

# Introduction to geopolymers

J L PROVIS and J S J VAN DEVENTER,  
University of Melbourne, Australia

**Abstract:** This introductory chapter provides a brief overview of some important aspects of geopolymer technology, in particular its historical development and the terminology by which geopolymers are described. An introduction to geopolymer technology from a scientific viewpoint is also given. The scope of this review is confined to predominantly low-calcium materials, i.e. ‘traditional’ alkali-aluminosilicate geopolymers, to the exclusion of alkali-activated slags and other related materials.

**Key words:** geopolymer, inorganic polymer, aluminosilicate, alkali activation.

## 1.1 History of geopolymer technology

The term ‘geopolymer’ was coined in the 1970s by the French scientist and engineer Prof. Joseph Davidovits, and applied to a class of solid materials synthesised by the reaction of an aluminosilicate powder with an alkaline solution (Davidovits 1982a, 1991, 2008). These materials were originally developed as a fire-resistant alternative to organic thermosetting polymers following a series of fires in Europe, and products based on this initial work have since found application as coatings for fire protection for cruise ships (Talling 2002), as a resin in high-temperature carbon-fibre composites (Lyon *et al.* 1997), in thermal protection of wooden structures (Giancaspro *et al.* 2006), as a heat-resistant adhesive (Bell *et al.* 2005, Krivenko and Kovalchuk 2007), as a monolithic refractory (Comrie and Kriven 2003, Kriven *et al.* 2004), and in various other niche applications. However, as can be seen from a brief perusal of the Table of Contents of this book, the primary application for geopolymer binders has since shifted to uses in construction. This is primarily due to the observation, first published by Wastiels *et al.* (1993), that it is possible to generate reliable, high-performance geopolymers by alkaline activation of fly ash, a by-product of coal combustion.

The synthesis of construction materials by alkaline activation of solid, non-Portland cement precursors (usually high-calcium metallurgical slags) was first demonstrated by Purdon (1940). Detailed lists of key historical references and milestones in the development of alkali-activated binders have been presented in various review papers (Malone *et al.* 1985, Krivenko 1994, Roy 1999, Krivenko 2002); the majority of these relate to the alkaline

activation of blast furnace slags, and so are beyond the scope of the current discussion. A very extensive review focussed predominantly on alkali activation of metallurgical slags has recently been published (Shi *et al.* 2006), and the reader is referred to that excellent book for information in that area. The key distinction to be made here is that the alkaline activation of slags produces a fundamentally calcium silicate hydrate-based gel (Richardson *et al.* 1994, Wang and Scrivener 1995, Shi *et al.* 2006), with silicon present mainly in one-dimensional chains and some substitution of Al for Si and Mg for Ca, whereas the geopolymer gel is a three-dimensional alkali aluminosilicate framework structure (Duxson *et al.* 2007b). The role of calcium in geopolymers is a matter still under investigation; some of the subtleties of calcium chemistry in geopolymers will be discussed throughout this book.

Much of the early published research into aluminosilicate geopolymers was published in the patent literature (for example: Davidovits 1982b, 1984), and so contains little scientific detail. Probably the most valuable documents summarising work throughout the 1980s are the proceedings of a conference (*Geopolymer '88*) held in France in 1988 (Davidovits and Orlinski 1988), and a review paper authored by Davidovits (1991). Shortly after this, Palomo and Glasser published the first detailed scientific study of metakaolin geopolymers (Palomo and Glasser 1992), followed shortly afterwards by an extremely valuable three-part series by Rahier *et al.* (1996a, 1996b, 1997). These papers laid the groundwork for both broader and deeper study of metakaolin geopolymers in the ensuing decade, in particular work by groups in Spain (Granizo and Blanco 1998, Palomo *et al.* 1999b, Alonso and Palomo 2001), New Zealand (Barbosa *et al.* 2000, Barbosa and MacKenzie 2003), Germany (Kaps and Buchwald 2002, Buchwald *et al.* 2003, Buchwald 2006), and Australia (Yip and van Deventer 2003, Duxson *et al.* 2005, Perera *et al.* 2005, Singh *et al.* 2005, Steveson and Sagoe-Crentsil 2005). The proceedings of Geopolymer conferences held in 1999 (Davidovits *et al.* 1999), 2002 (Lukey 2002) and 2005 (Davidovits 2005) also provide valuable information regarding both technical developments in the field and the worldwide growth in geopolymers research during this period. A book published recently by Davidovits (2008) also summarises a good deal of work that was only previously available in the patent literature.

Research into fly ash geopolymers has grown from the aforementioned conference paper by Wastiels *et al.* (1993) to now form the bulk of applications-oriented research in this field. Fly ash has long been used in Portland cement concretes to enhance flow and other properties (Diamond 1986, Bouzoubaâ *et al.* 1999, Manz 1999), to reduce the carbon footprint of concrete, as well as simply a means of disposing of some of the many millions of tonnes of fly ash produced worldwide each year. Additional early reports of geopolymerisation of ASTM Class F (low-calcium) fly ash were provided by a number of researchers (van Jaarsveld *et al.* 1997, 1998,

Palomo *et al.* 1999a, van Jaarsveld 2000, Krivenko and Kovalchuk 2002, Lee and van Deventer 2002, Swanepoel and Strydom 2002, Fernández-Jiménez and Palomo 2003, Rostami and Brendley 2003, Hardjito *et al.* 2004, Palomo *et al.* 2004), along with a proliferation of patents. Possibly due to the inherent difficulty associated with detailed scientific analysis of highly heterogeneous fly ash-based geopolymers, the level of understanding of fly ash geopolymers currently appears to lag behind their metakaolin-based counterparts. Metakaolin geopolymers are often used as a ‘model system’ by which the more commercially relevant fly ash-based materials may be better understood (van Deventer *et al.* 2007), and the exact degree to which this relationship holds has been the subject of some recent scrutiny (Lloyd 2008).

It is also necessary to note that various theories have been proposed attempting to link aspects of geopolymerisation technology to the construction of ancient structures, most particularly the Pyramids of Egypt (Davidovits and Davidovits 2001, Barsoum *et al.* 2006). While the veracity of such arguments is still under quite intense debate in some circles, it is clear that whether or not the Pyramids were ‘poured’ as synthetic stone blocks, the chemistry involved in such an undertaking would have been some distance away from the alkali-activated aluminosilicate systems which today are described as geopolymers (Barsoum *et al.* 2006). However, it is not the role of this Introduction to attempt to speculate regarding such issues.

## 1.2 Geopolymer terminology

In the context of this book, a ‘geopolymer’ is in general defined as a solid and stable aluminosilicate material formed by alkali hydroxide or alkali silicate activation of a precursor that is usually (but not always) supplied as a solid powder. The same term has also been used to describe organic polymers formed under geological conditions (e.g., coal); in spite of some highly speculative discussions to the contrary (Davidovits 2008), these materials are entirely unrelated to aluminosilicate geopolymers and will not be discussed in detail here.

The materials referred to here as ‘geopolymers’ have also been described in the academic literature as ‘mineral polymers’, ‘inorganic polymers’, ‘inorganic polymer glasses’, ‘alkali-bonded ceramics’, ‘alkali ash material’, ‘soil cements’, ‘hydroceramics’, and a variety of other names. The major impact of this proliferation of different names for essentially the same material is that researchers who are not intimately familiar with the field will either become rapidly confused about which terms refer to which specific materials, or they will remain unaware of important research that does not appear upon conducting a simple keyword search on an academic search engine. A prime example of this is the very valuable early work of Rahier and colleagues

(Rahier *et al.* 1996a, 1996b, 1997), who used the term ‘inorganic polymer glass’ rather than ‘geopolymer,’ and so these papers have received far fewer citations than their quality and importance deserve. The terms ‘geopolymer’ and ‘inorganic polymer’ are gaining increasing ubiquity in the academic research field, and will be used essentially interchangeably throughout this book. Geopolymers are a subset of the broader class of alkali-activated binders (Shi *et al.* 2006), which also includes materials formed by alkali-, silicate-, carbonate- or sulfate-activation of metallurgical slags and giving a product that is predominantly calcium silicate hydrate, as mentioned in Section 1.1. The defining characteristic of a geopolymer is that the binding phase comprises an alkali aluminosilicate gel, with aluminium and silicon linked in a three-dimensional tetrahedral gel framework that is relatively resistant to dissolution in water (MacKenzie 2003, Rees *et al.* 2007).

More than 25 years ago, Davidovits introduced the ‘sialate’ nomenclature to describe aluminosilicate structures (Davidovits 1982a). The linkage type Si-O-Al was named a sialate bond, and Si-O-Si a siloxo bond. This provided a means of describing the composition of geopolymers according to their Si/Al ratio, with a ratio of 1.0 being a poly(sialate), 2.0 being a poly(sialate-siloxo), and 3.0 a poly(sialate-disiloxo). Unfortunately, the term ‘sialate’ was already in use (since the 1950s) to describe any of the salts of sialic acid, a nine-carbon monosaccharide and an important component of several biochemical systems within the human body. Also, this system of nomenclature implies certain aspects of the geopolymer gel structure which do not correspond to reality; firstly, it describes only integer Si/Al ratios, and secondly, it provides a one-dimensional description of a three-dimensional network, which will almost invariably prove inadequate. This nomenclature system did for some time find relatively widespread use in academic research (Barbosa *et al.* 2000, Zoulgami *et al.* 2002, Zhang *et al.* 2005, Subaer and van Riessen 2007), often to describe systems with non-integer Si/Al ratios but generally without comment as to its applicability in such cases, but appears to be fading in popularity as researchers discover its limitations.

### 1.3 Geopolymer science

Given that a large part of the purpose of this book is to provide an overview of the state of the art in various aspects of geopolymer science, it would be superfluous to provide a detailed description in this Introduction. Nonetheless, some preliminary comments are in order.

Initially, it must be said that geopolymers are a complex class of materials. The principal means of synthesising geopolymers is to combine an alkaline solution with a reactive aluminosilicate powder, in particular metakaolin (calcined kaolinite clay) or fly ash (a by-product of coal combustion). This results in the formation of a disordered alkali aluminosilicate gel phase,

known as the geopolymeric gel binder phase. Embedded within this phase are unreacted solid precursor particles, and the pore network of the gel contains the water that was used in mixing the precursors (usually supplied via the alkaline ‘activating solution’). Unlike in a calcium silicate hydrate gel, the water does not form an integral part of the chemical structure of a geopolymer binder; from a practical perspective this presents both advantages and disadvantages. The fundamental framework of the gel is a highly connected three-dimensional network of aluminate and silicate tetrahedra, with the negative charge due to  $\text{Al}^{3+}$  in four-fold coordination localised on one or more of the bridging oxygens in each aluminate tetrahedron and balanced by the alkali metal cations provided by the activating solution. There have been a variety of attempts to draw schematic diagrams of the three-dimensional geopolymer structure; such efforts will almost certainly be fraught with difficulty due to the disorder inherent in the geopolymer and also the difficulty of accurately representing a three-dimensional framework in two dimensions. The picture presented recently by Rowles *et al.* (2007) is probably the most useful of those currently available.

It has also been shown that the geopolymeric gel binder displays structural similarities, on an atomic to nanometre length scale, to zeolitic materials. In some cases – particularly in the presence of high water content, elevated synthesis temperature and low Si/Al ratio – this extends so far as to be visible as the formation of nanocrystallites within the geopolymer gel (Provis *et al.* 2005). However, even where none of these factors is present and the geopolymer displays no structural ordering on a length scale exceeding 1 nm, there are still strong structural motifs on an atomic length scale which correlate well with those observed in zeolites (Bell *et al.* 2008).

From this basis, the structural analysis presented in various chapters of this book represents the results of detailed investigations by various research groups over a number of years. Very little about the structural analysis of geopolymers is straightforward, as they comprise a mixture of various X-ray amorphous phases (reaction product as well as unreacted precursor material), and are formed in a corrosive reaction environment which complicates in situ analysis (as discussed in detail in Chapter 4). Nonetheless, much information has been obtained through careful experimental design and data analysis. In most areas of science, it is the case that either ‘easy’ (i.e. routine) methods of analysis are applied to ‘challenging’ materials, or ‘challenging’ methods of analysis are applied to ‘easy’ (i.e., pure and well characterised) material classes. Geopolymers, in common with Portland cements, are a ‘challenging’ class of materials whose chemistry necessitates the use of ‘challenging’ techniques for characterisation; this means that the science involved in understanding ‘low-technology’ construction materials is in fact at the cutting edge of materials science in general.

## 1.4 Geopolymer applications

As was mentioned in Section 1.1, the primary area of application of geopolymer technology is currently in the development of reduced-CO<sub>2</sub> construction materials as an alternative to Portland-based (calcium silicate) cements. Various other properties of geopolymers provide technological advantages over traditional construction materials, but performance in itself will not be sufficient to drive a revolutionary change in construction materials technology (Duxson *et al.* 2007a). A new material cannot be forced onto an unwilling market; the market itself must demand a new material, and this is beginning to be the case for geopolymers in construction, as will be discussed in detail in Chapter 17 of this book.

Other applications for geopolymers include as a host matrix in waste encapsulation, as a low-cost ceramic (either used directly or as a precursor for calcination), and in fire protection of structures. Part III of this book is dedicated to the description of some of the prime applications for geopolymers at present.

## 1.5 Conclusions

Geopolymers are a class of materials, whose potential remains to be fully unlocked. It is only through a detailed understanding of geopolymer science that full use can be made of the properties of geopolymers in specific applications. However, such science would rapidly become irrelevant in the absence of commercial success; a material that is well characterised but not used in the real world is in effect useless. From a scientific perspective, debates regarding nomenclature and semantics are entirely counterproductive, so long as the existing nomenclature is adequate to the task at hand. What is more important is that the understanding of geopolymers is built to the point where binder properties can be tailored *a priori* by rational mix design, and the understanding of the binder structure is sufficient to explain why these properties can be expected to last for a sufficient period of time to render the material fit for purpose in an engineering sense.

There is a growing demand for new construction materials that have low greenhouse gas emissions associated with their manufacture. Therefore, geopolymeric concrete could potentially be used widely as a replacement for Portland cement concrete, but this will only happen when both an efficient supply chain for raw materials and a distribution network for the products are in place. Recent commercial initiatives in this regard are encouraging, but it will take some time to make geopolymeric concrete a scaleable commodity available on a global basis. In the meantime, it is imperative that the localised demonstration of geopolymer technology grows, especially for converting coal ash into concrete with a low carbon footprint. This book

provides essential background to those interested in pursuing this exciting technology.

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