



**LOW CARBON LIVING
CRC**

State of Practice: High Volume Applications of Fly Ash and Barriers to Commercialisation

Research Project: RP1004-II



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EXECUTIVE SUMMARY

Australia is heavily reliant upon the use of coal for electric power generation with approximately 74.9% or 170,822 GWh of electricity in year 2010 to 2011 being generated through coal-fired power plants. Australia's coal powered generators produce about 14 million tonnes of fly ash per year. Currently, only 42% of by-product fly ash is used in various construction-related applications and the remainder placed into onsite storage dams or dumped into landfill sites potentially causing serious environmental issues. The principal aims of this study are to review the existing fly ash utilisation industry and to examine the potential high volume applications of fly ash.

The widespread utilisation of Geopolymer concrete in the industry is certainly the most promising pathway to increase the rate of fly ash utilisation. Geopolymer concrete is the result of the reaction of materials containing aluminosilicate such as fly ash with alkalis to produce an inorganic polymer binder. As there is no Portland cement in geopolymer concrete mix and geopolymer binder can provide reduction of embodied CO₂ of up to 80% compared to Ordinary Portland Cement. Indeed, carbon emissions due to the manufacture of Portland cement are second only to burning fossil fuels. Its share of CO₂ emissions in Australia is estimated at 8 million tonnes/year.

The considerable sustainability benefits of using a geopolymer binder system composed almost entirely of recycled materials has led to considerable research on geopolymer concrete (GC) in recent years in Australia and three established commercial suppliers of GC: Wagners in the Queensland supplying Earth Friendly Concrete (EFC), Zeobond in Victoria supplying the E-concrete technology and Rocla, part of Fletcher Building group with their Head Office in Chatswood, New South Wales. Geopolymer concrete has yet to enter the mainstream of concrete construction. The main barriers for widespread adoption of geopolymer concrete in the industry and the pathway to overcome those barriers

have been clearly identified and are reported in the CRC-LCL RP1004-I (Berndt et al., 2013).

Fly ash based manufactured synthetic lightweight aggregate for concrete appears to be the second most promising pathway to increase significantly the rate of fly ash utilisation. Lightweight concretes offer superior insulation properties that can reduce energy consumption in buildings, reduce the dead weight and material handling cost in construction. Further, the rapid depletion of quality natural aggregate quarry sources close to most major metropolitan regions of Australia, emphasize why the need to explore alternative economic sources has become imperative to support increasing vital infrastructure development, including housing, roads, bridges, schools and hospitals.

INTRODUCTION

Background

Coal is a major fuel for energy and steam production in coal-fired power plants worldwide. It is estimated that there are over 1004 billion tonnes of coal reserves worldwide (WCA, 2012). In 2011, total world coal production reached a record level of 7.7 billion tonnes. At the current production rates, coal resources are enough to last for more than 130 years. Coal currently provides 30.3% of global primary energy needs and generates 42% of the world's electricity. WCA (2012) predicts that utilisation of coal is expected to rise over 50%, from current levels, by 2030, with developing countries responsible for 97% of this increase, primarily to meet improved electrification rates. Demand for coal use in energy generation continues to grow within both developing and developed economies.

Australia too is heavily reliant upon the use of coal for electric power generation with approximately 74.9% or 170,822 GWh of electricity in year 2010 to 2011 being generated through coal-fired power plants (ESAA, 2012). Policy shifts towards low carbon technologies and strong rejection by the environmentalist and conservationist groups as well as cheaper prices for renewable and/or cleaner energy may prevent new coal fired power stations been built in Australia (Hannam, 2013). However, it is anticipated that the current coal fired power stations will continue to operate and generate electricity at the current capacity into the future (ESAA, 2012). By year 2021, a total of 50.8% of the total electricity in Australia will still be generated by burning coal, as shown in Figure 1 (ESAA, 2012).

Combustion residues from coal-fired power stations include fly ash from the electrostatic precipitator (ESP) or bag house of pulverised coal-fired boilers, bottom ash at the bottom of the furnace, residues from flue gas desulphurisation (FGD), fluidised bed combustors and from gasifiers used for power generation (Smith, 2005). In Australia, fly ash generally constitutes to about 80% of the coal combustion residues with bottom ash making up

the remainder. Flue gas desulphurisation and clean-up technologies are not used (French and Smitham, 2007).

These combustion residues are industrial by-products that if not put to beneficial use, are recognised as environmental pollutants. The production of coal combustion residues has increased significantly over the last two decades. Back in the early 1990s, the total world coal combustion residues production was estimated at 460 million tonnes (Manz, 1997). From the data in 2010, the worldwide production of coal combustion residues was approximately 780 million tonnes with some 415 million tonnes or 53% were reported as utilised (Heidrich et al, 2013).

The remainder of the unused combustion residues is dumped into landfill sites, ash ponds or flushed out directly into the ocean, potentially causing serious environmental damages to marine life (Malhotra, 1999). With the increase in combustion residues production, more land and reserves will be required for storing the ash and these large ash lagoons, if breached, could cause significant environmental damage, as well as significant distress to the local community. An example of such an environmental disaster is the 2008 Tennessee coal ash spill incident in United States (Lynnfield, 2009).

Forecast of principal generation capacity (MW) 2011 to 2021

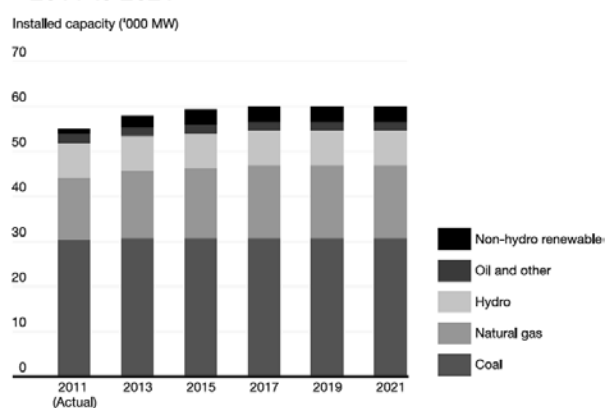


Figure 1: Forecast of electricity generation from 2011 to 2021 (ESAA, 2012)

Steel furnace slag, a by-product of steel making, is produced during the separation of molten steel from impurities in steel-making process in the basic oxygen

system. Value added applications for steel furnace slag are investigated as well.

Scope of Study

The principal aims of this study are to review the existing fly ash utilisation industry, examine the potential high volume applications of fly ash and identify the barriers to commercialisation and/or utilisation. Recommendation to increase rate of fly ash utilisation accompanied by suggestions for further research is also provided. It should be noted at this point that numerous studies on the utilisation of fly ash have been undertaken by many researchers; for example, Roy et al. (1981), Openshaw (1992), Heeley (2003), Smith (2005, 2006), Ahmaruzzaman (2010), Blissett and Rowson (2012), but to list a few.

The utilisation and application of other coal combustion residues such as bottom ash and flue gas desulphurisation residues are not within the scope of this study and will not be considered.

In this study, potential applications of steel furnace slag are review as well.

FLY ASH

Introduction

Traditionally, fly ashes are generated at 1200°C to 1700°C from the various inorganic and organic constituents of the feed coal. Because of the scale of the variety of the components, fly ashes are one of the most complex anthropogenic materials with approximately 316 individual minerals and 188 mineral groups identified in different sources and batches of fly ash (Vassilev and Vassileva, 2005). The formation of fly ash particles is represented schematically in Figure 2 (Tomeczek and Palugniok, 2002). The coal particles when heated up, release volatiles and burn as char particles. Consequently, they reach temperatures much higher

than the extraneous mineral particles containing not more than 10% of organic matter. The fine inherent minerals (<0.1 µm) transform within the char particles and gradually are released during the char fragmentation. Decomposition of minerals and conversion in solid phase leads to formation of gases that undergo homogeneous chemical reactions with subsequent heterogeneous or homogeneous condensation. The homogeneous condensation and the fragmentation of inherent minerals are the source of fly ash of size 0.02 µm to 0.2 µm. Coalescence of the fine fragments of mineral matter produces ash particles of medium size 0.2 µm to 10 µm. The largest ash particles (10 µm to 90 µm) are from the transformed extraneous mineral particles.

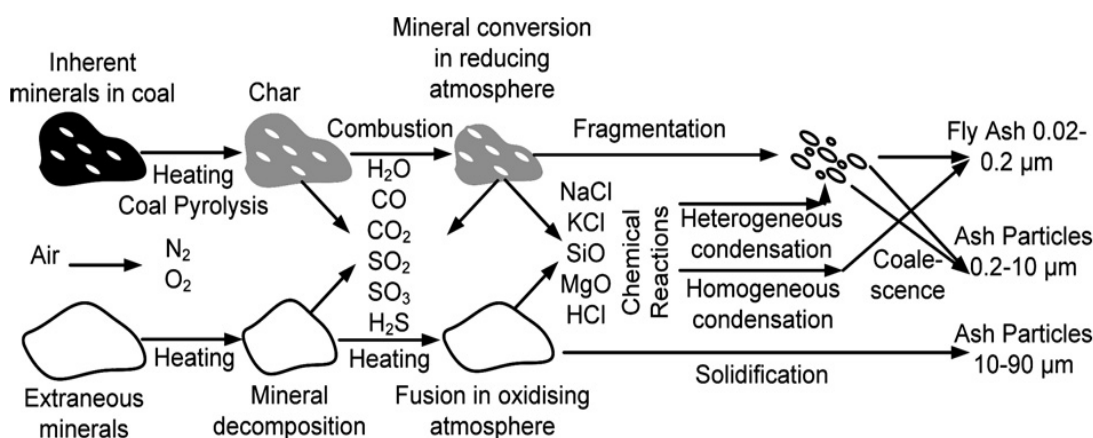


Figure 2: Mechanism of fly ash formation from pulverised fuel combustion (Tomeczek and Palugniok, 2002)

In the following sections, the properties of fly ash obtained from the conventional pulverised fuel combustion are briefly discussed. The properties of fly ash including composition, mineralogy, surface chemistry and reactivity are of fundamental importance in the development of various applications of fly ash. It is important to note here that as nitrous oxide (NO_x) emissions controls are becoming increasingly stringent and the power generators in Australia, and internationally, are increasingly updating their burners to low NO_x types, the properties of fly ash generated from these low NO_x combustions are different. Limited

published literature is available on the properties of the low NO_x combustion fly ash. This issue is addressed in details in Section 7.5.4 of this report.

Physical properties

The physical properties of fly ash particles vary widely depending on the type of feed coal, boiler type, carbon content in the coal, combustion temperature, cooling rate and the setup of the pulverised ash collection system (Basu et al., 2009; Ahmaruzzaman, 2010; Blissett and Rowson, 2012). Generally, fly ash consists of fine, powdery particles that are predominantly spherical in

shape, either solid or hollow and irregular unburned carbon (Ahmaruzzaman, 2010; Blissett and Rowson, 2012). As mentioned in Section 2.1, fly ash particles are usually finer than 100 µm (Chang et al., 1977; Roy et al., 1981) and have a silt loam texture. The specific gravity of fly ash usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m²/kg (Roy et al., 1981; Tolle et al., 1982; Mattigod et al., 1990). The colour of fly ash can vary from tan to grey to black, depending on the amount of unburned carbon in the ash (Ahmaruzzaman, 2010).

Mineralogy

The mineralogical composition of fly ash, which depends on the geological factors related to the formation and deposition of coal, its combustion conditions, can be established by X-ray diffraction (XRD) analysis. Fly ash can be regarded as essentially consisting of three types of components:

- Crystalline minerals;
- Unburnt carbon particles; and
- Non-crystalline aluminosilicate glass.

The dominant crystalline mineral phases in fly ash are quartz, kaolinite, mullite, hematite, magnetite, calcite and hematite (Hodgson and Holliday, 1966; Wang, 2008). Quartz and mullite are the major crystalline constituents of low-calcium ash, whereas high-calcium fly ash consists of quartz, calcium aluminate (C₃A), calcium silicate (CS) and calcium aluminosilicate (C₄AS) (Blissett and Rowson, 2012).

Chemical properties

The chemical properties of fly ash are influenced to a great extent by the type of the coal being burned. Two types of coal, viz, black and brown coals, are mined and burnt in Australia. In most power stations in Australia, black coal is burnt. Black coal consists of anthracite, bituminous and sub-bituminous coals. In the state of Victoria, brown coal, also known as lignite, is burnt. The fly ashes derived from these two coals have substantially different characteristics.

The principal components of black coal fly ash are the oxides of silicon (Si), aluminium (Al), Iron (Fe) and Calcium (Ca), with varying amounts of carbon, as measured by the loss on ignition (LOI). Brown coal fly ash is characterized by higher concentrations of calcium and magnesium oxide and reduced percentages of aluminosilicate and iron oxide, as well as lower carbon content, compared with black coal fly ash. Brown coal fly ash also has a higher concentration of sulphate compounds than black coal fly ash. Table 1 compares the typical range of the chemical constituents of black coal fly ash with those of brown coal fly ash derived in Australia.

Table 1: Chemical composition of black and brown coal fly ashes.

Component	Australian fly ash	
	Black coal ^{1,2}	Brown coal ³
Silica, SiO ₂	44.5 – 71.0	1.4 – 60.4
Alumina, Al ₂ O ₃	21.8 – 30.7	1.8 – 13.3
Iron oxide, Fe ₂ O ₃	0.7 – 14.4	8.5 – 24.5
Calcium oxide, CaO	0.1 – 5.9	1.0 – 28.4
Magnesium oxide, MgO	0.3 – 4.2	1.0 – 18.8
Sodium oxide, Na ₂ O	0.1 – 3.7	2.1 – 11.0
Potassium oxide, K ₂ O	0.4 – 2.9	0.4 – 1.2
Titanium oxide, TiO ₂	0.9 – 1.9	0.1 – 1.7
Sulphur trioxide, SO ₃	0.0 – 0.7	2.4 – 21.7
Loss on ignition (LOI)	0.2 – 10.0	7.6 – 11.7

¹ Ward and French (2003) ² Heidrich (2003) ³ Macphee et al. (1993)

As shown in Table 1, aside from the major components in fly ash, i.e. Aluminium (Al), Iron (Fe) and Silicon (Si), smaller concentrations of Potassium (K), Sodium (Na), Titanium (Ti) and Sulphur (S), other components are also present. Mattigod et al. (1990) suggested that during the combustion of coal at temperatures of 400°C to 1500°C, a large portion of the inorganic compounds in

the feed coal vaporise and condense on fly ash particles. Davidson et al. (1974) established correlation between mineral concentrations with the particle size. They noted that inorganic compounds including Aluminium (Al), Calcium (Ca), Iron (Fe), Potassium (K), Magnesium (Mg), Sodium (Na) and Titanium (Ti) exist in all sizes of fly ash particles with little or no enrichment with the particle sizes.

In Australia, the Ash Development Association of Australia has undertaken an on-going monitoring program to determine the total heavy metal contents in fly ashes. Table 2 summarises the heavy metal element concentrations of fly ashes in Australia.

The pH of fly ash varies depending on the source of the coal. Fly ash is known to be both acidic and alkaline and its pH varies from 4.5 to 12.5 (Plank and Martens, 1974; Theis and Wirth, 1977) depending on the sulphur content of the feed coal, the amount of oxalate extractable iron, the water soluble calcium content and the type of coal used for combustion which affects the sulphur content of fly ash (Theis and Wirth, 1977; Page et al., 1979). Research performed by Theis and Wirth (1977) shows that the pH of fly ash appears to control the desorption of metals from the surface of the fly ash; desorption increases as the pH decreases. Hollis et al. (1988) also found this to be true. Boron concentration in solution increased 100 times by changing the pH from 12.5 to 7.0.

Fly Ash Classification

Current classification of fly ashes is mostly based upon the American Society for Testing and Materials (ASTM). ASTM have grouped fly ash into two categories on the basis of the SiO_2 , Al_2O_3 , and Fe_2O_3 contents, viz, Class C and Class F, as shown in Table 3 (ASTM, 2012). Class F fly ash has a combined SiO_2 , Al_2O_3 , and Fe_2O_3 mass content of greater than 70% compared to greater than 50% for Class C fly ash. In general, the high-calcium Class C fly ash is normally produced from the burning of brown coal and has cementitious and self-hardening properties when reacted with water (Ahmaruzzaman, 2010). On the other hand, the low-

calcium Class F fly ash is commonly produced from the burning of black coals that are pozzolanic in nature and only hardening when reacted with alkaline solution or with calcium hydroxide (Ca(OH)_2) in concrete.

In Australia, the ASTM classification may not be directly applicable to or adequately reflect the variability found in Australian fly ashes both with respect to chemistry and mineralogy (French and Smitham, 2007). The Australian Standard AS3582.1 (1998) classified fly ashes into three different grades based on the physical properties or the fineness of the ashes as shown in Table 4. The Australian Standard classification is mainly tailored for the cement and concrete industry.

Similarly in Japan, the fly ash is categorised to suit the cement and concrete industry. There are four classes of fly ash in JIS A 6201 (1999) in Japan (Nagataki et al., 2001) and the main differences among fly ash classes are the LOI content and the fineness of the ashes. Table 5 shows the fly ash classification according to Japan's JIS A 6201 (1999).

Table 2: Heavy metal element concentrations of fly ashes in Australia (ADAA, 2007, 2009)

Element	Total Metal (mg/kg)			
	Black Coal		Brown Coal	
Year	2007	2009	2007	2009
No. of samples	26	11	2	3
Silver (Ag)	0.1	-		0.26
Arsenic (As)	8.2	7.36		13.2
Boron (B)	63.0	49.5		210
Barium (Ba)	1157.0	271.5		181
Beryllium (Be)	5.1	2.07		2
Cadmium (Cd)	0.2	0.25	1.1	0.12
Cobalt (Co)	17.8	6.7		11.2
Chromium (Cr)	18.3	10.55		32
Cooper (Cu)	22.7	18.45		31.6
Mercury (Hg)	0.2	0.15	5.4	1.54
Manganese (Mn)	201.7	161.77		1393.8
Molybdenum (Mo)	15.2	6.95		5.2
Nickel (Ni)	28.8	11.34		62.4
Lead (Pb)	16.7	10.18	5.5	8.2
Antimony (Sb)	1.1	-		-
Selenium (Se)	3.3	4.05		20.4
Tin (Sn)	3.0	2.34		2.1
Titanium (Ti)		-		-
Zinc (Zn)	64.8	44.55		149.4

Table 3: Properties of Class C and Class F fly ash (ASTM C 618, 2012)

Properties	Fly Ash Class	
	Class F	Class C
Chemical Properties		
Silicon Dioxide (SiO ₂), Aluminium Oxide (Al ₂ O ₃), Iron Oxide (Fe ₂ O ₃), minimum weight in %	70.0	50.0
Sulphur Trioxide (SO ₃), maximum weight in %	5.0	5.0
Moisture Content, maximum weight in %	3.0	3.0
Loss on Ignition (LOI), maximum weight in %	6.0	6.0
Physical Properties		
Fineness, % maximum retained on 45µm sieve	34	34
Water requirement, % maximum of control	105	105
Autoclave expansion, soundness, % maximum	0.8	0.8

Table 4: Australian Standard AS3582.1 (1998) fly ash classification

Grade	Fineness, by mass passing a 45 μ m sieve (% maximum)	Loss on Ignition (% maximum)	Moisture content (% maximum)	SO ₃ content (% maximum)
Fine	75	4.0	1.0	3.0
Medium	65	5.0	1.0	3.0
Coarse	55	6.0	1.0	3.0

Table 5: Japanese JIS A 6201 (1999) fly ash classification (Nagataki et al., 2001)

Fly ash	Class-I	Class-II	Class-III	Class-IV
LOI, % maximum	3.0	5.0	8.0	5.0
Fineness, % maximum on 45 μ m sieve or Blaine method, cm ² /g	10 5000	40 2500	40 2500	70 1500
Flow ratio, % lower limit	105	95	85	75
Density, g/cm ³ lower limit	1.95	1.95	1.95	1.95
SiO ₂ , % lower limit	45.0	45.0	45.0	45.0
Moisture content, % upper limit	1.0	1.0	1.0	1.0

CURRENT APPLICATIONS OF FLY ASH

Introduction

In Australia, fly ash has predominantly been used as a substitute for material in the construction and mining industries. Approximately 11.8 million tonnes of fly ash was generated in Australia in 2011 but only 20.4% or 2.4 million tonnes of the fly ash was beneficially utilised

(ADAA, 2012). Of the ash that is utilised, 87% or 2.1 million tonnes was used in the cement and concrete industry; 9.2% or 222.2 hundred thousand tonnes goes into bulk fill applications such as mine site backfilling, controlled low strength material (CLSM) fill and structural fill; 0.36% or 8.8 thousand tonnes being used to stabilise and solidify mining waste; and 3.4% or 80.8 thousand tonnes was used in road base construction. Figure 3 summaries the utilisation of fly ash in Australia.

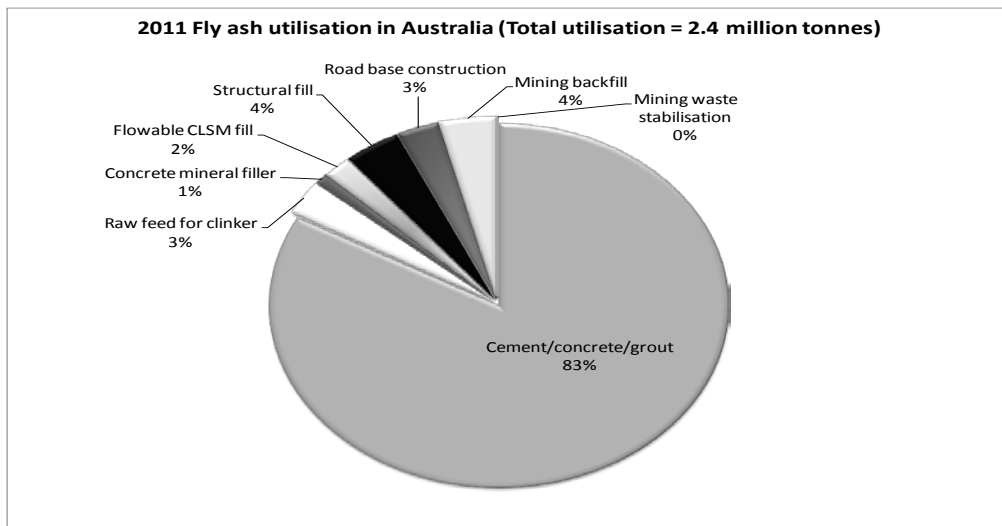


Figure 3: Distribution of fly ash utilisation in Australia (data taken from ADAA, 2012)

Fly Ash in cement and concrete industry

There are essentially two distinct applications for fly ash in the cement and concrete industry, including:

1. use as raw material for cement clinker production; and
2. partially replace Portland cement to produce blended cement

Raw material for cement clinker production

The main raw materials used in the cement production are limestone, sand, shale, clay, and iron ore. Fly ash can be added and replace natural clay as raw material for cement clinker production (Naik et al., 2003). Fly ash contributes silica, alumina, iron and calcium to the raw material mix. The amounts of fly ash used, however,

depend primarily on the raw material available at a cement manufacturing plant, that is, on the clay and lime content of the limestone and marl deposits used in manufacturing cement clinker (Smith, 2005). The limit in which the amount of fly ash can be used in cement raw material is differed from each cement manufacturing plant and country. If the clay content in the limestone is high, no additional clay or fly ash is required to make up the silica and alumina content of the cement clinker. For example, the chemical composition of Indian fly ashes is similar to that of clays and they may be used as a clay substitute. However, the limestone used in making cement clinker also contains around 8% to 10% silica, or more, and the primary fuel contributes argillaceous components so that the amount of fly ash may be limited in many cases (Sharma et al., 2003). In Japan, the limestone is near pure, containing on average 92% to

98% of lime or calcium oxide (CaO) whereas it may only contain 80% CaO in some regions of Europe. Hence, a greater proportion of the clay is substituted by fly ash in Japan (Smith, 2005). Some European limestones may contain sufficient clay minerals without adding clay and this may limit the amount of fly ash which can be added to the raw materials.

In order to use fly ash as a raw feed for clinker production, the process of transportation of fly ash from power station and mixing of fly ash needs careful design as fly ash is required in a dry state (Smith, 2005). Benefits of using fly ash as part of the cement raw material are that natural materials are saved and less ash has to be stored (Smith, 2005). Greater quantities of fly ash are claimed to be usable in green cement, developed in Australia and using magnesium carbonate to replace part of the limestone in the cement kiln. The eco-cement incurs less carbon dioxide (CO₂) emissions in its manufacture and then absorbs more CO₂ in the products than Portland cement (ENDS, 2004).

In some cement manufacturing plants, fly ash is used to alter the chemistry of the cement. The sodium and potassium alkali in the final product is reduced by adding low alkali fly ash to the raw meal. This has environmental and practical benefits, reducing the kiln temperature and producing a more saleable, lower alkali product (Sear, 2002). In India, Reddy (2003) reports that clinker quality is improved when using fly ash compared to clay in the raw meal. The alumina to ferrous ratio was higher when using fly ash and the reactive silica in fly ash improved the quality. In addition the raw meal was finer, improving the grindability of the raw mix.

In the United States, Goss (2003) suggested that replacing clinker raw materials, natural clays, shales and other ores, with fly ash has the advantage because the ASTM quality standards are not mandatory as if it is used in concrete applications. Fly ash containing high amounts of unburnt carbon (up to 21%) can be used and help to reduce the energy requirements of the cement kiln. This reduces costs, for example, at a kiln in Illinois, use of fly ash yielded a 10% production increase and a 4% fuel saving.

Fly Ash Blended Cement and Concrete

Portland cement is the most cost and energy intensive component of concrete. Fly ash has pozzolanic properties and can be used as partial replacement of cement in producing concrete and the unit cost of concrete is, hence, reduced. The use of fly ash for blended cement also contributes to the reduction of greenhouse gases emissions. The production of Portland cement releases large amounts of greenhouse gases, namely carbon dioxide (CO₂), nitrous oxide (N₂O) and methane (CH₄) and contributes to about 7% of global anthropogenic CO₂ emissions (Malhotra, 2002a) and accounts for 4% of man-made global warming (McCaffrey, 2002). Every tonne of Portland cement replaced with fly ash is estimated to avoid the emission of about a tonne of CO₂ to the atmosphere. The CO₂ is emitted by decarbonation of limestone and fuel burning in the cement kilns is estimated at 0.7 to 1.0 tonne for each tonne of Portland cement production (Humphreys and Mahasenan, 2002; Gartner, 2004; Josa et al., 2004).

Producing fly ash blended cement uses much less energy than that of conventional Portland cement, which requires significant amounts of energy. The energy consumed in the production of Portland cement is estimated to be 4.88 MJ/kg (Struble and Godfrey 2004) with 85% of this energy used to burn the raw materials to form cement clinker in the kiln. The remaining 15% is divided about equally between preparation of raw materials entering the kilns and grinding the cement clinker that is discharged from the kiln (Walker, 1975). It is the third most energy intensive industry after aluminium and steel production and accounts for approximately 2% of the global primary energy consumption, or almost 5% of the total global industrial energy consumption (WEC, 1995).

The use of fly ash in blended cements is a well-established technology but rarely comprises more than 40% of the cementitious materials. In the mid-1980s, Malhotra and his fellow researchers achieved a milestone in concrete industry by introducing high volume fly ash (HVFA) concrete (Mehta, 2002). In HVFA

concrete, up to 60% of OPC content is replaced by ASTM Class F fly ash (Bilodeau and Malhotra, 1998, Bouzoubaâ and Fournier, 2002). This type of concrete possesses excellent mechanical properties, low permeability and shows superior durability and has compressive strength of about 8 MPa at 1 day and more than 110 MPa after 10 years (Bouzoubaâ and Fournier, 2002). At present, HVFA concrete has been put into the practice. It has been used to build the 22 storey Purdy's Wharf office complex in downtown Halifax, Nova Scotia, Canada, (Malhotra, 2002b) and Liu Centre for the Study of Global Issues in the University of British Columbia, Canada (Bilodeau et al., 2001). It is also used in foundations, structural elements for small buildings, roller compacted concrete, massive elements, slabs on ground, and pavements.

High volume usage of fly ash in roller compacted concrete (RCC) application is also possible. RCC is a well-established technology that has been used extensively in roads, dams, and large floor construction (Hansen and Reinhardt, 1991; Nanni et al., 1996; Delagrave et al., 1997). The use of class C fly ash for rapid hardening hydraulic cements is now possible at over 80% fly ash substitution, with various additives (Smith, 2005). According to Hicks (2003), masonry cements using 80% to 90% class C fly ash have improved workability, better board life, reduced shrinkage and are sulphate and acid resistant. Studies on 100% replacement of cement using ASTM Class C fly ash has also been undertaken by Cross et al. (2005) and Berry et al. (2011). Concrete with slump of 152.4 mm was obtained without using water reducing admixtures. Early strengths of 27.5 MPa and long terms strengths of up to 55.2 MPa after a year have been produced.

Two major factors affecting the function of fly ash in blended cement concrete are fineness and the unburnt carbon residue or loss on ignition (LOI) content (Smith, 2005). These two factors form the basis of the most fly ash specifications and standards, including the European Code BS EN450-1 (2012), the Australian AS3582.1 (1999) and the Japanese Standards JIS A 6201 (1999) (Nagataki et al. 2001). The finer the fly ash

and the lower the carbon content, the better is the quality of the fly ash. Both greater fineness and a low carbon content reduce water demand. Finer fly ash improves the performance of the concrete to sulphate attack. Lower carbon content in fly ash improves the efficiency of chemical admixtures in the concrete, especially those governing air entrainment. Frost resistance of concrete is also expected to decrease with LOI above 10% (Miskiewicz et al., 2003).

The utilisation of fly ash is not only based on economic and environmental grounds, as pozzolan for partial replacement of cement, but also its engineering beneficial effects, such as lower water demand for similar workability, reduced bleeding and lower evolution of heat (Ahmaruzzaman, 2010). Fly ash blended cement has been used particularly in mass concrete applications and large volume placement to control expansion due to heat of hydration and also helps in reducing cracking at early ages. Generally the setting and hardening rates of fly ash blended cement mortar and/or concrete are slower when ASTM Class F fly ash is added to it, especially under cold weather conditions. Fly ash blended cement concrete has an extended hydration period, making it more sensitive to curing conditions. For example, the setting time of concretes with 15% conventional cement replaced by fly ash increases by 30 to 60 minutes than that of concrete without fly ash. A 30% cement replacement by fly ash increases the setting time by two to three hours. Krüger (2003) reported that boron was the most likely trace element responsible for the retarding effect on the setting time due to some fly ashes in concrete. On the other hand, ASTM class C fly ashes have shown both rapid and delay setting of concrete depending on their properties and the quantity used. The setting behaviour can be accelerated using heat or steam curing (Ahmaruzzaman, 2010) and more readily modified when chemical admixtures such as water reducer, superplasticiser, retarder, or gypsum are used in mixtures containing fly ash. Studies involving chemical admixtures are detailed by Naik et al. (2001) and Payá et al. (2001).

The use of fly ash blended cement in concrete enhances the workability of concrete. The rounded particles of fly ash improve the workability of concrete when mixed with the more angular shapes in cement and some aggregates and enable easier finishing with trowels and other tools (Ahmaruzzaman, 2010). This also leads to greater compaction and produces concrete with less permeability because of the spherical particles and, therefore, improved packing; that is more dense paste and pozzolanic reaction. Being finer than cement, fly ash fills voids in concrete normally occupied by water. The reduced water demand usually helps to avoid segregation and bleeding in fresh concrete as well as improving strength and long-term durability (DTI, 2002; Kruger, 2003; UKQAA, 2001; Walker et al., 2002).

Fly ash also reacts with excessive or free lime produced from Portland cement hydration process to form stable calcium silicate and aluminate hydrates. These hydrates fill the voids within the concrete, removing some of the lime (UKQAA, 2000). Indirectly, this increases the resistance of steel reinforcement to corrosion in reinforced concrete as the ingress of corrosive liquids is limited due to the reaction of fly ash with lime in cement to form a stable, cementitious compound of calcium silicate hydrate. The lime produced from Portland cement hydration is soluble, whereas the calcium silicate hydrate is less soluble in fly ash blended concrete, thereby reducing the possibility of leaching of lime from the concrete. In addition to calcium silicate hydrate being less soluble, the calcium silicate hydrate produced from fly ash tends to the filling of capillary voids in the concrete mixture, thereby reducing permeability of concrete. Further, once fly ash reacts with free lime, it reduces the risk of damage due to expansive reactions between the free lime and certain chemicals (mainly sulphates). This improves the durability of concrete structures that are placed in aggressive environments.

Fly ash reduces the alkali silicate reaction (ASR). This phenomenon causes premature and severe cracking and is due to the development of chemical reactions between the siliceous materials in concrete aggregate

and the alkali hydroxides in cement. The reactive silica in fly ash combined with the cement alkalis (NaOH and KOH) more readily than the silica in aggregate. The resulting calcium-alkali-silica gel is non-expansive, unlike the water-absorbing expansive gels produced by conventional alkali-aggregate reactions. Hence fly ash increases ASR resistance, improving the ultimate strength and durability while lowering the cost of the concrete (Knowles, 2004). For example, the use of 30% fly ash to replace cement in concrete effectively prevents the ASR reaction occurring (UKQAA, 2001), although the amount required depends on the calcium content of the fly ash. A 15% replacement of cement with low calcium (<2% CaO) Class F fly ash is considered sufficient to mitigate ASR. A low addition of fly ash can increase ASR so it is important to establish the correct dose (Knowles, 2004).

In a study undertaken by McCarthy (2003), it was indicated that both dry and conditioned fly ash is effective in limiting ASR with little difference in expansions for a wide range of fineness of the fly ash. Play et al. (2003) also presented detailed results of a long-term study of the effectiveness of fly ashes with different alkali contents to prevent ASR in concrete. Two fly ashes were used; one with a low alkali content of 2.12% and the other with a higher total alkali content of 3.36%. Both had less than 7% LOI, less than 40% retained on a 45 µm sieve, silica, aluminium oxide and iron oxide totalling more than 70% and a low calcium content (class F). The results after five years of testing showed that the fly ash with higher alkali content also prevented ASR. The efficiency of the fly ashes to inhibit expansion of the concrete was influenced by the reactivity of the aggregates. Use of two reactive aggregates reduced expansion when using 30% fly ash but the most reactive aggregates (siliceous limestone) caused expansions, although lower than those of control concretes without fly ash. This suggested it was preferable to use a greater rate of fly ash replacement (more than 30%) in cases where the aggregates are highly reactive.

ASTM Class C fly ashes or high calcium fly ashes show variable performance with respect to sulphate resistance. The ASTM C 1012 mortar bar expansion test for sulphate resistance was carried out by Shashiprakash and Thomas (2001) using Portland cements with varying content of calcium and aluminium oxides, high calcium fly ashes, an ultra-fine fly ash and silica fume. The performance of high calcium fly ashes could be improved by addition of 3% to 6% of silica fume, or by 8% to 16% of ultra-fine fly ash. The high calcium fly ash appeared to perform well when blended with a moderate or low tricalcium aluminate (C_3A) cement. It is suggested that these blends provided sulphate resistance by reducing the permeability of the mortar but not necessarily its chemical resistance. The mechanisms determining sulphate resistance are discussed and may involve not only the CaO content of the fly ash but the ratio of reactive alumina to sulphate in the fly ash blended cement.

The alumina content of fly ash is thought to bind chlorides and reduce its diffusion, improving chloride resistance. This phenomenon also improves the corrosion resistance of reinforced concrete. The low permeability of the microstructure hinders migration of sodium and potassium ions. Finally the lower heat of hydration reduces cracking (DTI, 2002; Kruger, 2003; UKQAA, 2001; Walker et al., 2002).

Fly ash for road construction

Fly ash has been used in subgrade base course material, as a fine aggregate, a bituminous pavement additive and mineral filler for bituminous asphalt concrete. Construction of road embankments using fly ash, involves encapsulation of fly ash in earthen core or with RCC facing panels (Ahmaruzzaman, 2010). Since there is no seepage of rainwater into the fly ash core, leaching of heavy metals is also prevented. When fly ash is used in concrete, it chemically reacts with cement and reduces any leaching effect. Even when it is used in stabilisation work, a similar chemical reaction takes place which binds fly ash particles. Hence the chances

of pollution due to use of fly ash in road works are negligible.

Use of fly ash in road works is reported to have a reduction in construction cost by about 10 to 20% (Ahmaruzzaman, 2010). Fly ash is available free of cost at the power plant and hence only transportation cost, laying and rolling cost are there in case of fly ash. Hence, when fly ash is used as a fill material, the economy achieved is directly related to transportation cost of fly ash. If the lead distance is less, considerable savings in construction cost can be achieved.

Similarly, the use of fly ash in pavement construction results in significant savings due to savings in cost of road aggregates (Ahmaruzzaman, 2010). If environmental degradation costs due to use of precious top soil and aggregates from borrow areas quarry sources and loss of fertile agricultural land due to ash deposition are considered, the actual savings achieved will be much higher and fly ash use will be justified even for lead distances up to say 100 km.

In Australia, fly ash is permitted to be used as a mineral filler for asphalt concrete (Austroads, 2007; AS 2150, 2005; RMS 2012).

Mine backfill

Fly ash mine backfilling has demonstrated to be an attractive option to dispose fly ash beneficially for power stations located near the coal mine (Ahmaruzzaman, 2010). Backfilling of underground mines is technically vulnerable and especially holds good potentials for those areas where sand is scarce. Open cast mine filling can again be considered as land reclamation.

Fly ash grout injection is currently being considered for use at a closed underground mining site (Ahmaruzzaman, 2010). The injection process would reduce acid mine drainage (AMD) by neutralising the AMD and preventing contact between water and pyritic materials. Acid mine drainage occurs in areas that have previously been mined for coal and contain pyritic materials in spoil piles or in mine shafts, where the pyritic material is in contact with both water and

atmospheric influences. The spoil piles and mine shafts contain iron pyrite in the tailings that chemically react with oxygen, water and Thiobacillus bacteria, resulting in acid mine drainage.

Fly ash mine void filling has been carried out in controlled circumstances and in actual field applications in both Australia and internationally (Ward et al., 2006). Mine void filling is undertaken for numerous reasons, the first being for the control of AMD, where the groundwater table intersects the mining rubble. The second reason for fly ash grout injection compliments AMD control by filling mine voids and providing support to areas where standing coal pillars are crumbling and causing land subsidence on the surface. The third use for fly ash injection is mine fire control.

Underground coal mining operations conducted many years ago removed large volumes of coal, leaving only small pillars to maintain the structural stability of the surrounding land surface (Ward et al., 2006; Ahmaruzzaman, 2010). Environmental weathering over time caused the pillars to crumble and AMD to occur due to the exposure of the pyritic material, surrounding the coal seams, to the groundwater and atmosphere. Through the use of high pressure injection, even areas that have partially collapsed can be filled with fly ash grout material to prevent further subsidence, while disposing of large quantities of fly ash at the same time. The procedures for conducting underground mine void filling with fly ash for AMD control, subsidence control and fire abatement are identical (Magnuson and Malenka, 1970). Two methods can be used, dry fly ash injection or wet slurry injection. Dry fly ash injection consists of drilling 150 mm diameter boreholes into the mine void and placing steel casing down to that level. The dry fly ash is then injected at relatively low pressure into the mine void. The dry fly ash easily flowed in either direction from the borehole along the shaft as it filled to the mine roof. The ash had an angle of repose of only 8 degrees from the horizontal exhibiting excellent 'flow' characteristics. The eventual filling at the roof covered 4.5m in either direction from the borehole and provided an airtight seal for the mine shaft. Moisture from

surrounding strata eventually provided the fly ash with the water needed for hydration and the fly ash hardened, exhibiting no signs of shrinkage or settling.

Fly ash-water slurry injection is conducted in much the same manner as dry ash injection with the exception of the use of higher injection pressures and a slightly larger borehole, 200mm in diameter, being drilled (Magnuson and Malenka, 1970). Experimental results determined that an ideal water content equating to approximately 100 gallons per ton of fly ash (25% water by total mix weight), produces slurry that pumps easily and does not shrink upon drying.

Bulk quantities of coal fly ash have been used to replace the conventionally used sand for reclaiming underground mines (Ahmaruzzaman, 2010). The potential application of coal fly ash in reclaiming abandoned coal mine is of practical significance.

Geotechnical Applications

Fly ash is commonly used in geotechnical applications. Geotechnical is a broad term that encompasses its use in different applications: sub-grade stabilisation, general engineering fill, controlled low strength material (CLSM) fill, structural fill, soil amendment and infill (ADAA, 2012; González et al., 2009).

Fly ash has been used as a stabiliser for soil because of the beneficial properties it imparts. It is found that the addition of fly ash to soils tends to decrease the propensity for the soil to absorb water and, thus, less swelling of the soil results. For soils with high montmorillonite content, the swelling problems can be severe; they tend to expand when wet and shrink when dry. This movement exerts pressure that can crack pavements, basement floors, driveways, pipelines and foundations. It is thought that the addition of fly ash to the soil changes the mineralogy due to pozzolanic reaction. The soil becomes more granular and holds less water which results in a decrease of swelling associated with water absorption (Nalbantoglu, 2004; Zha et al., 2008). Fly ash has found to have equal or higher shear strength for embankment stabilisations (Lin, 1971). The

higher shear strength in fly ash is likely because of its self-hardening or pozzolanic properties.

Cenospheres

Fly ash also contains some hollow spherical particles, called cenospheres, which is one of the most important value-added components of fly ash. Cenospheres are similar in composition to the fly ash though they tend to have a larger particle size (Hirajima et al., 2010). The unique properties of cenospheres, namely their sphericity and their low density relative to water, make them amenable to a variety of different applications.

The existing method of extraction of cenospheres relies on the storage of fly ash in large lagoons from where the cenospheres can be removed from the surface of the water. The fact that they float on water is of special interest to researchers investigating new photocatalysts. They can be used as a buoyant carrier to enhance catalytic activity as they increase the exposure of the particle to light sources (Nair et al., 2009; Huo et al., 2009; Suriolia et al., 2010; Wang et al., 2011). They are easily recovered from water after the reaction. This feature has also attracted interest for their use in water purification applications such as the removal of excess fluoride from drinking water; this was achieved by producing magnesia loaded cenospheres using a relatively simple wet impregnation method of magnesium chloride (Xu, et al., 2011). This principle can be extended by applying functional layers onto the fly ash cenosphere. A process of electroless plating of nickel followed by hydrothermal synthesis of the zeolite ZSM-5 has been used to create a cenosphere/Ni/ZSM-5: a composite structure that is a molecular sieve, floatable, and magnetic (Tao et al, 2009).

Cenosphere properties have also been altered by coating with various metals. Their use as lightweight materials in the fields of electromagnetic interference shielding, electromagnetic wave absorbance, and high light reflectivity has been suggested by some researchers (Blissett and Rowson, 2012). A variety of different methods of plating have been used but some of the most widely investigated include electroless plating

(Aixiang et al., 2005; Wang et al., 2009; Hu et al., 2010; Pang et al., 2011), magnetron sputtering (Cai et al., 2007), and heterogeneous precipitation (Liu et al., 2008; Meng et al., 2010). The advantages of using a cenosphere as the carrier are its sphericity, low weight, and high strength. This makes it ideal for its incorporation into materials such as silicone rubber in order to increase the conductivity of the rubber. Furthermore, this enhances its suitability for use as an electromagnetic wave absorbing material that can be used in electronic and radar applications (Pang et al., 2011).

The lightweight nature of the cenospheres renders them suitable for the design of light weight composite materials. A variety of different composites have been evaluated, such as fly ash incorporation into concrete (Blanco et al., 2000; Barbare et al, 2003), geopolymer concrete (Ng, 2011), polymers and resins (Johnson et al., 1970; Chand et al., 2010; Deepthi et al., 2010) and metal alloys (Jha et al., 2011; Luong et al., 2011; Rohatgi et al., 2011). Their use in these applications reduces the extent to which energy intensive and resource dependent materials are used. For metal alloys, cenospheres also confer some advantages to the composite structure. Traditionally, porosity in cast metal is an undesirable property, however, by using the cenospheres to enclose porosity inside strong hollow structures embedded inside metals several properties of the composite are enhanced, and the structural weight is decreased. This type of material is highly suitable for the use in weight sensitive applications such as the automotive and aerospace industries (Rohatgi et al., 2011).

The use of hollow spheres in ceramic composite foams has also been of significant interest. They are being investigated for their likelihood to exhibit high temperature performance and low thermal conductivity particularly for refractory materials (Ozcivici and Singh, 2005). Other studies have taken a different approach and evaluated the possibility of using them as coating materials for similar reasons. They were coated onto a silicon carbide substrate using an electrophoresis

method; they exhibited a lower thermal conductivity relative to pure fly ash coatings, but they were extracted based on size rather than density so caution should be exercised in the interpretation of the results (Chavez-Valdez et al., 2011).

Economically the use of cenospheres makes sense in applications that have traditionally used manufactured hollow spheres made of glass. For this reason they were assessed for their potential to act as a sensitiser for emulsion explosives. Their performance was comparable to the glass spheres (Anshits et al., 2005).

NEW AND EMERGING APPLICATIONS OF FLY ASH

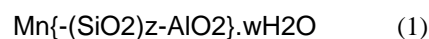
In addition to the current established application of fly ash, extensive research have been undertaken to search for new applications of fly ash. Among the successful findings are the use of fly ash in manufacturing geopolymer, lightweight synthetic aggregates, bricks, zeolites, glass and ceramic, use to amend agricultural soil, use as a catalyst and use as an absorbent for waste and toxic substances. Further, some of these applications have gained community and market acceptance and have been adopted in the practice. The following sections review new and emerging applications of fly ash.

Fly ash based geopolymer

Geopolymer or alkali-activated aluminosilicates technology, first developed in the 1970s by Joseph Davidovits, is manufactured by reacting aluminosilicate and alkali metal silicate solutions under strongly alkaline conditions. Geopolymer is amorphous or semi-crystalline polymeric structures of Si–O–Al bonds. Geopolymers exhibit good physical, chemical, and mechanical properties: these include low density, micro and nanoporosity, low shrinkage, high mechanical strength, good thermal stability, durability, surface hardness, fire, and chemical resistance. Given these desirable properties they are seen as potential alternative materials for industrial applications such as concrete, transport, aerospace, mining, and metallurgy (Swanepoel and Strydom, 2002; Barbosa and MacKenzie, 2003). Fly ash contains high amount of aluminosilicate and can be used to make geopolymer and replace the use of conventional cement as a binder in concrete production. The utilisation of fly ash in geopolymerisation was investigated extensively in recent years by Van Jaarsveld et al. (1999), Xu and Van Deventer (2002), Van Deventer (2000), Phair and Van Deventer (2002), Swanepoel and Strydom (2002), Krivenko and Kovalchuk (2002a), Krivenko and Kovalchuk (2002b), Bakharev (2005), Palomo et al. (1999), Fernández-

Jiménez et al. (2003, 2006), Rangan (2008), Ng (2011), but to list a few.

Davidovits (1991) suggested that the structural backbone of this geopolymer is “poly-(sialate)”. Poly- implies many and sialate is an abbreviation for silico-oxo-aluminate. The polysialate network is a framework that consists of three-dimensional structures of SiO₄ and AlO₄ tetrahedral linked in all directions with varying degrees of aluminate substitution. Positive ions or cations must be present in order to neutralize the negatively charge AlO₄⁻ tetrahedral units within the polysialate network (Lee, 2002). The cation can be any one of the metals or alkaline earth metals available such as potassium (K), sodium (Na), calcium (Ca) or magnesium (Mg). Polysialate has the following empirical formula (Davidovits, 1991; 1994):



where 'M' is a cation, 'n' is a degree of polycondensation, '-' indicates the presence of a bond and 'z' is the degree of aluminate substitution (Davidovits, 1991; Davidovits, 1994; Lee, 2002). The varying degrees of aluminate substitution will produce different geopolymeric structures. When z = 1, the structure is termed 'poly-sialate'; when z = 2, the structure is called 'poly-sialate-siloxo'; and when z = 3, it is known as 'poly-sialate-disiloxo'. The three different types of polysialate of geopolymer backbone are shown in Table 6.

The geopolymerisation process is an exothermic reaction where heat is released. Some examples of the chemical reactions in synthesizing geopolymer can be schematised in Figure 4 and Figure 5 (Davidovits, 1991, 1994).

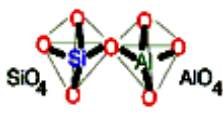
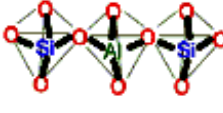
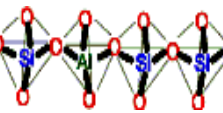
The mechanisms of geopolymerisation are not completely understood. Davidovits (1991, 1999), Xu and Van Deventer (2001) and Duxson et al. (2007) summarised the steps of geopolymerisation, as outlined in Figure 6.

Xu and Van Deventer (2002) asserted that when solid aluminosilicate source materials come in contact with alkaline solution, leaching of Al and Si atoms in the

source materials starts. The level of leaching depends on concentration of the alkaline solution, type of alkaline solution, mixing speed, leaching period and the structure and composition of aluminosilicate source materials. Among all of these factors, the properties of the aluminosilicate source materials, the concentrations of the alkaline solution and the types of alkaline solution are believed to be dominant (Xu and Van Deventer, 2000; Phair and Van Deventer, 2001; Phair and Van

Deventer, 2002). Van Deventer (2000) and his fellow researchers concluded that the aluminosilicate materials show a higher extent of dissolution with an increase in concentration of alkaline solution (Xu and Van Deventer, 2000; Xu and Van Deventer, 2001; Van Jaarsveld and Van Deventer, 1999a; Phair and Van Deventer, 2001). Likewise, they have also shown that the aluminosilicate materials dissolve more in sodium hydroxide (NaOH) solution than potassium hydroxide (KOH) solution.

Table 6: Type of Geopolymeric Structures (Davidovits, 1991, Davidovits, 1994)

Category of Polysialate	Molar Ratio of Si/Al	Schematic Structure	Molecular Graphics
Poly-sialate	1	$M_n-(\overset{ }{\text{Si}}-\text{O}-\overset{ }{\text{Al}}-\text{O}-)_n$ <div style="display: flex; justify-content: center; gap: 20px;"> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> </div>	
Poly-sialate-siloxo	2	$M_n-(\overset{ }{\text{Si}}-\text{O}-\overset{ }{\text{Al}}-\text{O}-\overset{ }{\text{Si}}-\text{O}-)_n$ <div style="display: flex; justify-content: center; gap: 20px;"> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> </div>	
Poly-sialate-disiloxo	3	$M_n-(\overset{ }{\text{Si}}-\text{O}-\overset{ }{\text{Al}}-\text{O}-\overset{ }{\text{Si}}-\text{O}-\overset{ }{\text{Si}}-\text{O}-)_n$ <div style="display: flex; justify-content: center; gap: 20px;"> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> <div style="text-align: center;"> ○</div> </div>	

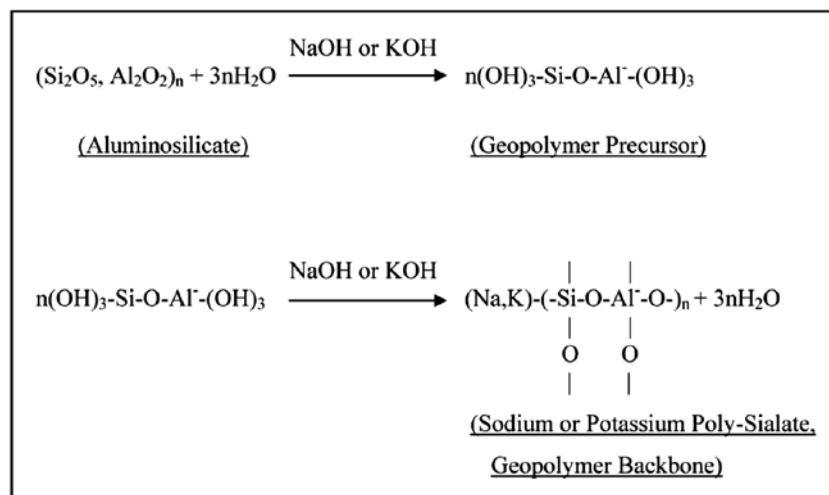


Figure 4: Formation of Poly-Sialate (Davidovits, 1991)

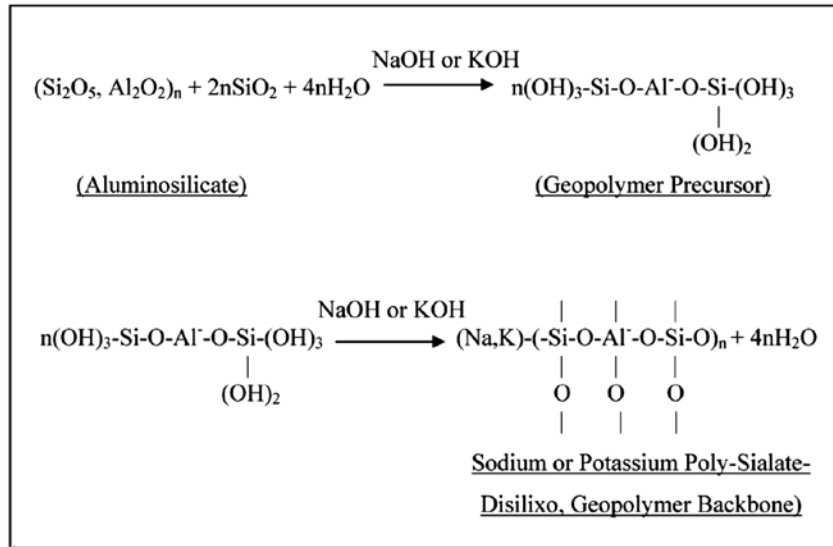


Figure 5: Formation of Poly-Sialate-Disilixio (Davidovits, 1991)

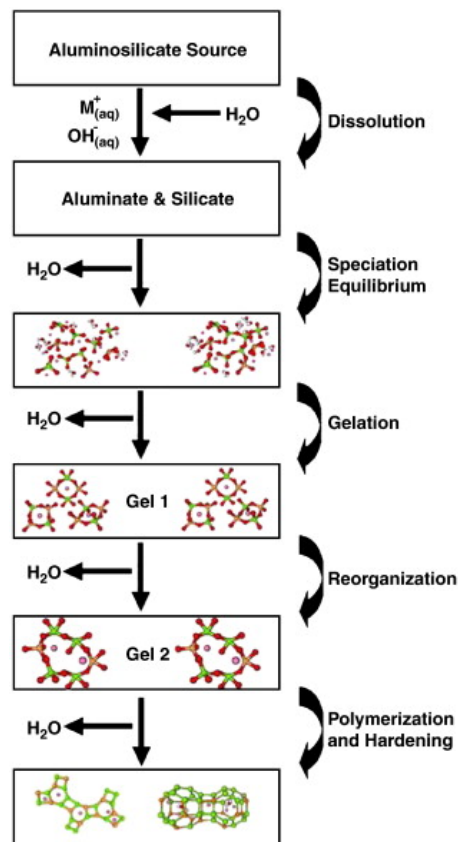


Figure 6: Conceptual Model of Geopolymerisation Process (Duxson et al., 2007)

After being leached from the surface of the aluminosilicate source materials, Al and Si atoms are transported and diffused into the gel phase, which reduce the concentrations of the Al and Si atoms at the aluminosilicate source material surfaces and, therefore, stimulate further leaching of Al and Si atoms (Xu and van Deventer, 2002). During the diffusion step, the time and the intensity of stirring are dominant factors. A longer leaching period and a more intense stirring can maximize the capacity to dissolve the Al and Si atoms from the surface and break the barrier between the Al-Si particle surface and the gel phase so as to accelerate diffusion of the Al and Si atoms (Xu and van Deventer, 2002).

Xu (2002) also said that during the hardening step, there is no obvious movement of particles. However, leaching and diffusion between aluminosilicate particle surface and the gel phase may still be occurring and a slight movement of paste in capillary pores may also take place. Temperature and air circulation are two main factors to determine the mechanical properties of geopolymer and the existence of cracks in geopolymer.

ASTM Class F fly ash based geopolymer does not harden at room temperature (Rangan, 2008) while Class C fly ash based geopolymer hardens rapidly at room temperature (Kumar et al., 2007; Chindaprasirt et al, 2011). This is likely due to the presence of calcium in Class C fly ash. To-date, large-scale manufacturing of geopolymer concrete are starting to become commercialised (Van Deventer et al., 2012).

Hardjito and Rangan (2005) and Ng (2011) have developed a fly ash based geopolymer concrete with an achievable compressive strength of 90 MPa. Based on Rangan (2008) study, there is no substantial gain in the compressive strength of heat cured fly ash based geopolymer concrete with age. Therefore, fly ash geopolymer concrete could achieve 90 MPa after just 24 hours of curing.

However, fly ash based geopolymer concrete has a low Young's modulus for its compressive strength (Ng, 2011). Using fly ash, sand, and granite type of aggregate

to manufacture geopolymer concrete, Hardjito and Rangan (2005) found that the Young's modulus is approximately 25% lower than that of OPC concrete. Similarly, Fernández-Jiménez et al. (2006) found that the Young's modulus of fly ash based geopolymer concrete is low compared to OPC concrete. They found that for the same strength of fly ash based geopolymer concrete and Portland concrete, the Young's modulus of the geopolymer concrete is approximately one half that of Portland concrete. Ng (2011) developed a predictive model to estimate the elastic modulus of fly ash based geopolymer concrete.

Fly ash based geopolymer concretes do not require the addition of water in their manufacture and have a much lower shrinkage than OPC concrete (Van Jaarsveld et al., 1997; Wallah and Rangan, 2006). Wallah and Rangan (2006) concluded that the heat cured fly ash based geopolymer concrete undergoes little drying shrinkage, in the order of just 100 micro strains after one year. This value is significantly smaller than the 800 to 1000 micro strains that can be expected from OPC concrete. This may indicate that geopolymer concrete has better durability than OPC concrete but long-term testing is needed to test this hypothesis.

Fly ash based geopolymer concrete has a superior chemical resistance than OPC concrete. Wallah and Rangan (2006) have demonstrated that heat cured fly ash based geopolymer concrete has an excellent resistance to sulphate attack. In their tests, the sulphuric acid attack caused degradation in the compressive strength of heat cured geopolymer concrete; however, the severity of the degradation is much lower than OPC concrete.

Muntingh (2006) found that the chloride diffusion rate of fly ash based geopolymer concrete is lower than 3×10^{-9} mm²/s, i.e. more than 300 times lower than that of Portland cement concrete. Therefore, in marine environment, provided the geopolymer concrete is uncracked, the time needed for the chloride ions to diffuse through geopolymer concrete cover and initiate depassivation of the steel increases dramatically.

Sumajouw and Rangan (2006) manufactured and tested twelve reinforced columns and twelve reinforced beams with heat cured low-calcium fly ash based geopolymer concrete. The compressive strength of geopolymer concrete ranged from 40 MPa to 60 MPa. For the geopolymer concrete columns, the investigation parameters were the longitudinal reinforcement ratio and load eccentricity. The longitudinal reinforcement ratios were 1.47% and 2.95%. All columns had a cross-section 175 mm square. It was found that the behaviour and failure modes of reinforced geopolymer concrete columns were similar to those observed for the case of reinforced Portland cement concrete columns and can be predicted with the Australian Concrete Structures Standard AS 3600 (2009).

In the Sumajouw and Rangan (2006) investigation, the geopolymer concrete beam cross section was 200 mm wide by 300 mm deep, and 3300 mm in length. The test parameters were the concrete compressive strength and the longitudinal tensile reinforcement ratio. The longitudinal tensile reinforcement ratios were 0.64, 1.18, 1.84, and 2.69%. The behaviour and failure mode of reinforced geopolymer concrete beams were as would be expected for the case of reinforced Portland cement concrete beams designed to the Australian Concrete Structures Standard AS 3600 (2009).

Chang et al. (2007) studied the shear and bond strengths of reinforced geopolymer concrete beams. The failure modes and crack patterns observed for reinforced geopolymer concrete beams were similar to those reported in the literature for reinforced Portland cement concrete beams. The design provisions in the Australian Concrete Structures Standard AS 3600 (2009) and the American Concrete Institute Building Code ACI 318-08 (2008) were found to give conservative predictions for the shear strength and bond strength of reinforced geopolymer concrete beams.

Ng (2011) undertook a series of studies on fly ash based geopolymer concrete. He proposed a framework for designing high performance fly ash based geopolymer mortar and concrete. Further, Ng (2011) investigated the material behaviour of steel fibre reinforced fly ash based

geopolymer composite and proposed constitutive tensile model. It was found that the bond strength between the steel fibres and fly ash based geopolymer concrete is superior than that of conventional cement concrete. Ng (2011) and Ng et al. (2013) investigated the shear carrying capacity of steel fibre reinforced fly ash based geopolymer concrete beams without stirrups. The results indicate that an increase in fibre volumetric content enhanced the shear capacity of the beam. It was also found that the failure mechanism of fly ash based geopolymer concrete is similar to that of conventional cement concrete. In addition, Ng (2011) also developed some high performance lightweight fly ash based geopolymer mortars. The mortar has a similar strength to that of a conventional concrete at one-half of its density.

Geopolymer binder can provide reduction of embodied CO₂ of up to 80% compared to OPC. The considerable sustainability benefits of using a binder system composed almost entirely of recycled materials has led to considerable research on GCs in recent years in Australia and three established commercial suppliers of GC: Wagners in the Queensland supplying Earth Friendly Concrete (EFC), Zeobond in Victoria supplying the E-crete technology and Rocla, part of Fletcher Building group with their Head Office in Chatswood, New South Wales. The widespread utilization of Geopolymer concrete in the industry is certainly the most promising pathway to increase rate of fly ash utilisation. Geopolymer concrete has yet to enter the mainstream of concrete construction. The main barriers for widespread adoption of geopolymer concrete in the industry and the pathway to overcome those barriers have been clearly identified and are reported in the CRC-LCL RP1004-I (Berndt et al., 2013).

Fly ash for manufacturing synthetic aggregate

Fly ash can be used to manufacture synthetic aggregate to produce lightweight concrete. Lightweight concretes offer superior insulation properties that can reduce energy consumption in buildings. Further, the rapid depletion of quality natural aggregate quarry sources

close to most major metropolitan regions of Australia, emphasize why the need to explore alternative economic sources has become imperative to support increasing vital infrastructure development, including housing, roads, bridges, schools and hospitals. There are a number of advantages in manufacturing synthetic fly ash aggregate and/or bricks. Among these benefits are (Kayali, 1984, 2005a):

- Recycle fly ash;
- Conserve the natural and very scarce materials of coarse aggregates and sand from the use as aggregate;
- Spare the countryside, river beds and beaches from the scarring and damaging activities of aggregate mining;
- Improve durability and decreasing shrinkage cracking by drawing on the enhanced strength and bond of the concrete matrix to the aggregate;
- Establish an industry for lightweight aggregates with export potential especially to countries where natural aggregates are depleted or, are of extremely inferior quality as in the oil rich Middle East states;
- Lighter in weight, reduce the dead weight and material handling cost in construction.

By heating the fly ash until it is sintered but not pelletized, Kayali (2005a) produced a patented synthetic aggregate named Flashag. Flashag aggregates are reported by Kayali to be superior to previously known lightweight aggregates. It is claimed that concrete made from Flashag is not only lightweight but possesses low porosity, high strength and has a high durability potential. With the same cement content and comparable workability, Flashag concrete achieved 25% more compressive strength than concrete made with fly ash pellets, while concrete made using Flashag aggregates is more than 21 % lighter than normal weight Granite and Dacite aggregate concretes. Moreover, Flashag concrete is reported to possess at least 30 % lower drying shrinkage value than normal weight high

strength concrete and thus is better in resisting shrinkage crack formation.

Much research has been undertaken in the manufacture of sintered fly ash lightweight aggregates as a possible step to promote large volume utilisation of fly ash (Ahmaruzzaman, 2010). To-date, there are many fly ash based lightweight aggregates commercially under different trade names, such as Terlite, Lytag, Waylite corsonalite and sinterlite. After Geopolymer concrete application, fly ash based manufacture synthetic aggregate for concrete appears to be the second most promising pathway to increase rate of fly ash utilisation.

Fly ash for brick production

Fly ash can also be used in brick production. In addition to the advantages listed above in Section 4.2 for the use of fly ash for manufacturing synthetic aggregates, fly ash bricks are lighter than the clay-fired bricks and require less energy and firing time to produce fly ash brick than that of clay-fired bricks (Reidelbach, 1970; Kayali, 2005b):

Several studies including Lingling et al. (2005), Cicek and Tanriverdi (2007) and Kayali (2005b) indicate that fly ash bricks are a superior building material than burnt clay bricks. The use of fly ash bricks provides a stronger, more durable construction that is better protected from efflorescence and salinity with meaningful savings in construction costs. Fly ash has found to improve the compressive strength of bricks and make them more resistant to frost (Xu et al., 2005). Cicek and Tanriverdi (2007) observed the positive effect of the addition of fly ash, sand and hydrated lime in the compressive strength of the bricks. The porosity of the brick depends directly on the mineralogical composition of the raw material and the firing temperature, but generally, bricks fired at high temperatures are more vitreous and undergo the greatest changes in size and porosity (Cultrone et al., 2004). It has been found that fly ash bricks are as durable as clay bricks and in fact in certain aggressive environments perform better than clay bricks. Fly ash can be used in the range of 40% to 70%. The other ingredients are lime, gypsum, cement, sand, and stone

dust or chips. Minimum compressive strength at 28 days of 7 MPa can be achieved and a strength of 25 MPa can be attained if cured in autoclave.

The technical quality of compositionally different groups of solid bricks fired between 800 and 1000°C was evaluated by Cultrone and Sebastian (2009). The textures of the bricks with fly ash were found to be similar to the textures of those without it, except that the samples with the additive contained spherical fly ash particles with diameters ranging from 0.1 to 10 mm. These particles led to a reduction in the density of the bricks and a substantial improvement in their durability, with less decay being caused by salt crystallization in the pores. This is because fly ash causes a reduction in the number of micropores, the pores that make porous materials most vulnerable to salt-induced decay. Use of this additive could have practical implications as a means of recycling and for achieving cost savings in brick production.

Fly ash in a wet state with low quality was also used as raw material to replace clay to make fired bricks (Xu et al., 2005). The effect of fly ash with high replacing ratio of clay on firing parameters and properties of bricks were investigated. The results indicate that the plasticity index of mixture of fly ash and clay decreased dramatically with increased replacing ratio of fly ash. Additive can be chosen to improve the plasticity index of mixture to meet plastic extrusion used in most brick making factories. The sintering temperature of bricks with high replacing ratio of fly ash was about 1050°C, which is 50 to 100°C higher than that of clay bricks. The properties of fired bricks were improved by using pulverized fly ash. The fired bricks with high volume ratio of fly ash were of high compressive strength, low water absorption, no cracking due to lime, no frost and high resistance to frost-melting.

In Australia, Kayali (2005b) produced a type of brick named FlashBrick. It is made of fly ash, water and commercially protected, cheap, commonly available plasticiser in minor quantities. The brick is reported to be 28% lighter than clay brick, has a 40 MPa compressive strength (25% higher than clay brick), has three times higher the modulus of rupture, excellent mortar bond

strength, durability, low absorption capacity and low initial rate of absorption. Similar to clay brick production, FlashBrick needs to be cured for 3 days prior to firing for few hours at temperature between 1000 to 1300°C. However, these curing and firing durations are significantly lower than that of conventional clay bricks, i.e. 7 days of curing time and 1 to 7 days of firing time and, hence, it consumes only two-third of the energy when compared to standard clay brick during production.

In addition to brick products, fly ash has been utilized in the manufacture of lightweight roofing products such as rigid roofing tiles (Ahmaruzzaman, 2010). The roofing tiles have the advantage of being both lighter than clay products and providing a class A fire-rating making them an excellent replacement for cedar shake roofing in high fire danger areas.

Fly ash for agriculture industry

Fly ash can be used as a soil amendment or amelioration agent in the agriculture industry. Jala and Goyal (2006), Pandey and Singh (2010), Yunusa et al. (2006) and many others have undertaken extensive review and research on the use of fly ash to improve soil for agricultural purposes.

Most crops will have an optimum growth when the pH of the soil media is between 6.5 and 7. Fly ash, which can be alkaline or acidic, can be used to neutralise the soil. The addition of alkaline fly ash to acidic soil can raise the pH (Pandey and Singh, 2010). Pandey and Singh (2010) have demonstrated the ability of fly ash to raise the pH of acidic soil use ASTM Class C fly ash, i.e. ash with high CaO contents (>15%). It has been shown that for the most part of ASTM Class F fly ashes with low CaO content have limited potential to ameliorate soil acidity with the exception of ashes that contain relatively high calcium contents. Pandey and Singh (2010) have also noted other beneficial effects of the application of fly ash soil systems and include:

- Improving the texture of the soil;
- reducing the bulk density of the soil;

- improving soil aeration, percolation, and water retention in the treated zone;
- reducing crust formation;
- reducing the consumption of other soil amelioration agents such as fertilisers or lime;
- serving some purpose as an insecticide; and
- decreasing the mobility and availability of metal in the soil.

However, Pandey and Singh (2010) reported on harmful effects such as the reduction in bioavailability of some nutrients resulting from application of alkaline fly ash. Other undesirable effects of fly ash application to soil include excess salinity and a high content of phytotoxic elements.

In Australia, Yunusa et al. (2006) found that the application of fine (<20 µm) fly-ash to coarse textured sandy soil can reduce the hydraulic conductivity by 25% and improve the soil water-holding capacity. For similar treatment of fine textured clayey soil with coarse (>20 µm) fly-ash would increase conductivity by up to 20%. They also reported that fly ash can increase the early growth of canola vigour and seed by 20%. Heidrich (2003) also reported that the use of fly ash can: improve the crop yields, increase the turn-around time for turf farming harvests, improve growth colour and general health, improve water take up and reduce watering requirements.

Fly ash as adsorbent

Fly ash has been investigated for its direct use as an adsorbent in both gaseous and aqueous applications. Adsorbents are often used in pollution control applications and the use of fly ash for this purpose provides an excellent example of how mutually beneficial industrial synergies can be built. Fly ash is an inferior adsorbent relative to activated carbon (Blissett and Rowson, 2012). However, its low cost could make it an economically viable alternative for the removal of organics from wastewater; for example, fly ash was considered as a potential adsorbent to remove Copper

(II) ions from industrial wastewaters (Panday et al., 1985). Recently, the use of mixed fly ashes with different chemical compositions has been evaluated for the removal of a variety of different heavy metal ions from wastewaters: Cu, Pb, Zn, Mn, Cd, Cr and Ni (Mohan and Gandhimathi, 2009; Itskos et al., 2010). Ahmaruzzaman (2010) reviewed the use of low cost adsorbents for the removal of heavy metals from industrial waste and concluded that fly ash has great potential for use in the treatment of wastewater. However, he also suggested that the potential of fly ash utilisation is limited by the variability in its chemical composition and large volumes that might be required for it to be effective.

Aksu and Yener (1999) investigated the potential for fly ash to be used in place of activated carbon for the adsorption of phenol. They reported an adsorption capacity of 27.9 mg/g for the fly ash compared to 108.0 mg/g for activated carbon. Kao et al. (2000) and Aksu and Yener (2001) also suggested the use of fly ash to remove 2-chlorophenol and 2,4-dichlorophenol. Fly ash has also been found to be effective for the removal of two types of polychlorinated biphenyls (PCB): 2,3,4-trichlorobiphenyl (PCB No. 21; TCB) and 2,20,3,30,4,5,6-heptachlorobiphenyl (PCB No. 173; HeCB) (Nollet et al., 2003).

Fly ash for manufacturing ceramic and glass

Fly ash can be used as a low cost raw material for the manufacture of ceramics, glass–ceramics, and glass materials as it contains high amount of SiO₂, Al₂O₃, CaO, and Fe₂O₃ (Erol et al., 2008). The basis of manufacture ceramics, glass–ceramics, and glass is to activate the fly ash at various temperatures and adding co-reagents to form glass or ceramic. Erol et al. (2008) successfully manufactured glass, glass and ceramic and ceramic material from fly ash without any additional additives. Physical and mechanical properties of the fly ash based glass and ceramic materials are found to be comparable with other glasses and ceramics made of other materials.

Fly ash has been considered as a replacement for kaolinite in the manufacture of the ceramic cordierite (He

et al., 2005). Fly ash has been used in a 60 to 40 weight ratio with kaolinic clay to manufacture category BIII ceramic tiles according to EN 14411 (Sokolar and Vodova, 2011). They reported that the firing shrinkage was reduced but at the expense of an increase in porosity, a decrease in bending strength, and an increase in SO₂ in the flue gases.

Jedidi et al., (2009) produced ceramic microfiltration tubular membranes from fly ash for filtering the effluent from textile dyeing processes. The membrane included both a macroporous support and a microfiltration active layer. The support was manufactured in two stages; the fly ash is first calcined and then mixed with binding agents to form a paste. The paste is extruded into tubes and sintered. The microfiltration layer was applied using ground fly ash with particle sizes between 0.5 and 2 µm. The layer was deposited on the support using a slip-casting method in dip solution containing fly ash and polyvinyl alcohol as a binder. When the prepared ceramic membrane was used for the cross flow membrane treatment of textile dye effluent, it was found to achieve a 75% removal of chemical oxygen demand (COD) and 90% removal of colour. The overall stabilised permeate flux (ca. 100 L/mh) was the same as that of a conventional alumina ceramic membrane highlighting the potential of fly ash for this application. A similar study undertaken by Fang et al. (2011) reported that a double coated membrane had a smaller pore size and narrower size distribution than a single coated membrane.

Fly ash for synthesising zeolites

The manufacturing of zeolites requires a source of Si and Al ions, an alkaline environment, and usually an elevated temperature (Barrer, 1981). Zeolitisation times may be of the order of hours, days, weeks, or even months depending on the nature of the reactants and the temperature employed. Höller and Wirsching (1985) used fly ash as a source of Al and Si ions for alkaline hydrothermal synthesising of zeolites. Many studies have also been conducted to manufacture zeolites from fly ash using a one stage hydrothermal method (Berggaut and Singer, 1996; Querol et al., 2001;

Murayama et al., 2002). The type of zeolite produced depends from the experimental conditions. Some of the key factors include activating solution to fly ash ratio, temperature, pressure, and reaction time (Querol et al, 2001). However, the main obstacle to synthesising zeolites from fly ash is that, to speed up the reaction, temperatures in the range of 125 to 200°C must be applied in order to dissolve the silica and alumina. Under these conditions the formation of many of the larger pore, and more valuable, zeolites (A and X) is hindered.

Fly ash as catalyst

The use of fly ash in catalytic applications has been investigated for its potential to reduce the consumption of materials that have limited reserves and/or that are costly to manufacture. An extensive review of the use of fly ash in catalytic applications has been undertaken by Wang (2008). The application of fly ash as material to be used in heterogeneous catalysis has received a great deal of attention. Heterogeneous catalysis is appealing because it is often easier to recover the catalysts after reaction completion relative to homogeneous catalysts. For heterogeneous catalysis, catalytic materials can be supported on other materials and their activity depends on both the active component and its interaction with the support matter. Commonly catalyst supports include a range of metal oxides such as Al₂O₃, SiO₂, TiO₂, and MgO (Wang and Lu, 2007). Given that fly ash is primarily made up of Al₂O₃ and SiO₂, fly ash offers desirable properties such as thermal stability for use as a support.

Fly ash has also been employed as the catalytically active component. Fly ash has been used as a support material for nickel in the application of CO₂ methane reforming. It was found that treatment of the fly ash with CaO prior to Ni loading could produce catalysts capable of high conversion and stability with activities close to the well reported Ni/Al₂O₃ and Ni/SiO₂ systems (Wang and Lu, 2007). Study by Xuan et al. (2003) has shown the potential for the selective catalytic reduction of NO by ammonia with fly ash supported Fe, Cu, Ni, and V catalysts; the Cu loaded fly ash displayed the highest activity.

Other applications of fly ash

Fly ash is a valuable industrial by product and its application is almost limitless. In addition to the common applications of fly ash described previously, there are many other fields and areas where fly ash has high potential to be utilised; these include:

- Use as filler for polymer matrix composite (Naik et al., 2003; Nath and Bandyopadhyay, 2011); and
- Use as filler for metal matrix composite (Naik et al., 2003).
- Produce inorganic fibre by fusing, melting and fiberisation of coal fly ash (Ishikawa, 2005). The fibre can be used as an alternative material of glass fibre and rock fibre.
- Extract raw mineral materials in the fly ash. Among the minerals are:
 - Aluminium (Nayak and Panda, 2010; Shabtai and Mukmenev, 1996);
 - Titanium (Shabtai and Mukmenev, 1996);
 - Carbon (Ban et al., 1997; Soong et al., 2002);
 - Magnetic concentrate or mineral (Sokol et al., 2002);
 - Germanium (Ramdoo, 2011); and
 - Gallium (Ramdoo, 2011).
- Use for manufacturing mesoporous silica (Kumar et al., 2001).
- Use as the raw or support materials for carbon dioxide capture and storage technology (Wee, 2013).

Future applications of fly ash

In this section, some potential high volume uses of fly ash are identified.

Fly ash to replace sand in coal seam gas mining

With the realities of climate change, the scramble for sustainable energy sources is rapidly expanding. One potential source of energy in the Australian context is the extraction of gas from coal seam gas, shale gas, basin-centred gas and tight gas.

Coal seam gas largely consists of methane and is bonded to the surface of coal particles (Geoscience Australia, 2012). In some areas, such as low permeability coals, hydraulic fracturing or 'fracking' is necessary to enable a more effective release and flow of gas from the coal seam. Fracking can unlock an area of low productivity potential, it can convert a non-productive well into a productive one and it can increase the drainage area of each well. This means that fewer wells need to be drilled in order to produce the same amount of gas. Hydraulic fracturing of the coal seam is done by pumping large volumes of water and sand at high pressure down the well into the coal seam, which causes the coal seam to fracture. The sand carried in the water is deposited in the fractures to prevent them closing when pumping pressure ceases. The gas then moves through the sand-filled fractures to the well. Fly ash may be potentially used to replace sand in this instance. Further study and prototype trial tests, however, are required.

Innovative and advanced systems for building infrastructure

The concrete infill wall system consists of a permanent formwork system for concrete walling for external and internal walls. It consists of lightweight sandwich panels created by bonding hard-wearing fibre cement, gypsum or plaster board to a stud frame (see Figure 7). The panels can be erected quickly and easily on site and then core-filled with concrete to achieve loadbearing walls that are fire and sound rated. The fibre cement,

gypsum or plaster board remains in place as sacrificial formwork, and provides a substrate for applied finishes such as skim coating, acrylic render and paint. The wall system can vary in size and thickness to suit a variety of architectural and engineering design requirements.

The use of concrete infill partition wall system on the building is gradually increasing in Australia and overseas. Some proprietary products include AFS LOGICWALL® in Australia and PRIMA™ SOLIDWALL and RBM Building System in Malaysia. This type of wall system is more durable and environmental friendly when compared to the traditional wall cladding system. In the traditional wall cladding system, rock wool or stone wool batt is used as wall insulation. Rockwool is made by melting volcanic rock at approximately 1500°C and its production is high energy intensive and requires significant amount of natural rocks. Further, concrete infill partition wall system can have thinner footprint with similar if not higher acoustic and fire ratings to that of traditional wall cladding systems. It also allows speedy construction, less labour intensive and, hence, has lower cost when compared to conventional wall cladding system or brick wall systems.

Instead of using conventional cement concrete or mortar to infill the wall, fly ash based product may be used (Figure 7). In the case of low rise building, cellular, foamed or lightweight expanded polystyrene high volume fly ash blended cement or fly ash based geopolymer concrete can be used. There are studies in literature that indicated fly ashes reacted adversely with foam reagents to produce cellular concrete (Smith, 2005) and, therefore, future research in this area and search for a new type of foam reagent are needed. Colaizzi (2003), for instance, has developed a type of lightweight, high heat resistance, cellular concrete using fly ash.

Fly ash based product infill wall system can also be extended to modular and tilt-up construction system as an alternative to precast concrete panel. It can be pre-fabricated off-site and assembly in-situ. For medium rise building or structures that required load bearing wall such as lift well/core, normal or high strength, high

volume fly ash blended cement or fly ash based geopolymer concrete can be used.

With similar concept, fly ash based product can also be used to infill steel hollow section columns, which will increase the column compressive load carrying capacity.

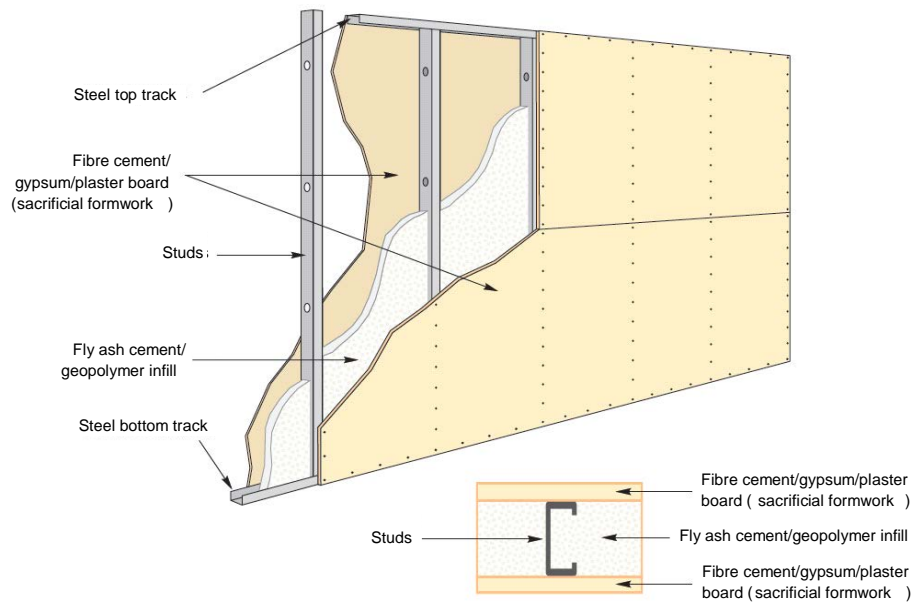


Figure 7: (Lightweight/foamed) fly ash cement or geopolymer concrete wall system (graphic obtained from Hume Cemboard Industries Sdn Bhd Malaysia and modified with permission)

Multi- component fly ash processing and utilisation system

Sections 3, 4 and 5 present the direct application of fly ash. There is an obvious benefit to being able to use the fly ash directly, but this may come at the expense of effectiveness. For example, although fly ash is used directly as an absorbent in wastewater treatment and soil amelioration agent for agriculture applications, there are issues regarding potentially leaching and mobilisation of heavy metals, which will cause secondary pollution of the wastewater effluent or the toxic elements and heavy metals being applied to soil which is being used to grow crops.

The variability in chemistry, mineralogy, and morphology of different fly ash batches also hinders its use directly. Each component may be useful or inert in a particular application but actively detrimental in another. For example, excess or variable carbon or LOI content in fly ash hinders its use in concrete applications due to its propensity to adsorb the speciality surfactants that are used in concrete mixtures to stabilise air bubbles (Pedersen et al., 2008). On the other hand, the adsorption capacity of the carbon in fly ash could be advantageous in wastewater treatment applications. Hence, by separating fly ash components physically and/or chemically, it can substantially enhance the effectiveness of fly ash in various applications and improve its utilisation rate.

Fly ash sequential separation for multi-component utilisation

A fly ash processing company named RockTron International Limited (RockTron) in United Kingdom uses a proprietary sequential separation process to recycle both fresh and stockpiled fly ash waste from coal-fired power stations. Figure 8 shows the sequential separation schematic process of RockTron.

Based on communication with RockTron founding director, Mr Philip Michael, RockTron is currently operate in United Kingdom and the technology is transferred to

Russia and licensed to Malaysia. RockTron has commercial plant capacity ranges from 25 tph to 100 tph. Their plant at Fiddler's Ferry Power Station in United Kingdom operated at up to 120 tph. They recycle 100% fly ash for the use as pollution abatement, polymers, elastomers, coatings, and adhesives to replace expensive raw materials and make valuable savings in production costs. Three main products produced by RockTron are:

- MinTron™ consists of a range of coated and uncoated micron sized classified solid aluminosilicate glass spheres: <1 to +200 m. With a Mohs hardness of 5-6, MinTron™ offers greater scratch resistance and lower oil absorption, reducing the amount of expensive resin required. MinTron™ can be used as fillers in plastics, rubber, coatings and adhesives applications.
- MagTron™ consists of a range of dense, solid magnetite spheres: <1 to +100 m. MagTron™ offers improved rheology and higher incorporation levels at a significant cost advantage compared to milled magnetite. MagTron™ can be used in sound absorption and other shielding applications.
- CenTron™ consists of a range of clean, classified hollow glass cenosphere products: <1 to 300 m. CenTron™ may allow higher filler levels and substitution of more expensive fillers in numerous applications including lightweight formulations for fillers and coatings.

Further, from communication with Mr Philip Michael, it was understood that at once stage, RockTron had considered licensing their technology to Australia and had held discussions with a number of institutions in Australia from Financial through Process Design Contractors and end users. However, it did not proceed finally and the reason is not disclosed.

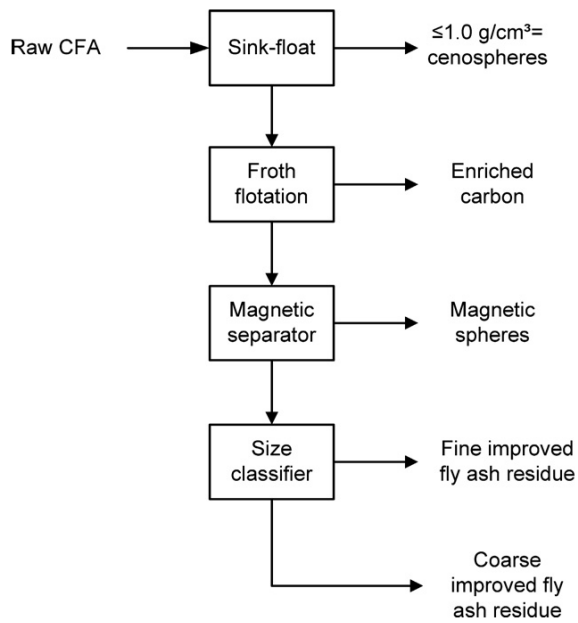


Figure 8: Sequential fly ash separation process of RockTron (Blissett and Rowson, 2012)

Fly ash activation processing for multi-component utilisation

Blissett and Rowson (2012) demonstrated a series of chemical, thermal, and/or mechanical activation processing technique to produce and recover the useful components from fly ash. This is potentially of significance with respect to the design of new fly ash derived products.

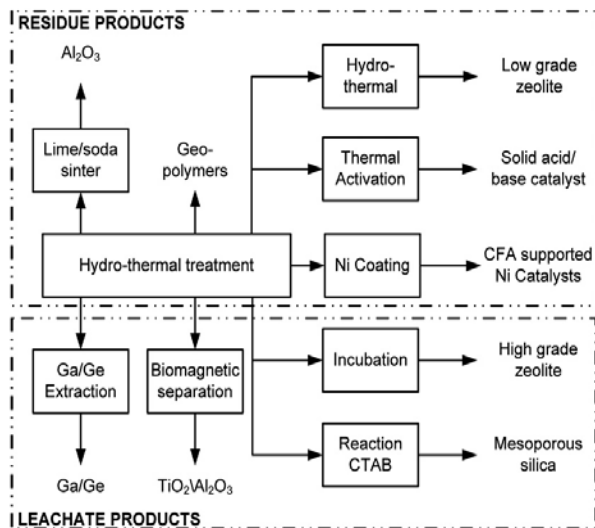


Figure 9: Chemical, thermal, and/or mechanical activation processing technique of fly ash for multi-component utilisation

Industrial integration with multi-component fly ash utilisation

Blissett and Rowson (2012) also suggested an industrial synergy process to substantially increase the fly ash utilisation. Figure 10 and Figure 11 show the concept proposed by Blissett and Rowson (2012). It is suggested that through the process, the net material input to the system can be lessened and, consequently, less virgin material is used.

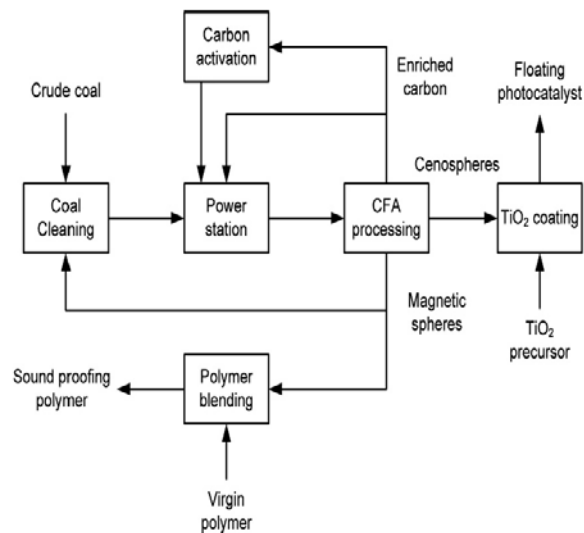


Figure 10: Industrial integration with fly ash cenospheres, enriched carbon and magnetic spheres (Blissett and Rowson, 2012)

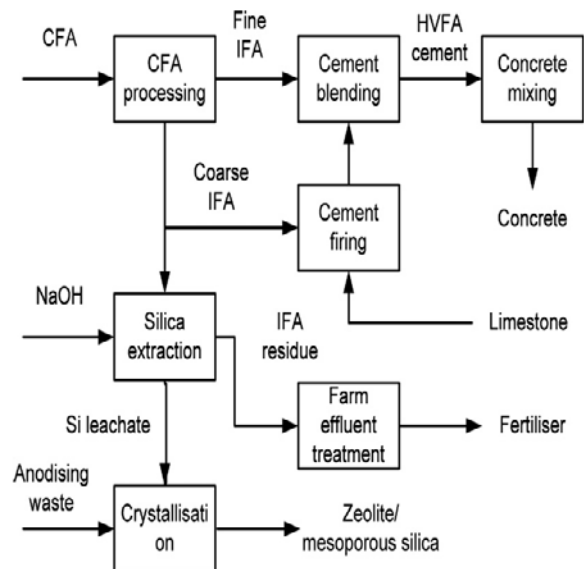


Figure 11: Industrial integration with improved fly ash residue (Blissett and Rowson, 2012)

BARRIERS TO COMMERCIALISATION OF FLY ASH

There are a number of potential technical, economic and legal barriers to the use of large quantities of coal fly ash. Each of these barriers is not mutually exclusive. For example, strict legal requirement may prohibit technological and technical advancements of fly ash. The following sections present the barriers to commercialisation and utilisation of fly ash.

Economic barriers

Economic barriers to increase the use of fly ash include the cost of transporting and competition from locally available natural materials (Kalyoncu, 2002). The previous study undertaken by the Cooperative Research Centre for Coal in Sustainable Development (CCSD) has also identified the cost of transportation and economics of ash production as the major barriers in the large volume utilisation of fly ash (Heeley, 2003). Storage may be an issue for dry fly ash, used in high value applications. In many cases, the highest production of fly ash does not occur at the time of greatest demand from the construction industry. Hence, storage capacity in the silos may limit the chances of a utility delivering its fly ash to the market. Wet fly ash may be stored easily but is mostly used in landfill. This practice is becoming less acceptable in many countries. For example, in the United States, the low cost of landfilling fly ash have been a barrier to utilisation (Walker et al., 2002).

Environmental barriers

As discussed in Section 2.4, fly ash contains trace amounts of heavy metal. In United Kingdom, the leachates and radon emissions from embankment built with fly ash between 1967 and 2000 were measured (Sear et al., 2003). It was found that the concentration of Mg, Se, K, Na and sulphate were above normal drinking water quality values. In Australia, the heavy metal element concentrations and leachate tests were undertaken by ADAA (2007, 2009) but they were found to be well within the maximum acceptance criteria of

Queensland EPA and NSW Department of Environment and Climate Change. However, for unbound fly ash applications such as structural fills, mining backfills, and usage of fly ash in agriculture industry, which are close to the water supply catchment or has high potential to interact and contaminate groundwater, it is recommended that the heavy metal element concentrations and leachate test results to be compared against the Australian Drinking Water Guidelines (2011) and Australian Guidelines for Water Recycling (2008) requirements.

Legal barriers

Environmental legislation is being applied in a way which hinders rather than furthers deployment of fly ash in various applications. CCSD has reviewed the legislation relevant to ash disposal both in Australia and internationally (Riley, 2004). For a comprehensive review of the legislation, the authors refer the reader to Riley (2007).

In United States, the Environmental Protection Agency (EPA) did not regulate fly ash as hazardous under Subtitle C of the Resources Conservation and Recovery Act (RCRA) prior to the 2008 Tennessee coal ash spill incident.

Having fly ash being regulated in some countries while not in other countries may be an obstacle to the higher utilisation of fly ash in this global environment. As the economies of the world are increasingly becoming interdependent, technical professionals such as engineers are required to work as part of international teams and devise solutions.

The authors are not familiar with the legislation both in Australia and internationally and, hence, it is recommended that other parties to the CRC (law and commerce) be engaged to review the current state of legislation with regard to environmental management and waste disposal legislation, as may be relevant to the project. Together with the environmental barriers identified in Section 7.2 above, a well-designed, comprehensive and systematic environmental management policy and risk management plan may be

developed by others in the CRC with waste management and legal expertise in which the plan and policy can potentially be acceptable by the lawmakers as a way for recycling and beneficial reuse of fly ash.

Technical barriers

Limitation of the amount of fly ash in blended cement concrete

There are strict standards governing the use of fly ash in cement and concrete such as EN 197-1 (EN, 2011) in Europe and ASTM C 595 (2003) in United States. The use and the amount of fly ash in blended cement are

defined by EN 197-1 (EN, 2011) as shown in Table 7. For cement to be certified to meet the EN 197-1 specification, the maximum permissible fly ash content is 50% and for ASTM C 595, the limit of substitution is 40%. Australian Standard AS 3972 (2010) does not impose any limitation on the amount of fly ash used in blended cement as long as the fly ash meets the AS3582.1 (1999) specification. However, some state-specific specifications have restricted the amount of fly ash permitted in blended cement. For instance, in NSW, the Roads and Maritime Services limits the maximum permissible fly ash content to 40% (RMS, 2012).

Table 7: Selected fly ash blended cement product defined by EN 197-1 (EN, 2000)

Types	Cement Product		Composition (percentage by mass)			
	Name	Notation	Cement Clinker	Fly ash		Other
				Siliceous	Calcareous	
CEM II	Portland fly ash cement	CEM II/A-V	80-94	6-20	-	0-5
		CEM II/B-V	65-79	21-35	-	0-5
		CEM II/A-W	80-94	-	6-20	0-5
		CEM II/B-W	65-79	-	21-35	0-5
	Portland composite cement	CEM II/A-M	80-94	6-20		0-5
		CEM II/B-M	65-79	21-35		0-5
CEM IV	Pozzolanic cement	CEM IV/A	65-89	11-35	-	0-5
		CEM IV/A	45-64	36-55	-	0-5
CEM V	Composite cement	CEM V/A	40-64	18-30	-	18-35
		CEM V/B	20-38	31-50	-	31-55

However, in United States, a new performance based ASTM C 1157 (2011) places no limit on the components of blended cements, and the International Building Code (IBC 2012) refers to ASTM C 618 (2012) and states that the optimum amount of fly ash is determined by the required properties of the concrete and is to be established by testing.

Inadequacy of current fly ash classification standards

The current fly ash classification standards such as ASTM C618 (2012), EN 450-1 (2012) and AS 3582.1

(1998) are developed for the use of fly ash in cement and concrete and, thus, may not be applicable for other uses. A certain percentage of fly ash passing 45 μm is usually defined in the fly ash standards as fine particle size is important in cement applications. Finer fly ash particles allow for more efficient blending and promote greater lime-silica reaction (Mehta, 1999). Particle size also has an influence upon other properties such as surface area and packing density. Sear (2001) studied the dependence of cement strength on the fineness of fly ashes from a range of fly ash from United Kingdom and the results are shown in Figure 12.

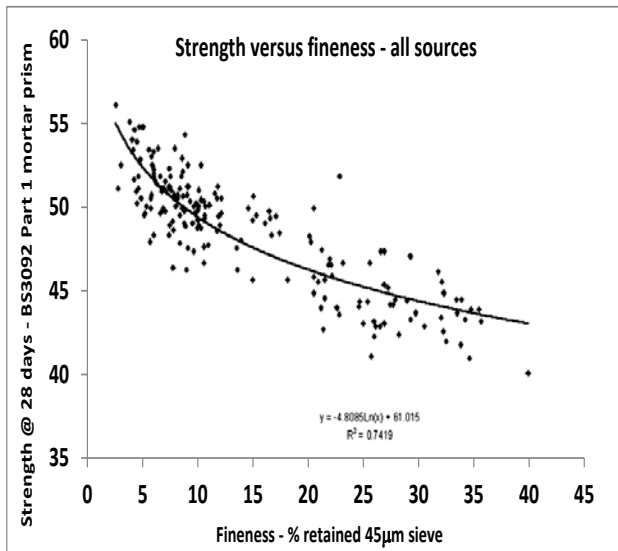


Figure 12: Relationship between the strength of fly ash mortar prisms and the fineness of fly ash (Sear, 2001)

In Australia, AS 3582.1 (1998) is the only fly ash classification standard and has been used not only for cement and concrete but also has been referenced by AS 2150 (2005) for asphalt pavement filler application. Filler is portion of mineral matter passing a 75 µm sieve according to AS 2150 (2005) but AS 3582.1 (1998) classifies fly ashes based on its fineness (percentage passing a 45 µm sieve). Some state-specific specifications have even imposed further restriction on the grade of fly ash for asphalt pavement filler. For instance, in NSW, the Roads and Maritime Services only permits fine (more than 75% passing a 45 µm sieve) to medium (more than 65% passing a 45 µm sieve) grade fly ash to be used as asphalt pavement filler (RMS, 2012). It is, hence, recommended that a new fly ash classification and rating system be developed that applies for all applications.

Variation in fly ash composition and current state of knowledge

As discussed in Section 2.3, fly ash consists of three types of mineral components. The glass component of fly ash is the principal component involved in the chemical reactions associated with fly ash utilisation, such as in the geopolymer, conventional cement and concrete industries or in zeolite production. Ward and French (2003) evaluated the mineralogical and chemical

characteristics of fly ashes from nine Australian power stations and found a wide variation in the percentage of glass in the Australian fly ash, ranging from 45 to 80%. The inferred large variation in glass composition data suggests that the characteristic and reactivity of fly ash from different power stations are dissimilar. Likewise, Fernandez-Jimenez and Palomo (2003) and Van Jaarsveld et al. (2003) reported that fly ash obtained from different sources as well as different batches of ash from the same source have various concentrations of constituents. Further, they also discussed that for a given type and source of coal, the composition of fly ash is generally determined by the operating temperature within the combustion process as well as the mineralogy and inorganic geochemistry of the original feed coals. For those reasons, to-date, each batch of fly ash is needed to be characterised experimentally and the end products are to be tested and undergo stringent quality control. Such activities add to the production cost for the industry, providing a barrier to its use.

A study was undertaken by French and Smitham (2007) to correlate the physical and chemical characteristics of fly ash with respect to the feed coal properties. They have identified the knowledge gaps and future research opportunities; those knowledge gaps of French and Smitham's study are reproduced in Table 8 and Table 9; six years since the publication, no or limited studies have been undertaken to fill the knowledge gaps.

Effect of low NO_x burner

Further, as power generators are increasingly upgrading their burner to low NO_x type to reduce nitrous oxide emissions in recent years, previous studies on fly ash conducted prior to the upgrading works may no longer be applicable. It is well documented that low NO_x burners change the form and quantity of fly ash, as well as introducing possible ammonia compounds (Hemmings et al. 1997; Bijen and van Seist, 1992; Golden, 2001; Fox and Constantiner, 2007). Low NO_x burner fly ash has greater and more active carbon contents, more coarse particles, slightly less glass composition and lower strength activity index (SAI) when compared to fly ash obtained from conventional burners.

Hence, it is recommended that a project to be scoped by the CRC to investigate and the properties of fly ash produced from low NO_x burner and together with the quantification of the fly ash characterisation as discussed in Section 7.4.4 previously.

Table 8: Current state of knowledge of influence of feed coal properties on key physical fly ash characteristics for Australian Coals (French and Smitham, 2007)

Physical Characteristics	Relationship of characteristic to coal properties	
	Available Australia data	Summary of available literature data
Particle size	Very little data	One Study showed difference for two coals
Surface area	Some data indicating relationship exists	Two studies conflicting evidence coal type vs operation conditions
Bulk density	Some data indicating relationship exists	One Study suggests possible relationship
Permeability	Not known	
Viscosity	Not known	
Compressive strength	Not known	
Shear strength	Not known	
Moisture content	Not known	
Slurry pH	Not known	
Color	Not known	

Table 9: Current state of knowledge of influence of feed coal properties on key chemical fly ash characteristics for Australian Coals (French and Smitham, 2007)

Chemical Characteristics	Relationship of characteristic to coal properties	
	Available Australia data	Summary of available literature data
Major Elements	Data available	Several Studies show relationship of ash chemistry to coal chemistry
SiO ₂	Data available	As described for major elements
Al ₂ O ₃	Data available	As described for major elements

Fe ₂ O ₃	Data available	As described for major elements
CaO	Data available	As described for major elements
MgO	Data available	As described for major elements
Alkalis	Data available	As described for major elements
SO ₃	Data available	As described for major elements
Free lime	Not known	
Trace Elements	Data available	Many laboratory studies few of power stations which show operating conditions also have an influence
Radioactivity	Very little data	Some information which suggest may be influenced by mode of occurrence of radioactive elements in coal
Unburnt Coal	Data available	Contradictory most studies suggest operating conditions more important but some indicate coal type also significant
Trace Organics	No data	
Pozzolanicity	No data	
Mineralogy	Limited quantity data	Very limited quantitative data which suggest that a relationship may exist

Fly ash from co-firing combustion

The authors are not aware of any co-firing coal power station in Australia. However, this kind of practice has been adopted overseas to reduce greenhouse gas emissions and study on pilot scale co-firing of biomass and coal boiler has been undertaken by CCSD in Australia (Zulfiqar et al., 2006). Therefore, it is possible that existing plants may be upgraded for co-firing of coal with secondary fuels. Co-firing combustion with great proportions of secondary fuels, such as biomass, have reported to have in more varied ash composition (Smith, 2005) and there are also concerns on the increase in the composition of mercury and other trace elements in the fly ash from co-firing of coal and biomass (Meij and te Winkel, 2003). For these reasons, it is recommended to the CRC that study on the effects and properties of fly

ash from co-firing combustion to be included in future projects.

Longer setting time of fly ash blended cement concrete

As mentioned in Section 3.2.2, fly ash blended cement concrete has an extended hydration period, required longer curing period and gained strength slower than that of conventional cement concrete. This is unfavourable for the construction industry as longer waiting time is required for stripping formworks and post-tensioning. The recommendation in Australian Standard AS 3600 (2009) for formwork stripping time also may not be applicable if fly ash blended cement concrete is used. According to Ahmaruzzaman, (2010) and many others, the setting behaviour can be accelerated using heat or steam cured and, hence, fly ash blended cement concrete is appropriate and suitable for precast concrete industry. Opportunities need to be investigated for a greater usage of fly ash based geopolymer products within the precast industry.

STEEL FURNACE SLAG: POTENTIAL VALUE ADDED APPLICATIONS

Introduction

Steel furnace slag, a by-product of steel making, is produced during the separation of molten steel from impurities in steel-making process in the basic oxygen system (BOS). The slag occurs as a molten liquid melt and is a complex solution of silicates and oxides that solidifies upon cooling (Chesner et al., 1998). Steel furnace slag can be subject to slight dimensional expansion until it fully hydrates and, hence, its potential to be reused and recycled is limited.

The principal aim in this section is to explore the potential value added applications for steel furnace slag.

Steel Furnace Slag Manufacturing Process

The BOS steel making process involves the removal of carbon, silicon and other oxidising elements from iron by an oxygen blast. In the process, the hot liquid blast furnace iron, scrap, and fluxes, which consist of lime (CaO) and dolomitic lime (CaO.MgO or 'dolime'), are charged to a vessel. High pressure oxygen is blown into the vessel and a violent chemical reaction takes place. The oxygen removes the impurities in the charge. These impurities consist of carbon as gaseous carbon monoxide, and silicon, manganese, phosphorus and some iron as liquid oxides, which combine with lime and dolime to form the steel furnace slag. At the end of the refining operation, the liquid steel is tapped and poured into a ladle while the steel furnace slag is retained in the vessel and subsequently tapped into a separate slag pot (Chesner et al., 1998). The slag is then transported into ground bay where after initial solidification the slag is cooled with water sprays (ASA, 2013). *Figure 13* shows the manufacturing diagram of steel furnace slag in steel making process.

Physical properties

Steel furnace slag is dark grey in colour and characteristically harder than blast furnace slag (BFS)

and has a density about 20 - 25% greater than basalt or BFS (ASA, 2013). Steel furnace slags are highly angular in shape and have rough surface texture (Chesner et al., 1998). They also have moderate water absorption, less than 3%. Steel furnace slag is very hard has high deformation resistance, high wet and dry strengths, high impact resistance and high abrasion and skid resistance (Hainsworth, 1995).

Mineralogy

McCallum (2005) studied the mineralogy of the Australian steel furnace slag. Through X-Ray Diffraction (XRD) analysis, he found that four main mineral phases present in the slag. These are as follows: Wustite (FeO), Magnetite (Fe₃O₄), Larnite (Ca₂SiO₄) and Srebrodol'skite (Ca₂Fe₂O₅). Some metallic iron is also found. McCallum suggested that there is substitution of Aluminium (Al), Manganese (Mn) and Magnesium (Mg) elements into the Larnite and Srebrodol'skite structures resulting in complex calcium silicates, calcium aluminium oxides and calcium iron silicates. Further, a definite separation of mineral phases in the slag, namely and Ca-Si rich phase as well as iron-rich and calcium-rich phases, was noted from the elemental maps derived from electron microprobe analysis and Ca-Si rich phase as well as iron-rich and calcium-rich phases is presence. He reported that Mg and most of the Mn present is associated with the Ca-Si rich phase whereas the Al would appear to be associated with the Ca-rich phase.

Chemical properties

The principal components of steel furnace slag are the oxide of Iron (Fe), Calcium (Ca), silicon (Si), and Magnesium (Mg). Table 10 shows the typical chemical constituents of steel furnace slag in Australia.

The cooling rate of steel furnace slag is sufficiently low so that crystalline compounds are generally formed (Chesner et al., 1998). The predominant compounds are dicalcium silicate, tricalcium silicate, dicalcium ferrite, merwinite, calcium aluminate, calcium-magnesium iron oxide, and some free lime and free magnesia (periclase). The relative proportions of these compounds

depend on the steel-making practice and the steel furnace slag cooling rate.

Free calcium and magnesium oxides are not completely consumed in the steel furnace slag and, hence, steel furnace slag generally exhibits a propensity to expand in humid environments (Chesner et al., 1998). The free lime hydrates rapidly and can cause large volume changes over a relatively short period of time (weeks), while magnesia hydrates much more slowly and

contributes to long term expansion that may take years to develop.

Steel furnace slag is mildly alkaline, with a solution pH generally in the range of 8 to 10 (Chesner et al., 1998). However, the pH of leachate from steel slag can exceed 11, a level that can be corrosive to aluminium or galvanized steel pipes placed in direct contact with the slag. In Australia, a pH of 12.4 was noted on the leachate of steel furnace slag (McCallum, 2005).

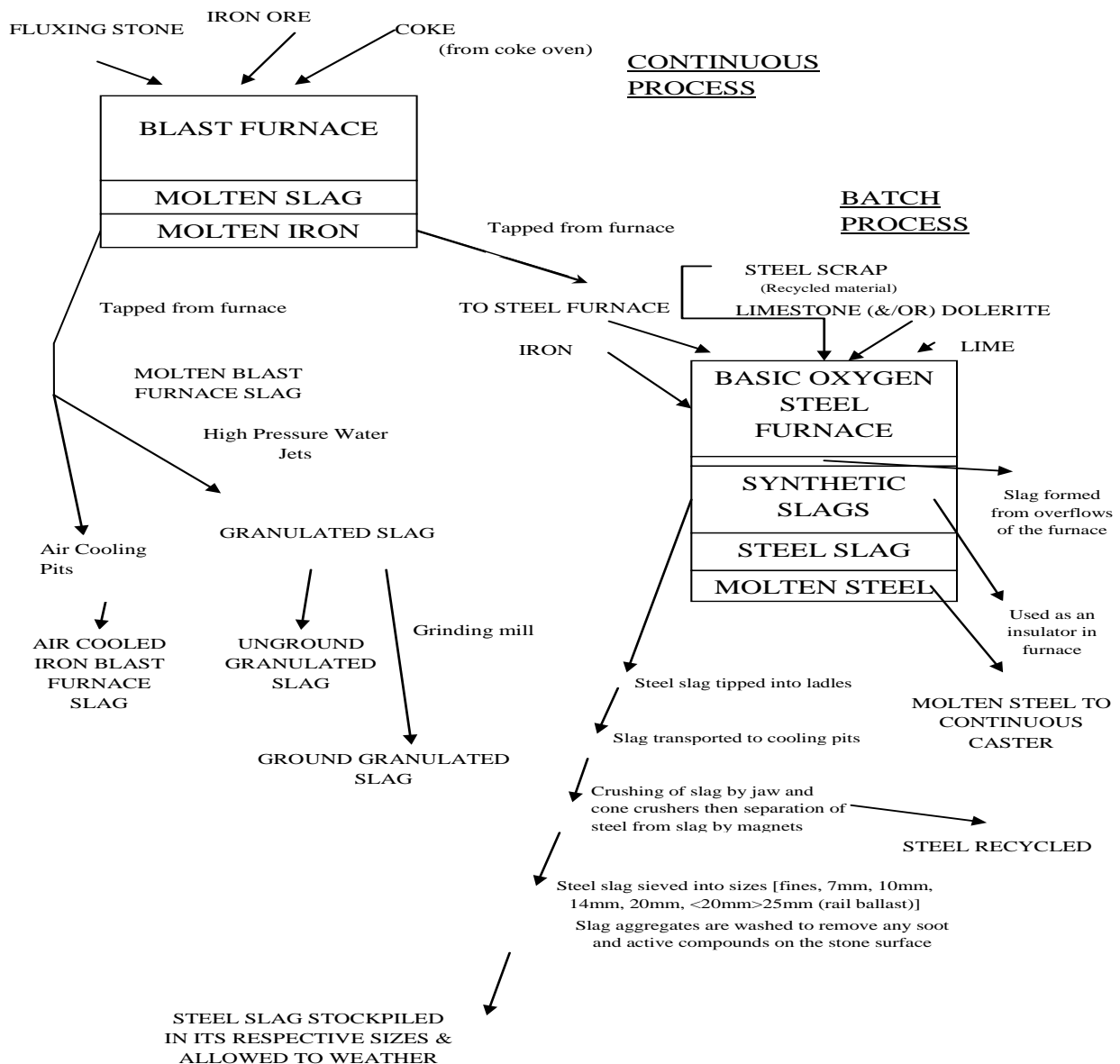


Figure 13: Production process of steel furnace slag or steel slag (Hainsworth, 1995)

Table 10: Chemical composition of steel furnace slag
(McCallum, 2005)

Component	Steel Furnace Slag
Silica, SiO ₂	10.4 – 12.5
Alumina, Al ₂ O ₃	2.8 – 3.49
Iron oxide, Fe ₂ O ₃	25.7 – 30.0
Calcium oxide, CaO	37.4 – 38.3
Magnesium oxide, MgO	9.9 – 10.6
Sodium oxide, Na ₂ O	0.06 – 0.07
Potassium oxide, K ₂ O	<0.01
Titanium oxide, TiO ₂	0.84 – 1.20
Sulphur trioxide, SO ₃	0.17 – 0.20
Phosphorus pentoxide, P ₂ O ₅	1.37 – 1.44
Manganese oxide, Mn ₃ O ₄	3.70 – 4.33
Chromium oxide, Cr ₂ O ₃	0.12 – 0.17
Vanadium oxide, V ₂ O ₅	1.43 – 1.90
Loss on ignition	0.07

Current Applications

In Australia, steel furnace slag has been fully utilised, predominantly used as a substitute for material in the construction industry. The demand of steel furnace slag exceeds its supply in 2011. A total of 573 thousand tonnes of steel furnace slag was generated and 597 thousand tonnes was utilised (ASA, 2012). *Table 11* presents the production and utilisation of steel furnace slag in Australia in 2011.

Table 11: Production and utilisation of steel furnace slag in Australia in 2011

Total produced	573,004 tonnes
Total utilised	597,334 tonnes
Breakdown of utilisation	
Feed stock for Clinker/Glass product	20,132 tonnes
Road base and sub base	203,894 tonnes
Asphalt aggregate	114,087 tonnes
Other	439,260 tonnes

This potentially expansive nature (volume changes of up to 10% or more attributable to the hydration of calcium and magnesium oxides) could cause difficulties with products containing steel furnace slag, and is one reason why steel furnace slag aggregates are not suitable for use in Portland cement concrete or as compacted fill beneath concrete slabs (Chesner et al., 1998).

Steel furnace slag use as aggregate requires to be stockpiled for several months to expose the material to moisture from natural precipitation and/or application of water by spraying (Chesner et al., 1998). The purpose of such storage (aging) is to allow potentially destructive hydration and its associated expansion to take place prior to use of the material in aggregate applications. There is a wide variation in the amount of time required for adequate exposure to the elements. According to Chesner et al. (1998), stockpile period up to 18 months may be needed to hydrate the expansive oxides.

However, steel furnace slag has an affinity for bitumen due to high skid resistance and the presence of free lime enhances its anti-stripping properties (Chesner et al., 1998).

New and Emerging (Value Added) Applications

Acid Mine Drainage Treatment

Simmons et al. (2002) studied the potential use of steel furnace slag to replace lime and to increase water pH and alkalinity and precipitate metals in acid mine drainage. Steel furnace slags with varying neutralization potentials were leached with acid mine drainage of a known quality using an established laboratory procedure. Leaching continued for 60 cycles and leachates were collected after each cycle and were analysed. Results from the tests showed that very little of the metals in the leachates originated from slag leaching, even under acidic conditions. These results indicate that many metals present in slag may be bound in insoluble forms that remain stable under a variety of pH ranges. Simmons et al. (2002) have also conducted a pilot test at an abandoned site in West Virginia, United

States. Steel furnace slag leach beds were constructed and acidic water which flowed through the leach bed is found to be neutralised.

Liming ameliorant for use in agriculture

Whatmuff et al. (2012) investigated the use of steel furnace slag as a liming ameliorant in agriculture industry. They found that the liming potential of steel furnace slag is equivalent to no more than 30% of finely ground agricultural limestone. Whatmuff et al. (2012) also reported that the metal uptake from steel furnace slag treated soils was generally low when compared to established background levels for plant tissue and relevant Australian food standard limits. Of the metals tested, increasing the rate of steel furnace slag application increased the plant tissue content of Cd and V on the sandy soil only. However, plant levels of these elements did not exceed Australian regulatory standards. Compared to background levels and soil contaminant limits, the application of steel furnace slag did not affect the total soil levels of Cu, Fe, Ni, Pb and Zn. Soil Cd, Cr and V levels were increased at higher application rates and only V approached regulatory limits at the highest application rate, but only on a soil with a high background V concentration. They also extracted contaminant metals from the steel furnace slag amended soils in order to assess the potential environmental impact. It was found that the concentration of water soluble metals in the extracts from steel furnace slag amended soils were below recommended irrigation and livestock drinking water limits. However, the abrasive nature of steel furnace slag was observed and worms avoided the steel furnace slag amended soils.

Steel Furnace Slag in Clay Brick Production

Bonazza et al. (2002) studied the feasibility of steel furnace slag recycling in clay brick manufacturing. The slags were coarse grained (1 to 10 cm) and rich in CaO and FeO with remarkable amounts of MnO and Cr₂O₃. After a preliminary grinding, they were introduced into clay bodies up to 2 to 3% by mass without any particular technological drawbacks, ensuring a complete inertisation of chromium and manganese. Additions of

slag up to 5 to 6 % by mass involved a significant increase of porosity and a decrease of mechanical properties.

Potential Value Added Applications

In this section, some potential high value uses of steel furnace slag are identified.

1. Steel furnace slag contains some significant amount of iron oxide (Fe₂O₃), up to 30%, and the iron can be potentially recovered.
2. Steel furnace slag contains high amount of free lime and is suitable to replace limestone and use as an absorbents in wastewater treatment. Piche and MultiServ (2001) have investigated the use of steel furnace slag in removing phosphate in wastewater treatment.

Further, as mentioned previously, in the current process, the cooling rate of steel furnace slag is sufficiently low so that crystalline compounds are generally formed. By quenching the molten steel furnace slag and allowing the slag to cool and solidify rapid, a more reactive amorphous compound may be formed and this type of slag when grind into powder form may be potentially suitable for a number of higher-value applications including:

1. Expansive agent for non-explosive demolition.
2. Shrinkage compensation cement concrete:
Due to its expansive properties, ground steel furnace slag may be used as an additive in cement to compensate and offset shrinkage in concrete.
3. Chemically prestressing or self-stressing cement concrete:

Due to its expansive properties, ground steel furnace slag may be used in self-stressing cement concrete for prestressing precast elements, such as hollow pipe. Concrete made of steel furnace slag can possibly be used to infill steel hollow section columns, providing confining pressure and increase the column compressive load carrying capacity.

4. Granulated or solid alkaline activator for geopolymer concrete manufacturing:

The use of ground steel furnace slag to replace conventional alkaline activator may be possible as steel furnace slag contains significant amount of free alkali substance.



CONCLUSIONS AND RECOMMENDATIONS

Australia's coal powered generators produce about 14 million tonnes of fly ash per year. Fly ash is a widely available by-product from coal fired power stations across Australia. Currently, only 42% is used in various construction related applications and the remainder placed into onsite storage dams or dumped into landfill sites potentially causing serious environmental issues. To make use of this abundant mineral resource, fly ash has been intensely investigated and has been commercially used for more than 60 years as a Portland Cement replacement material. Today, fly ash concretes are common place and are accepted by Standards Australia. However, Standards Australia limits the Portland cement replacement rate, typically up to 30-40%. As a result, blended cements still contain more Portland cement clinker than fly ash in most cases.

An increase in research activities related to the development of new low carbon concrete technologies, namely Geopolymer Concrete (GC), has occurred in recent years. GC is the result of the reaction of materials containing aluminosilicate such as fly ash with alkalis to produce an inorganic polymer binder. There is no Portland cement clinker in GC. The widespread utilisation of Geopolymer concrete in the industry is certainly the most promising pathway to increase the rate of fly ash utilisation. Moreover, geopolymer binder can provide reduction of embodied CO₂ of up to 80% compared to Ordinary Portland Cement. Indeed, carbon emissions due to the manufacture of Portland cement are second only to burning fossil fuels. Its share of CO₂ emissions in Australia is estimated at 8 million tonnes/year. Geopolymer concrete has yet to enter the mainstream of concrete construction. The main barriers for widespread adoption of geopolymer concrete in the industry and the pathway to overcome those barriers have been clearly identified and are reported in the CRC-LCL RP1004-I (Berndt et al., 2013).

Fly ash based manufactured synthetic lightweight aggregate for concrete appears to be the second most

promising pathway to increase significantly the rate of fly ash utilisation. Lightweight concretes offer superior insulation properties that can reduce energy consumption in buildings, reduce the dead weight and material handling cost in construction. Further, the rapid depletion of quality natural aggregate quarry sources close to most major metropolitan regions of Australia, emphasize why the need to explore alternative economic sources has become imperative to support increasing vital infrastructure development, including housing, roads, bridges, schools and hospitals.

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