

HIGH-PERFORMANCE REFRACTORY CERAMICS FROM WASTE MATERIALS

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ABSTRACT

Waste materials such as fly ash and bottom ash are increasingly being produced in high volumes owing to the dependence of numerous industries on coal-derived electricity. Even though a small fraction of these materials are being used in the construction industry, large volumes are dumped in landfill and man-made lakes, which negatively impacts on the environment and health. Work at UNSW in collaboration with Vecor Pty. Ltd. on waste material utilisation has resulted in the development of a patented materials and processing technology for the fabrication of interconnected percolated mullite fibre network using fly ash. Importantly, these materials have shown outstanding long-term stability at high temperatures, which makes it ideal for use as refractory ceramics. Furthermore, the characteristics of these unique ceramics can be further tailored to create ceramic composites with outstanding corrosion resistance and thermal shock properties, through careful control of chemical additions and processing conditions.

INTRODUCTION

Fly ash is the major component of coal combustion products (CCPs) in power stations. Currently, ~600 mT of CCPs are produced annually with 80% being fly ash (~500 mT)^[1,2]. The amount of fly ash produced is expected to increase tremendously in the coming decades owing to the rapid rate of growth in developing countries. The large volumes of ash produced annually have led to this material being considered as the world's fifth largest raw material resource. The utilisation of fly ash varies greatly globally; however the average global utilisation is only 16%. The major avenues for fly ash utilisation are in cementitious products and geopolymers, as soil conditioning agents, zeolites and filling materials for land reclamation, and glass ceramics^[2-4].

However, large volumes of fly ash are disposed of in landfill sites or in man-made lakes leading to major environmental issues such as leaching of toxic elements from the fly ash to the water sources and soil^[1]. These issues coupled with the increasingly tough environmental regulations on the disposal of fly ash have resulted in the drastic need for novel large-scale applications for these materials. Other factors limiting the utilisation of these materials include compositional variabilities and transportation issues^[1].

Fly ash generally appears grey to black in colour depending on the carbon content. The particles are spherical in shape and are composed of SiO₂-rich glassy spheres (Fig. 1). In addition, needles of mullite (3Al₂O₃•SiO₂) are present in the body of the spheres. The composition varies with the coal type and the combustion process used in the power station. However, the typical compositional ranges are as follows: SiO₂ (50-70 wt%), Al₂O₃ (20-40 wt%); Fe₃O₄ + Fe₂O₃ (1-15 wt%), CaO (1-30 wt%), TiO₂ (1-2 wt%) and Na₂O + K₂O (1-3 wt%)^[1,2,5].

The crystalline components are mullite (10-25 wt%), quartz (10-25 wt%), and iron oxides (1-15 wt%)^[2]. Mullite is the only stable intermediary compound in the Al₂O₃-SiO₂ system at atmospheric pressure and is used for several high-performance refractory applications owing to its high melting point, low thermal expansion, good chemical stability, and high strength at high temperatures^[6]. Mullite has an orthorhombic crystal structure and the stoichiometry can range from 3:2 to 2:1 Al₂O₃

to SiO₂ depending on the starting composition and processing conditions. Mullite grains are either acicular or equiaxed in morphology and the morphology is dependent on the relative proportions of Al₂O₃ and SiO₂, the sintering temperature, and presence of fluxes. The morphology of the mullite grains can be altered by the addition of oxides which either lower (V, Fe, and Mn) or enhance (Al and Ti) the glass viscosity^[6].

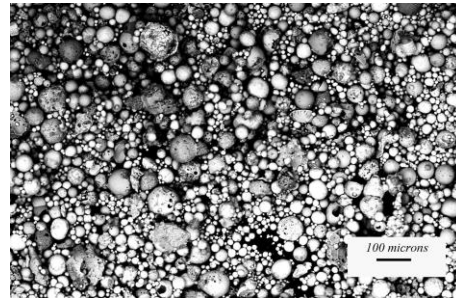


Fig. 1: SEM images of fly ash particles

The use of mullite for high-temperature applications is dependent on the operating conditions as well as the nature and composition of the grain boundaries in a polycrystalline material. Owing to the rarity of natural mullite, and the high processing and raw material costs for synthetic mullite fabrication, there is increasing focus on fabricating mullite from other raw materials. There has been increasing research on the fabrication of mullite ceramics from fly ash. Fly ash with high aluminium contents (Al₂O₃ >45 wt%) has been directly sintered to produce mullite without any additives, while other works involved pre-treatment with alkali/acid followed by sintering at 1500°-1600°C^[7,8]. Furthermore, stoichiometric 3:2 mullite has been fabricated by adding high amounts of Al₂O₃ to fly ash, followed by sintering at 1600°C^[9]. In fly ashes, the presence of unreacted SiO₂-rich glass and fluxes (alkali and iron oxides) can hinder their utilisation at high temperatures owing to the potential for glass softening and shape distortion of the ceramic.

Interestingly, patented work at UNSW has shown that an interconnected network of single-crystal mullite fibres (percolated) can be fabricated from fly ash. These materials display outstanding thermal stability during long-term heating at 1500°C, which is remarkable considering the glassy nature of the precursor materials, and the residual glass present in these samples^[10].

There has been limited work to examine the suitability of fly ashes of varying compositions for mullite production, and no reported work on the high-temperature behaviour of mullite ceramics produced from fly ash. The present work investigates the suitability of a range of fly ashes of varying compositions for high-temperature applications. Furthermore, the formation of a unique mullite ceramics and its properties and future potential is discussed.

MATERIALS AND METHODS

Ten fly ashes were obtained from different power stations in Australia, India, and China. The compositions of the fly ashes, determined using X-ray fluorescence spectroscopy (WDXRF; Panalytical Axios Advanced WDXRF, 4 kW) are provided in Table 1. The names of the power stations are not provided owing to proprietary reasons.

Table 1: Compositions of the fly ash showing the major species

| Fly Ash | SiO ₂ | Al ₂ O ₃ | Fe ₂ O ₃ | CaO | TiO ₂ | Na ₂ O | MgO | K ₂ O | LOI | Others |
|---------|------------------|--------------------------------|--------------------------------|-----|------------------|-------------------|-----|------------------|------|--------|
| A | 74.4 | 18.5 | 1.3 | 0.1 | 1.3 | 0.0 | 0.2 | 0.5 | 2.2 | 1.5 |
| B | 33.8 | 31.3 | 2.5 | 1.6 | 1.3 | 0.1 | 0.4 | 0.4 | 25.0 | 3.6 |
| C | 63.0 | 27.3 | 4.5 | 0.9 | 1.7 | 0.0 | 0.6 | 1.0 | 0.6 | 0.4 |
| D | 38.0 | 35.5 | 3.2 | 2.9 | 0.4 | 0.0 | 0.4 | 0.4 | 16.6 | 2.6 |
| E | 65.6 | 25.7 | 0.9 | 0.5 | 1.1 | 0.2 | 0.3 | 2.6 | 2.8 | 0.3 |
| F | 68.1 | 23.6 | 1.3 | 0.7 | 0.9 | 0.2 | 0.2 | 2.2 | 2.6 | 0.2 |
| G | 52.2 | 34.6 | 5.1 | 3.2 | 1.2 | 0.3 | 0.9 | 1.2 | 0.8 | 0.5 |
| H | 66.3 | 23.7 | 5.0 | 1.1 | 0.9 | 0.2 | 0.8 | 1.1 | 0.5 | 0.4 |
| I | 52.1 | 27.0 | 5.8 | 4.0 | 1.1 | 0.3 | 0.9 | 1.5 | 6.1 | 1.2 |
| J | 56.3 | 19.9 | 6.8 | 7.5 | 1.0 | 2.3 | 3.5 | 1.6 | 0.4 | 0.7 |

The mineralogical characteristics of some of the fly ashes are shown in Fig. 2. The mineralogical characteristics were determined using Philips X'Pert MPD (Multi-Purpose X-ray Diffraction System, 40 mA, 45 kV, CuK α radiation, 10°-70° 2 θ range, 0.026° 2 θ /min speed).

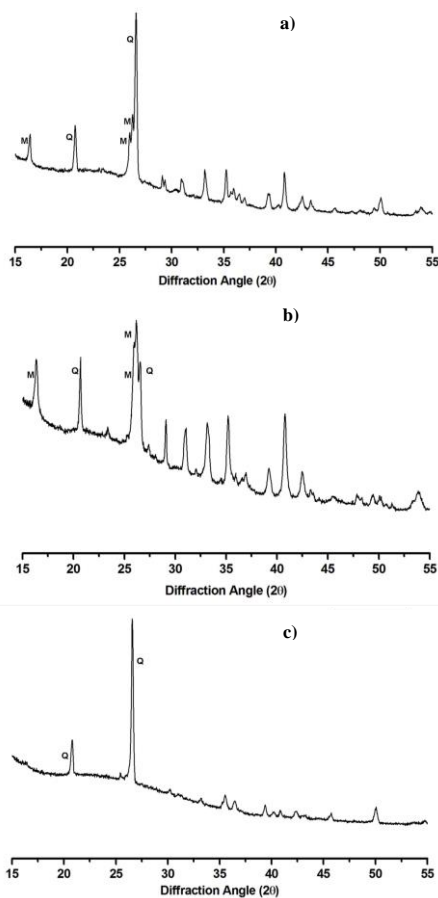


Fig. 2: XRD patterns of fly ash samples a) Typical (A), b) High-Al₂O₃ (B), and c) Low-Al₂O₃ (J) [Q – Quartz, M – Mullite]

The XRD patterns clearly show that quartz and mullite are the major crystalline species in these fly ashes, and that the mullite content generally shows a direct correlation with the Al₂O₃ content of the fly ash. A hump at ~26° 2 θ is indicative of the presence of glassy SiO₂-rich phase in the fly ash.

To 50 g of each fly ash, 0.5 wt% Na-CMC binder, and 5 mL distilled water were added, and then the mixture was manually mixed and then cast in a 20 mm diameter hardened steel die. The samples were then compacted at 10 kN load in an uniaxial press, and the resultant samples were heat treated at temperatures ranging from 1000°C to 1500°C for 5 h. For the heat treatment, the samples were placed on an aluminous insulating brick. The dimensional stability of the samples was

assessed by comparison of their shape and the extent of shrinkage after sintering at different temperatures. Based on these trials, three fly ashes were selected for long-term heat treatment trials at 1500°C for up to 96 h.

Scanning electron microscopy (SEM; Hitachi TM3000; 15 kV) was used to analyse the morphological characteristics of the sintered samples. Electrolytic etching in 5 vol% HF was conducted to reveal the mullite fibre characteristics of the samples after heat treatment at 1500°C. Application of a conducting coating with gold or chromium was not done to enable clear viewing of the etched mullite grain boundaries. XRD analysis was conducted on the heat treated samples to determine their mineralogical characteristics.

RESULTS AND DISCUSSION

Effect of Heat-Treatment

Figure 3 shows the effect of heat treatment on the mineralogy and microstructure of the sintered fly ash.

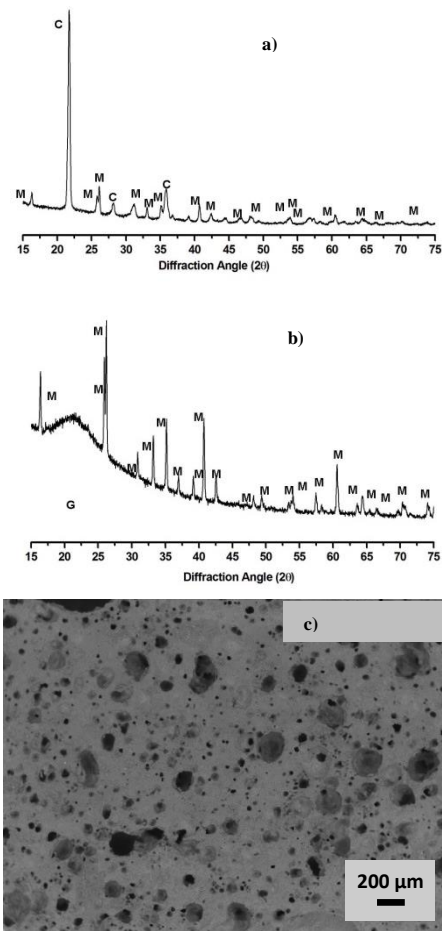
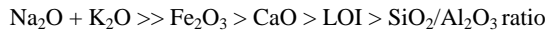


Fig. 3: XRD patterns of fly ash A a) after heat treatment at 1300°C [C – Cristobalite], b) after heat treatment at 1500°C, and c) SEM image after heat treatment at 1500°C

From the figures, it can be seen clearly that during heat treatment to 1300°C, the glassy hump disappears owing to the crystallisation of cristobalite. This is a common occurrence in aluminosilicate refractories with aggregates bonded by glass phases. However on heat treatment to 1500°C, the cristobalite redissolves and mullite is the major phase. In the absence of any aluminous additives, the increased intensity of mullite on heat treatment is a reflection of grain growth of the mullite fibres. The microstructure of the sintered sample appears dense and is composed of closed rounded pores.

Suitability for High-Temperature Applications

Based on the physical, microstructural, and mineralogical characterisation of the heat treated samples, the major criteria were identified that influence the high-temperature stability of the sintered fly ashes. The presence of fluxes (Na₂O, K₂O, CaO) would enhance glass formation and contribute to loss of shape on heating at high-temperatures; furthermore, Fe₂O₃ or Fe₃O₄ could transform to FeO at high temperatures, which also has a fluxing effect. The presence of high LOI would cause losses of high amounts of the material leading to unpredictable shrinkage during firing. A high Al₂O₃/SiO₂ silica ratio indicates high-temperature stability owing to minimisation of SiO₂-rich glass phases. With regard to the effects, the testing revealed that the stability is most significantly affected in the order:



Therefore, based on the results, the most suitable fly ashes for high-temperature applications were A, B, and C. It should be noted that the Fe-oxide content that is reported is composed of a mixture of Fe₂O₃ and Fe₃O₄ in almost similar proportions, and the latter can be removed by magnetic separation. This can enhance the potential of the material to be used for high-temperature applications. Blending with oxide additives is another potential approach that can be used.

Table 2: Suitability of different fly ashes for high-temperature applications (H – High, M – Moderate, L – Low; shaded boxes reflect most suitable characteristics)

| Fly Ash / Characteristics | Na ₂ O + K ₂ O | Fe ₂ O ₃ | CaO | SiO ₂ / Al ₂ O ₃ | LOI |
|---------------------------|--------------------------------------|--------------------------------|-----|---|-----|
| A | L | L | L | H | L |
| B | L | M | L | L | H |
| C | L | H | L | M | L |
| D | L | H | M | L | H |
| E | H | L | L | M | L |
| F | H | L | L | M | L |
| G | M | H | M | L | L |
| H | M | H | L | M | L |
| I | M | H | H | L | H |
| J | H | H | H | H | L |

Percolated mullite microstructures

Based on the results, fly ashes A, B, and C were heat treated at 1500°C for extended times. The results were remarkable in that these samples did not show any further deformation with increasing heat treatment time (Fig. 4), which is highly unusual for materials with high-SiO₂ contents. Examination of the microstructures of these samples at different time points revealed that with increasing heat treatment time at 1500°C resulted in increased coarsening of the mullite fibres and interconnectivity. This resulted in the formation of a three-dimensional interconnected mullite scaffold (Fig. 5) where the fibres were directly bonded to each other.

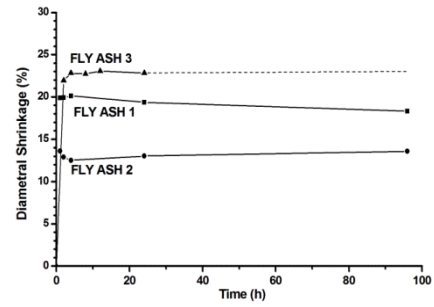


Fig. 4: Dimensional stability of sintered fly ash samples during heat treatment at 1500°C for extended times^[10]

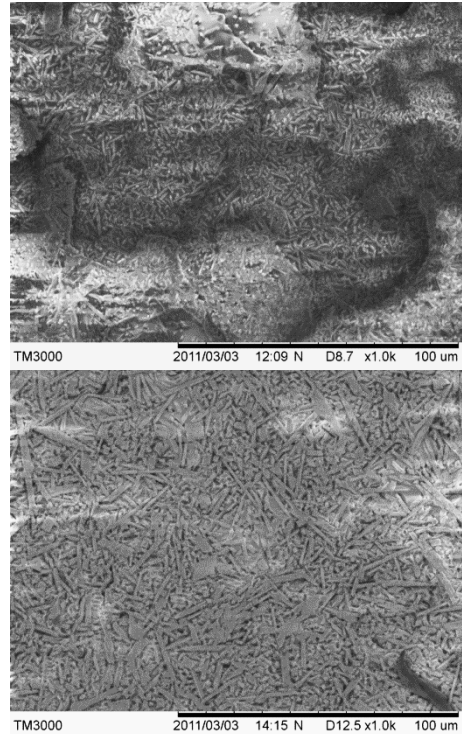


Fig. 5: Etched microstructures of the fly ash samples after sintering at 1500°C for short (top) and long (bottom) times^[10]

Another remarkable feature contributing to the improved high-temperature stability is that the growth of the interconnected mullite scaffold forces the glass phases to the interstices around the grains, thereby minimising their impact on the high-temperature stability and properties. Image analysis was conducted to quantify the changes in the microstructural characteristics. The data in Fig. 6 show clearly that the lengths of the fibres increased significantly with increasing heat treatment time. Further, the areal coverage of the microstructure by the mullite fibres increased significantly to ~95 vol% (not shown here) with increase with treatment time.

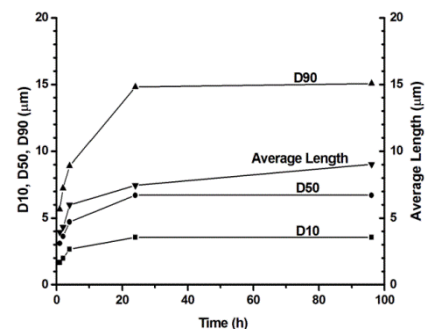


Fig. 6: Changes in average mullite fibre dimensions with heat treatment times^[10]

Further work has shown that the characteristics of the interconnected mullite network can be manipulated using different additives. This patented technology has been developed in partnership with Vecor Pty. Ltd., who are now working towards large-scale production of these mullitic materials in the form of aggregates and bricks for high-temperature refractory applications (Fig. 7).

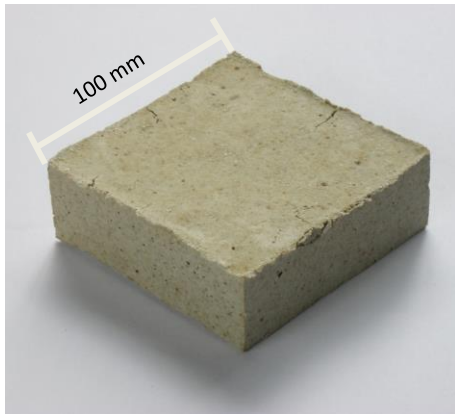


Fig. 7: Fly ash-based refractory brick sample

These materials show the following properties as listed in Table 3. As seen from the data, the materials possess high strengths and moderate thermal conductivity. The thermal expansion values are in the typical range of mullite refractories. The most remarkable property is the high-temperature stability which outperforms most commercial mullite-based products.

Table 3: Properties of percolated mullite products

| Properties | Values |
|---|---|
| Cold Compressive Strength | 45-80 MPa |
| Modulus of Rupture | 20-30 MPa |
| Thermal Conductivity | 0.7-1.8 W/mK |
| Thermal Expansion (25°-1000°C) | $4.5-6.0 \times 10^{-6}/^{\circ}\text{C}$ |
| High-Temperature Stability | $\geq 1600^{\circ}\text{C}$ |
| Thermal Shock Resistance (Adapted Japanese Standard of Immersion in Water from 950°C) | Good (Survived > 50 cycles) |

Work is underway on the fabrication of insulating refractory products using these aggregates. The work has involved careful selection of aggregate sizes and then sintering the gap-graded material at high-temperatures to obtain self-bonded insulating refractories with excellent thermal shock resistance. The microstructure of this insulating refractory is shown in Fig. 8. The apparent porosity of the product was determined to be ~50% as determined using the hydrostatic weighing method.

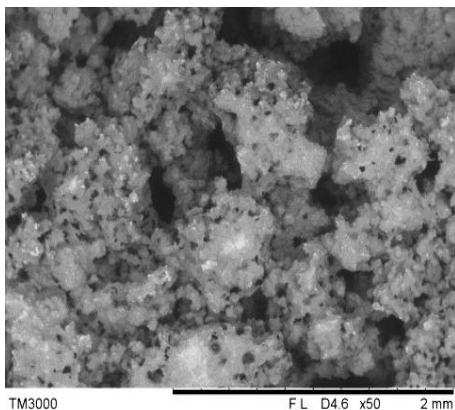


Fig. 8: SEM image showing the microstructure of the insulating refractory product

CONCLUSIONS

The collaborative research work between UNSW Sydney and Vecor Pty. Ltd. has led to the following successful outcomes:

1. Established the protocols for selection of fly ashes for high-temperature refractory applications.
2. Developed the patented processing steps (additions and heat treatment conditions) to obtain a percolated mullite refractory ceramic with excellent mechanical and high-temperature thermal properties.
3. Developed methods for the fabrication of percolated mullite aggregates for designing refractory products and ceramic composites with varying characteristics.

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