Article

Building Innovation through Geopolymer Technology

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Introduction

Geopolymer materials are inorganic polymers synthesised by reaction of a strongly alkaline silicate solution and an aluminosilicate source at near-ambient temperature.[1,2] The low energy process results in a fast-setting material that exhibits exceptional hardness and strength and, in this respect, geopolymers are similar to cements. The focus of our current research is to determine the potential of geopolymers as an alternative cementing system for high-value products.
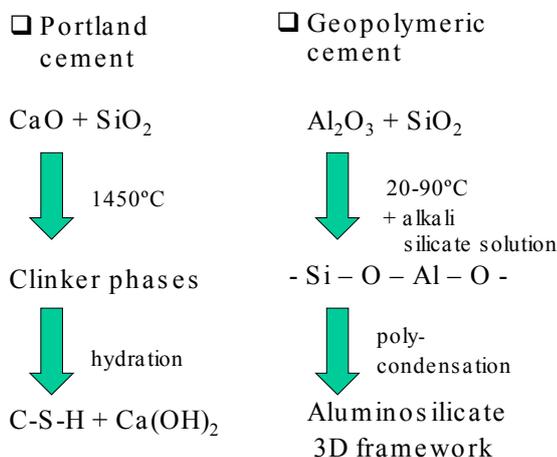
❑ Portland cement

$$CaO + SiO_2$$

⬇ 1450°C

Clinker phases

⬇ hydration

$$C\text{-}S\text{-}H + Ca(OH)_2$$

❑ Geopolymeric cement

$$Al_2O_3 + SiO_2$$

⬇ 20-90°C + alkali silicate solution

$$\text{- Si} – O – Al – O \text{ -}$$

⬇ poly-condensation

Aluminosilicate 3D framework

Fig. 1. Comparison of conventional and geopolymer-based cements.

A simple comparison of conventional and geopolymer cements is shown in Fig. 1. While traditional cements are composed of portlandite $[Ca(OH)_2]$ and calcium silicate hydrate (C-S-H) phases, geopolymer cement is based on an aluminosilicate framework. This difference is important in two respects. Firstly, aluminosilicate materials are much more resistant to chemical attack, *e.g.* by acids, than calcium-rich Portland cement and secondly there is no calcination step (heating to 1450 °C) in the synthesis, thus avoiding the release of CO_2. The former aspect means that geopolymer technology offers new opportunities for entering markets currently inaccessible to traditional cements while the latter illustrates that geopolymers offer significant environmental benefits, a fact important for the future. Geopolymers also possess physical and chemical properties that make them potentially suited for use in refractory applications and as waste immobilisation matrices.[3,4]

Synthesis and structure of geopolymers

Interest has centred on the types of aluminosilicate sources that can be successfully used in the geopolymerisation reaction. Naturally occurring clays and pumice as well as industrial wastes such as flyash and slag have been investigated. Particular emphasis has been placed on the waste materials with a view to developing geopolymers synthesised from the flyash obtained as a by-product of coal combustion in power stations. Our efforts have concentrated on locally-sourced aluminosilicate materials, including pumice, allophane, and bentonite, as well as the flyash produced at the Huntly power station. Flyash is extremely useful as it produces geopolymers with very high strengths. However, the composition of the flyash varies from batch to batch, depending on the composition of the coal being burnt in the power station at any given time.

Structural characterisation of geopolymers reveals that these materials are X-ray amorphous. Aluminium is mainly in tetrahedral coordination and silicon has a variety of coordination geometries. A cation, commonly Na^+ or K^+, provides charge balance. A structural model proposed by Barbosa *et al.*[5] is shown in Fig. 2.
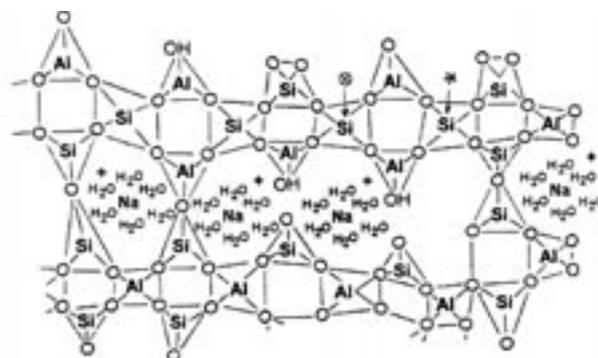

Fig. 2. Proposed geopolymer structure [5].

Characterisation

Any investigation of geopolymers requires characterisation methods applicable to amorphous materials and solid state nuclear magnetic resonance (NMR) spectroscopy and scanning electron microscopy (SEM) are particularly powerful. NMR is used routinely in our own work to determine whether a new product exhibits the chemical characteristics of geopolymers and to investigate on-going reactions within the solid state matrix over time. The nuclides of most interest are ^{23}Na, ^{27}Al and ^{29}Si; ^{11}B and ^{31}P may be used also for studies of boroaluminosilicate and phosphoaluminosilicate geopolymers, respectively.

For electron microscopy, sample preparation is critical in obtaining reliable SEM data. Standard polishing techniques are unsatisfactory for young, relatively soft samples, and for these resin impregnation or an examination of fresh fracture surfaces is preferable. Older samples

may have increased significantly in hardness on ageing and a standard polished section may be prepared.
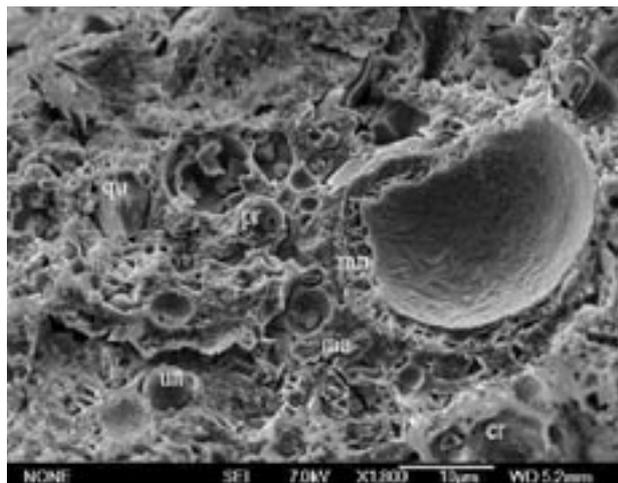
Fig. 3. SEM micrograph of geopolymer product - qu –quartz crystals; un – unreacted fly ash particle; pr – partially reacted fly ash particle, ma – geopolymer matrix; mn – mullite needles; cr – completely reacted flyash particle.

An annotated SEM micrograph of a flyash geopolymer (Fig. 3) shows a highly complex product morphology that consists of unreacted, partially reacted, and completely reacted flyash spheres that are surrounded by a matrix which also includes quartz crystals and mullite needles originating from the flyash. Energy dispersive X-ray analysis (EDX) shows that the material is extremely inhomogeneous. Of particular interest is the observation that products obtained using the Huntly flyash appear to contain two types of matrix (Fig. 4). A phase rich in sodium, aluminium, and silicon has a characteristic *dense* appearance and is an expected aluminosilicate geopolymer binder phase, while the second *spongy* phase is rich in calcium, sodium, aluminium, and silicon, reminiscent of the C-S-H phase of Portland cement. In fact, at higher magnification this dense phase is found to be quite porous, but the porosity is on a much finer scale in comparison with the spongy phase. These observations suggest the co-existence of aluminosilicate and cementitious binder phases in geopolymers synthesised from starting materials containing the high levels of calcium that Huntly flyash has.
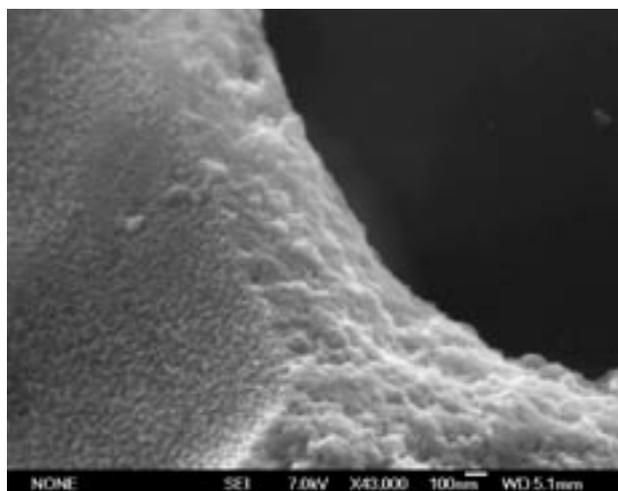
Fig. 4. SEM micrograph showing two types of geopolymer matrix.

Challenges in geopolymer chemistry

Relatively little is known about the chemistry of geopolymers such that a number of challenges present themselves to researchers. Two recent examples are in obtaining a desirable setting time, and in understanding the effect of processing variables.

Control of setting time

NZ flyash geopolymers show considerable promise in a wide range of industrial applications. However, Huntly flyash is *Class C* flyash due to its high lime content and it has extremely short setting times on activation by alkaline silicate solution. This limits the commercial exploitation of this and other Class C flyash as a raw material for geopolymers.

Our work has shown that addition of inorganic boron to the activator solution not only significantly extend setting times, but also allows a predefined setting time to be achieved by varying the amount and source of boron added. Subsequent characterisation of the products indicate that the boron is structurally incorporated in the matrix, giving rise to a novel class of boroaluminosilicate geopolymers. This work forms the basis of a patent application for commercial exploitation of Huntly flyash and other sources of Class C flyash worldwide.[6]

Effect of cure regime

The effects of processing conditions, particularly cure temperature and cure time, on the flexural properties of geopolymers synthesised from Huntly flyash have been investigated and the results are shown in Fig. 5. The most notable feature concerns the bend strength as there are the marked difference from low and high temperature cures. It appears that two different cure mechanisms may operate and on-going work is expected to elucidate the reasons for this.
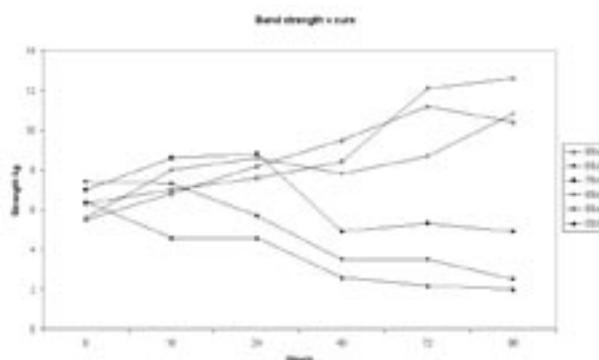
Fig. 5. Effect of cure regime on geopolymer tensile strength.

Future directions

In advancing our understanding of the chemistry and materials science of geopolymers, knowledge will be applied in the key areas of geopolymer composite materials synthesis and prediction of long-term durability.

Geopolymer composite materials

The building sector has signalled a need for reinforcement options for geopolymers, specifically through the design and fabrication of new fibre composites and structures.

This will permit increases in their strength, toughness, and elastic modulus, and generate a wider range of opportunities for new industrial products and applications.

The effects of incorporating solid pultruded rods as reinforcement in a flyash-based geopolymer are being investigated. Three different pultruded rods are currently under investigation, namely polyester resin, vinylester resin, and polyurethane resin with glass fibre as the rod reinforcement.

Durability and performance monitoring of geopolymers

In comparison with conventional cement and concrete systems, geopolymers are very new materials completely lacking the long service history that would enable robust prediction and control of structural deterioration. Performance requirements, drivers for deterioration, and means of predicting and characterising changes that will ultimately result in failure need to be assessed.

Electrochemical techniques such as the measurement of linear polarisation resistance and electrical impedance spectroscopy have been used by us to study the corrosion behaviour of steel and other representative engineering metals in flyash geopolymers for periods in excess of a year. In general terms, carbon steel, 316 stainless steel, and copper appear to perform well in flyash geopolymers. Each metal forms a reasonable bond with the geopolymer and does not undergo excessive corrosion. Zinc appears to suffer accelerated corrosion initially because of the high pH, but the reaction stabilises as the geopolymer sets. The vigorous reaction of aluminium in contact with liquid geopolymer damages the interface between it and the geopolymer, and prevents effective bonding.

As expected, carbon steel electrodes appear to form a protective film in high pH conditions. Corrosion potentials vary which may be a result of local breakdown of the protective iron hydroxide film at pH > 14. Copper and 316 stainless steel also appear to have only low corrosion rates after more that a year.

Conclusions

The cementing properties of geopolymer materials have been known for more than twenty years but key elements of their fundamental materials science remain unknown, undeveloped and unexploited. From an industrial perspective, geopolymer technology can only progress to successful commercialisation when the underlying science is fully understood. Our goal is to develop the knowledge, capability, and intellectual property in geopolymer materials ultimately to build a new technology platform from which commercial processes and products may be exploited for the benefit of NZ.

Acknowledgements

References

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