Geopolymers using waste materials to bring resource sustainability to construction and mining industries

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ABSTRACT

The 'holy grail' for environmental regulators is "zero waste" in which all waste is reused or recycled and no waste ends up as landfill. Innovative materials technologies, such as geopolymers, can deliver on the "zero waste" objective by creating commercially valuable products from materials that are otherwise high volume waste products. These waste materials include flyash, blast furnace slags, bauxite residues, clays, quarry waste and tailings. Waste generators are now recognising the value of working together, rather than disposing of these waste products on an individual basis, to economically and manufacture a range of products for the construction, building, mining and environmental management industries.

This paper outlines how Australia is leading the world in research and development to reduce waste materials by using geopolymer technology and presents results of this research which may lead to new products competing directly with 'traditional' building and construction material products.

1 ENVIRONMENTAL BENEFITS OF USING WASTE MATERIALS

Several Australian industry based research bodies, such as the Cooperative Research Centre for Sustainable Resource Processing (CSRP), are supporting research into transforming waste from mineral processing and metal production industries into valuable resources. The CSRP, based at the Curtin University in Western Australia has industry and government funding totalling AUS$90 million over the next seven years, with support from major mining companies including BHP Billiton, Rio Tinto and Alcoa. These bodies are conducting research on many projects, including the use of geopolymers, to reduce the ecological impact of resource processing and to progressively eliminate waste and emissions.

The 'holy grail' for environmental regulators and the community is "zero waste" in which all waste is reused or recycled and no waste ends up as landfill. Geopolymer technology can deliver on these "zero waste" objectives as it creates commercially valuable products from materials that are otherwise high volume waste products. These waste materials include flyash, bauxite residues, blast furnace slags, tailings and quarry wastes (Gourley 2003 and Hardjito et al 2004). Currently each waste generator deals with the disposal of these waste products on an individual basis.

Using geopolymer technology, construction and building products could be developed from a more diverse range of source materials, including waste materials, than are currently utilized. Many countries have shortages of raw materials and geopolymers from waste may replace the use of some natural raw materials to produce high quality concrete, building and construction products.

The total annual world production of Portland cement exceeds 1.5 billion tonnes and the gradual replacement of Portland cement products by geopolymer concrete would provide a significant reduction in greenhouse gas emissions. Over 0.5 tonnes of greenhouse gas emissions would be eliminated for every tonne of Portland cement replaced by geopolymer concrete (Davidovits 2005). The production of bricks, pavers and precast concrete products also requires elevated temperatures by burning fossil fuels during curing. Geopolymer concrete products could reduce or eliminate the need for this large energy requirement as they may be cured at ambient or moderate temperatures.

2 GEOPOLYMER TECHNOLOGY

Geopolymers are formed from the chemical fusion of aluminium and silica materials into concrete like products (Davidovits 1994). Geopolymers is the name given to a group of alkali activated alumino-silicate binders that are formed by mixing silica-rich and alumina-rich materials with a solution of alkali or alkali salts, resulting in a mixture of gels and crystalline compounds that eventually harden into a new strong matrix. This is in contrast to Portland cement products which use a pozzolanic reaction between silica and calcium carbonate to form calcium silicates as the binding matrix. Geopolymers may also be referred to as alkali activated cements (Krivenko 2005 and Shi et al 2006) or inorganic polymer concrete (Lukey & van Deventer 2005).

Geopolymer concrete products have high early strength and low shrinkage properties, are resistant to freeze-thaw, acid, fire, sulphate and alkali aggregate reaction (AAR) and have high thermal resistance qualities, which are useful for fire retardant walls, thermal banks and insulation panels (Davidovits 1994).

Geopolymer concretes may use similar batching processes to Portland cement products with workability improved by increasing water content, or the addition of super-plasticizers. Geopolymer concrete with high slumps of 240 mm can still achieve high strengths without any sign of aggregate segregation (Hardjito et al 2004). Ultimate compressive strengths and setting times of geopolymer concretes are dependent on curing temperature, water content, type of alkaline activator and the composition of source materials. Generally the presence of compounds other than silica (SiO_2) and alumina (Al_2O_3), such as calcium (CaO) or iron (Fe_2O_3) oxides, may reduce setting times (Hardjito et al 2004).

Geopolymer concretes can be produced from both calcined and non-calcined source materials. Calcined materials, such as metakaolin, fly ash and slags, generally yield high compressive strengths even after curing at room temperature. Non-calcined materials, such as naturally occurring kaolin clays, zeolites and reactive alkali silica minerals, can still yield moderate to high compressive strengths after curing at moderate temperatures (Hardjito et al 2004).

Geopolymer materials also exhibit very low permeability and have the potential for use as land fill liners and encapsulation of hazardous materials. The combination of low permeability and acid resistance properties can provide opportunities for the use of geopolymer concrete in applications not normally suitable for Portland cement products, such as storage and transportation of chemical compounds.

Geopolymer concretes can also immobilise toxic and hazardous materials, such as heavy metals, within the geopolymeric matrix and can act as a binder to convert semi-solid wastes into solids (Davidovits 1994). Heavy metals, such as copper (Cu) and lead (Pb), have been immobilised in fly ash based geopolymer products, using a combination of physical encapsulation, chemical bonding and adsorption (Van Jaarsveld et al 1998). In Eastern Europe, geopolymers have been used to encapsulate mine tailings containing normally occurring radioactive materials (NORM) derived from disused nuclear operations (Hermann et al 1999). The resultant geopolymer products are durable, provide ease of handling and storage and resist leaching of encapsulated contaminants.

Geopolymer products are currently being developed in the following areas:

- civil construction applications –stabilised fill, pavement materials, and soil stabilisation;
- building materials – bricks, blocks, tiles, pavers, lightweight/fire retardant/acoustic panels, pipes, precast concrete products and readymixed concrete products;
- mining – paste back-fill, tailings dams liners and capping media, shotcrete, and acid resistant concrete;
- environment / waste management – impermeable barriers, encapsulation of domestic, hazardous, radioactive and contaminated materials in a very impervious, high strength material; and
- specialist applications – rapid set binders, very high strength binders, lightweight products, low shrinkage, high temperature crucibles and acid resistant storage facilities.

Geopolymers have been around since the time of the Ancient Egyptians and Romans, yet are still considered a relatively new technology and limited commercial applications have been successful in recent history. Australia is currently leading the world in the research and development of geopolymer applications, with interest in the technology growing from within the mining, construction and engineering sectors. This interest is demonstrated by Australia conducting international conferences on geopolymers in Melbourne (2002) and Perth (2005).

A brief outline of each of the main waste materials, fly ash and blast furnace slag, on which industry is focusing research opportunities for using geopolymer technology, is provided below.

3 FLY ASH

Fly ash has been successfully used as a mineral admixture component of Portland-pozzolan blended cements for nearly 60 years. This is the largest single use of fly ash but generally only consumes about 10% of the fly ash production throughout the world. A further 10-15% of the fly ash produced is used for construction, building materials and beneficiation applications to produce lightweight concrete products such as panels and blocks, flowable fill, roadbase and structural fill products. The remaining 75-80% of fly ash is disposed of as waste, with power stations having significant environmental issues relating to the disposal of these large volumes of fly ash materials.

The majority of fly ash used in the cement industry is top ash derived from black or bituminous coal (Class F) because of its constant fineness and pozzolanic properties (Neville 2004). Bottom ash is coarser and more variable in its pozzolanic properties and only a small proportion of this fly ash is used for such applications as stabilised road pavement materials and dam construction. Class C fly ashes are derived from brown or sub-bituminous coals and lignites, and are generally higher in lime and coarser than Class F materials. This generally limits their use in the cement industry.

Fly ash is one of the most abundant waste materials available for use in the construction materials market because most power generation is located close to large metropolitan areas. Geopolymer technology is able to utilise all classes and grades of fly ash and has a great potential for reducing stockpiles of waste fly ash materials.

Many researchers are advancing the use of fly ash waste materials to reduce the use of Portland cement. The Curtin University of Technology in Western Australia is undertaking extensive research on the mechanical, chemical and workability properties of both high volume fly ash (HVFA) concrete (up to 60% fly ash) and geopolymer concrete (100% fly ash) and their applications in the construction industry *(*Hardjito et al 2004, Rangan 2005, Hardjito & Rangan 2005, and Wallah & Rangan 2006).

Results of their work on geopolymer concrete confirm the high early compressive strength of heat cured geopolymer concretes do not increase with age when compared to ambient cured concretes which gain strength with time (Rangan 2005, Figure 1). Mix designs were tested to determine optimum concentrations of fly ash, water, reagents, caustic and superplasticers, resulting in a workable high early strength 55MPa concrete product which was cheaper than comparable Portland cement concretes (Hardjito & Rangan 2005, Figure 2). Heat cured geopolymer concretes reported a 50% reduction in creep, up to 80% reduction in shrinkage and higher resistance to sulfate and sulphuric acid attack than similar Portland cement concrete mixes (Wallah & Rangan 2006). Research work continues on confirming the long term durability of geopolymer concretes to address issues relating to compliance to and modifying relevant Australian Standards, building codes and other industry specifications so that geopolymer concretes may gain commercial acceptance.

A private company, Siloxo Pty Ltd, was founded by researchers at the University of Melbourne and conducted studies for the commercialisation of a range of inorganic polymer products (Lukey & van Deventer 2005). This research was supported by Fletcher Constructions, a NZ based construction company, until early 2006 when Siloxo Pty Ltd ceased business. Australian construction companies Boral (Dumitru & Parashiv 2005) and Rocla (Gourley & Johnson 2005) have also conducted research into using fly ash and blast furnace slags to produce sleepers, pipes and precast concrete products.

Development of geopolymer products is not limited to black coal fly ash, with Latrobe Valley brown coal producers, Monash University and the Australian Sustainable Industry Research Centre (ASIRC) supporting the development of a geopolymer concrete freeway sound barrier and lightweight geopolymer concrete building panels using brown coal fly ash.

However, to date, commercialisation of fly ash geopolymer concrete products has failed in Australia, due to numerous barriers within the industry, including strict building codes and standards, which do not yet recognise geopolymer technology, conservative design engineers and entrenched businesses based on Portland cement.

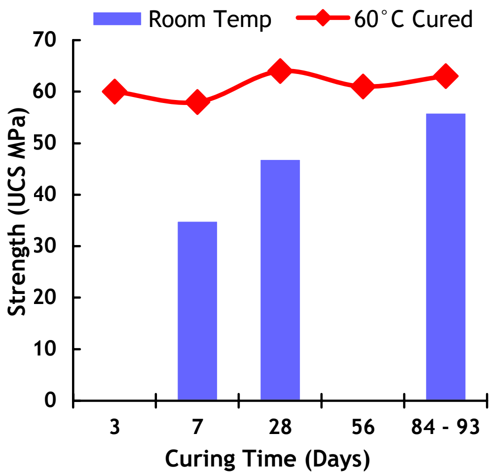

Figure 1: Comparison of room and heat cured 55MPa geopolymer concrete (Rangan 2005).

Figure 2: Curtin University of Technology 55MPa geopolymer concrete using 100% fly ash.

4 BLAST FURNACE SLAG

Molten blast furnace slag is formed during the process of manufacturing iron and other metals. Different forms of slag product are produced depending on the method used to cool the molten slag, which can be allowed to solidify slowly by air or rapidly by water cooling to form rock slag. The composition of the slag is dependent on the chemical composition of the ore material and the refining process. Blast furnace slag is non-metallic and consists primarily of silicates, aluminosilicates, and calcium-alumina-silicates with some residual metals.

Slags can be crushed like normal quarry products, for use as aggregates in concrete and pavement manufacture. They can also be further processed or ground to form Ground Granulated Blast Furnace Slag (GGBFS), which is used as a cement replacement for a range of end user products in the construction industry.

Around 3 million tonnes of slag are produced each year from iron and steel works in Australia (ASA 2003). Of this volume about 65% are sold as beneficiated slag products for use in the cement and construction industries. The remaining 35% are disposed of as waste, and producers are actively seeking opportunities for increasing sales to reduce stockpiles of waste materials. Slags are also produced from other metal refineries which also generally achieve very small sales volumes.

Slags are blended with Portland cements, as low cost fillers, but they also enhance concrete workability, density, durability and resistance to alkali-silica reaction (Neville 2004). Geopolymer technology is able to fully replace Portland cement with blast furnace slags of varied compositions.

Blast furnace slags have been used to produce geopolymer concretes (alkaline activated cements) in the Ukraine since early 1930's with over 60 specifications and standards developed in the former Soviet Union (Krivenko 2005 and Shi et al 2006). A wide range of industrial applications continue to be monitored by researchers for long term durability performances, and include the following:

- 9 storey buildings (built ~1960)
- 20 storey building (built ~1987, see Fig 3)
- Sewer pipes (built ~1966)
- Irrigation channels (built ~1962)
- Breakwater blocks (built ~1965)
- Road pavement (built ~1984)
- Railway sleepers (built ~1989, see Fig 4)
- Fire doors (built ~2000)

Long term durability trials of the Ukraine geopolymer concretes in seawall and freeze thaw conditions have shown strengths increase (40MPa to 57MPa in 5 years) and permeability decreases ($1x10^{-11}$ to $1x10^{-13}$ cm/sec in 7 years) with time (Krivenko 2005).

Figure 3: 24 storey residential building built in 1987-89 of slag alkaline concrete (Krivenko 2005).

Figure 4: Railway sleepers built in 1989 of pre-stressed slag alkaline concrete, Moscow – St Petersberg railroad (Krivenko 2005).

Research is being conducted by mining companies looking at opportunities to replace Portland cement in underground backfill applications with slags. However, the moderate pozzolanic properties of slags reduces their cementitious capability, especially for backfill products using mine tailings, and consequently large volumes of slag are required to achieve comparable strengths with Portland cement mixes. Trials have been undertaken at several Australian underground mines where Portland cement was replaced with GGBFS and a geopolymer reagent (Drechsler & Graham 2005). These trials found that slags can be high in reactive silica and alumina, and geopolymerisation may be further enhanced if mixed with tailings material that also contains reactive silica and alumina.

Research is also being conducted into opportunities for using blast furnace slags to produce lightweight building panel products based on geopolymer technology. The housing construction industry is seeing a growing trend towards the use of lightweight building panels and geopolymer technology could provide opportunities to use waste materials, such as slags and fly ash, to produce these products.

5 CONCLUSIONS

The ever-diminishing availability of both cement and clinker, particularly in the Asia-Pacific region, increasing transportation, energy and labour costs and the impost of carbon taxes to Australia in the near future will provide increased market pressures to use alternative raw material sources and "green" products such as geopolymers.

Industrial and mining companies in Australia are driving research into the use of innovative material technologies, such as geopolymers, for delivering objectives on reducing their waste materials and improving operating costs. The range of geopolymer products currently being developed includes backfill, geopolymer concrete, lightweight building panels, precast concrete, impermeable barriers and waste encapsulation products.

The use of innovative technologies must be embraced by the geotechnical community to meet growing pressures to improve resource sustainability from community, regulatory and industry stakeholders. Geotechnical professionals need to recognise that geopolymer technology is complementary to current technologies and that research is on the increase to find environmentally sustainable options for using waste whilst meeting strict standards and building codes.

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