ash was obtained from Lafarge Malayan Cement plant from Rawang, Selangor, Malaysia with SiO<sub>2</sub> content approximately 65% and relative density 2.10 (Alengaram *et al.*, 2008). Standalone coal fly ash was

used as the precursor for production of glass ceramics. The vitrification process was carried out in a muffle furnace. The samples were ground/crushed and homogenized before being put into separate ceramic crucibles. The samples were heated to 1400°C at 20°C/min and held for 2 hours before quenched in water to room temperature. In order to homogenize the resultant glassy material, the samples were crushed and ground, and re-fired under the same conditions. The samples were subsequently annealed by heating to 600°C at 10°C/min and held for 2 hours before being cooled at the same rate. The annealed glass samples were crystallized using a single-stage method. The nucleation/crystallisation temperature was fixed at 1000°C (Leroy *et al.*, 2001; Zhang *et al.*, 2007). This temperature was reached by heating at 20°C/min and held for 2 hours before the samples were cooled to room temperature at 10°C/min. Crystalline phases in the samples were determined using a Rigaku (D/MAX-2000/PC) X-Ray Diffractometer operated at 40 kV and 30 mA for the reflection angle (2θ) in the range 3° to 90°. Samples were crushed and ground prior to analysis. The surface morphologies of the samples were examined via Scanning Electron Microscope LEO 982. The samples were coated in gold using Thermo VG Scientific POLARON SC7620 sputter coater prior to SEM analyses. Rockwell hardness scale A (HRA) of the products was determined using a Series 600 Wilson/Rockwell indenter fitted with a hardened steel penetrator. Values of hardness were calculated from average of ten measurements for each sample. The toxicity of crushed products in terms of leachable heavy metals was determine via modified United States Environmental Protection Agency toxicity characteristic leaching procedure (TCLP) Method 1311 previously specified in Yin *et al.* (2008). This method was used to simulate typical leaching conditions on disintegrated landfilled glass-ceramics due to prolonged aging effects. Subsequent to completion of the 18-hour extraction, the leachate was filtered and analyzed for heavy metal content using Thermo Scientific iCAP 6000 Series Inductively Coupled Plasma Spectrometer.

### 3. RESULTS AND DISCUSSION

A smooth and matt brown glassy/ceramic-like material is produced. During the melting stages, a dark-brownish color is developed from the initial light grey color of the raw ash. However, this color appears to lighten after the heat treatment stage. Figs. 1 and 2 show the XRD patterns of the sample after annealing and crystallization stages, respectively. XRD patterns reveal phase, chemical and crystalline structure information data (Wahit *et al.*, 2009) which afford better understanding on the reaction products of the glass-ceramics. The diffraction intensities which are reflected by corresponding counts per second (cps) are used as the indication of changes among the patterns of various systems. The XRD patterns display a minimum number of peaks after the annealing process in which mullite is

dominant. Mullite is an aluminium-silicon-based oxide normally produced during high thermal processes and has a needle-like appearance. The patterns for sample after the crystalline process indicate prominent peaks associated with significant crystalline phase development, principally consisting of mullite, clinoenstatite, ferrosilite and quartz. This growth can be attributed to the choice of reasonable heat treatment stage conditions to enable nucleation. The presence of ferrosilite (FeSiO<sub>3</sub>) may have decreased viscosity and therefore, it increases the crystal growth rate since Fe<sup>3+</sup> ion can act as a modifier of the structure, that is, breaking of the Si-O-Si bonds (Barbieri *et al.*, 2002).

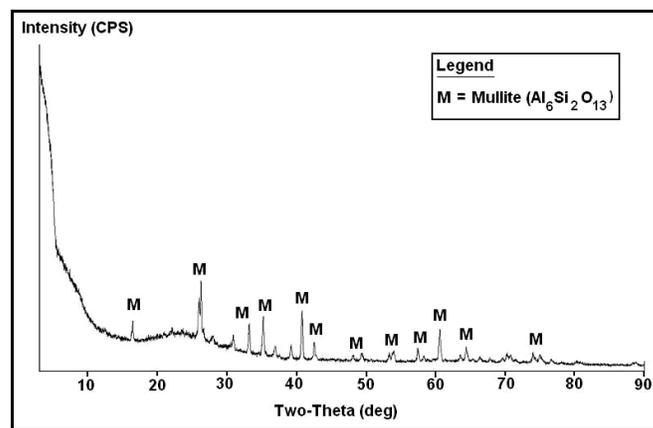


Figure 1 XRD patterns of sample after annealing process

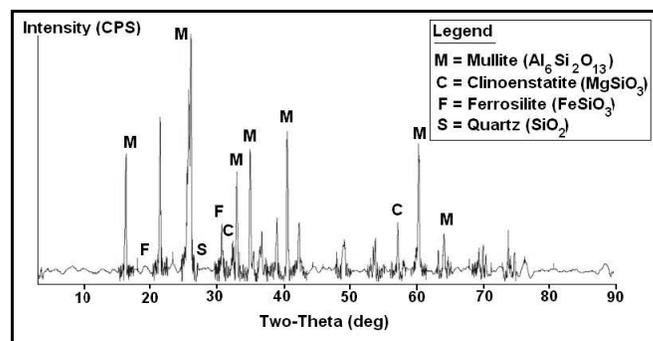


Figure 2 XRD patterns of sample after crystallization process.

Fig. 3 shows the micrograph of the coal fly ash. It is observed that the ash particles are spherical in shape, an observation similar to previous SEM observations for fly ash (Kutchko & Kim, 2006; Pengthamkeerati *et al.*, 2008). The majority of the particles ranged in sizes less than 20 μm. Figs. 4 and 5 show the micrographs of the sample after annealing and crystallization stages respectively. As expected, after the crystalline stage, the sample exhibits a more defined crystalline structure compared to the sample produced after annealing stage. This observation is consistent with result of the XRD analysis where amorphous elements are detected in the XRD pattern after annealing

stage. Needle-like formation is observed after the crystalline stage. This needle-like formation is most likely mullite. At this stage, the glass-ceramics appear to be very brittle and hard with the HRA measurements of the sample range from 1.4 to 87.5 kgf. The variation in hardness may be due to a lack of homogeneity in the sample.

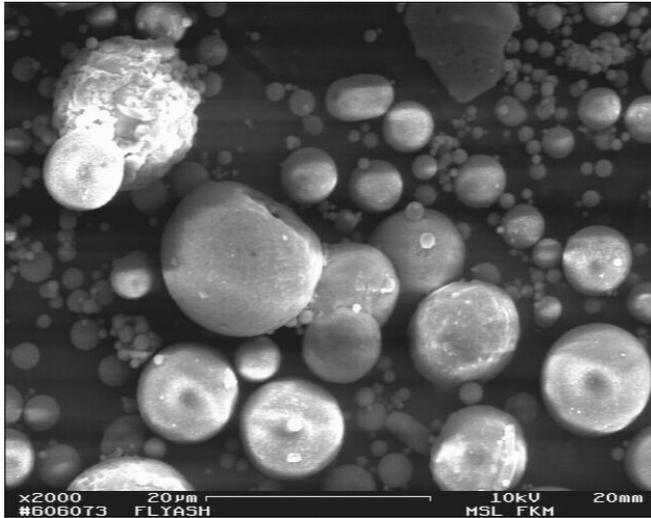


Figure 3 Micrograph of coal fly ash.

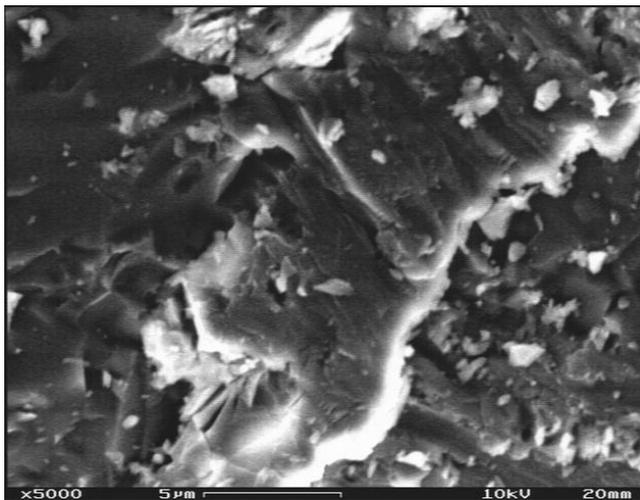


Figure 4 Micrograph of sample after annealing stage.

The TCLP test is used to determine the toxicity of contaminants of hazardous wastes or soils which determines the mobility of organic and inorganic analytes in the wastes. In this test, waste samples are crushed to particle sizes less than 9.5 mm and extracted with an acetic acid solution with pH either 2.88 or 4.93 depending on the alkalinity of the waste. Cadmium, chromium, copper and lead are not detected in the TCLP leachate while nickel concentrations are less than 0.1 ppm. Since the Malaysian leachability limits (Waste Evaluation Guidelines, Kualiti Alam Sdn Bhd,

Malaysia) for cadmium, chromium, copper, lead and nickel are stipulated to be 1, 5, 100, 5 and 100 ppm respectively (Yin *et al.*, 2008), it can be surmised that the produced glass-ceramics are not hazardous and they can be disposed

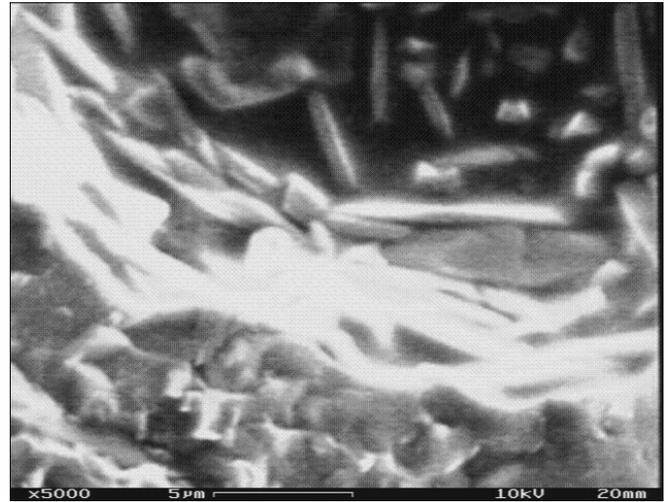


Figure 5 Micrograph of sample after crystallization stage.

off in a secure landfill after the end of their useful period. This observation is also in agreement with a previous study conducted by Zhang *et al.* (2007) in which they reported that glass-ceramic produced from Chinese coal fly ash was determined to be non-hazardous via TCLP method. They also reported that heavy metals present in fly ash (if any) were successfully immobilized into the glass matrix during the production process. In this case, the metals may have been infused in the solidified matrix which form very strong bonds and thus, significantly reduce metal leachability.

#### 4. CONCLUSION

It was technically feasible to produce glass-ceramics by vitrification of Class F fly ash since the resultant product exhibited sufficient strength. The following conclusions could be drawn:

Mullite was dominant after the annealing process while significant crystalline phase development, principally consisting of mullite, clinoenstatite, ferrosillite and quartz occurred after the crystallization process.

The glass-ceramic produced after the crystalline stage exhibited a more defined crystalline structure compared to after annealing stage.

TCLP results showed that the glass-ceramics were not hazardous and could be safely disposed off in a secure landfill after the end of its useful period.

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