

HISTORY OF DEVELOPMENTS IN GEOPOLYMER SCIENCE IN NEW ZEALAND: A BRIEF REVIEW.

Kenneth J.D. MacKenzie, D.Sc, FNZIC, FRSNZ
Professor of Chemistry and Emeritus Investigator
MacDiarmid Institute for Advanced Materials and Nanotechnology
School of Chemical and Physical Sciences,
Victoria University of Wellington, New Zealand

E-mail: Kenneth.MacKenzie@vuw.ac.nz
ORCID: 0000-0003-3460-6708

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Abstract.

This brief review covers some of the highlights of the research into the chemistry and various applications of aluminosilicate geopolymers carried out in the Chemistry Department of Victoria University of Wellington over the last 20 years. Because these materials are generally amorphous to X-rays, the technique of Nuclear Magnetic Resonance with Magic Angle Spinning (MAS NMR) played a unique and important role in these studies. Many potential applications of geopolymers, were investigated over this period, including their use as structural materials, catalysts for commercially important organic reactions, bioactive materials and photoactive materials. Most of the initial work was carried out on clay-based starting materials because of their purity, but more practical materials were also developed, based on the by-products of industrial processing (fly ash, blast furnace slag, red mud, etc) This work led to more than 62 published papers in international journals, some of which are discussed here.

Keywords: Geopolymers, Clay minerals, Solid state MAS NMR,



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A brief summary

Geopolymers, or inorganic polymers as we have preferred to call them because their origins are not necessarily from geological materials, were described by Joseph Davidovits [1] as X-ray amorphous materials formed by reacting dehydroxylated kaolinite clay with alkali. These materials were described by Davidovits as “sialates”, containing “siloxo” Si-O-Si units. This use of sialate terminology is confusing however, as the term had been used since the 1950’s to describe the salts of 9-carbon monosaccharide acid (sialic acid), and for this reason our group adopted the name “inorganic polymers” for these materials. Following the work of Davidovits, most of our initial studies were on clay-based materials, produced by the reaction of an alkali or alkali silicate with dehydroxylated kaolinite [3,4] or a mixture of silica fume and alumina [5], with the aim of producing pure products for advanced applications. However, we quickly realized that these clay-based materials are related to building materials reported much earlier, produced by reacting blast furnace slag or fly ash with alkali [6], and some of our later studies were on the formation and properties of geopolymers from fly ash [7,8,9], volcanic ash [10a,b] and water treatment residue [11]. A useful property of the geopolymers from water treatment residue was their ability to immobilize heavy metal contaminants in waste water [12].

The initial studies of our research group in Wellington were directed towards determining the atomic structure of metakaolinite-based geopolymers. Since these are X-ray amorphous, an analytical technique was required that did not depend on the crystallinity of the sample. Such a technique is solid-state nuclear magnetic resonance spectroscopy with magic-angle spinning (MAS NMR). This technique is also specific to a particular element in the structure, in this case Si and Al, and showed that both structural Si and Al are in tetrahedral coordination with oxygen [3]. Since the Al in the starting kaolinite is in octahedral coordination with oxygen, the charge imbalance accompanying the formation of a geopolymer must be compensated by the incorporation of hydrated cations from the activating alkali (commonly Na⁺, as confirmed by ²³Na solid-state MAS NMR [3]), but we showed by ³⁹K MAS NMR spectroscopy [4] that other monovalent cations such as K⁺ can also play a charge-balancing role. This proposed structure is shown in Figure 1.

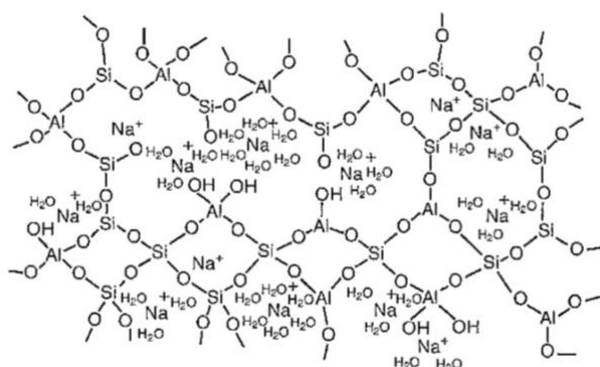


Fig.1. Proposed geopolymer structure based on MAS NMR measurements.

Further investigations showed that a much wider range of charge-balancing cations can be exchanged into the geopolymer structure, with complete exchange of Na by Ag^+ , NH_4^+ and Pb^{2+} , and a lower degree of exchange by Li^+ (82%), Cd^{2+} (78%) and Mg^{2+} (57%) [13]. The NH_4^+ form is particularly important as the starting compound for the incorporation of a number of other ions such as Eu^{3+} , Sm^{3+} and Mn^{3+} , to form geopolymers with photoluminescent properties [14,15].

Some of our early research was based on the premise that geopolymers might be formed containing tetrahedral units such as BO_4 [16] or PO_4 [17] units in place of AlO_4 , and this was shown by ^{11}B and ^{31}P MAS NMR spectroscopy respectively to be the case. Furthermore, the chemical similarity between gallium and aluminium, and germanium with silicon led to our successful synthesis of a geopolymer partially substituted with gallium [18] and a germanium-substituted geopolymer [19]. These syntheses, and our demonstration of the ion-exchange properties of geopolymers give an insight into the versatility of these materials and opened up the possibility of a range of further applications. Although most of our geopolymer research was conducted on the 1:1 layer-lattice aluminosilicate mineral kaolinite, we also investigated a 2:1 aluminosilicate (pyrophyllite), and found that although thermal dehydroxylation of this mineral at 800°C was insufficient to disrupt the structure and form a geopolymer, high-energy milling resulted in 4, 5 and 6-fold aluminium coordination, and successfully formed a geopolymer at 60°C [20]. Our attempt to form magnesium analogues of aluminosilicate geopolymers from the 1:1 layer lattice magnesiosilicate chrysotile was successful, as shown by ^{25}Mg MAS NMR, as was the product from chrysotile, but the 2:1 layer lattice mineral talc proved to be particularly resistant to geopolymerization [21].

One of the drawbacks to any application of geopolymers is that they fail in a brittle mode, a typical characteristic of inorganic materials. To overcome this problem, we have investigated embedding various types of fibres in a metakaolin-based geopolymer matrix. These unidirectional fibres include basalt [22] and the natural fibre New Zealand flax (phormium tenax); the incorporation of 10wt% of this fibre increased the flexural strength of the geopolymer from 5.8 MPa to about 70 MPa [23]. The effect of incorporating either coarse carpet wool or finer Merino wool fibres into a geopolymer was found to be improved by pre-treating the wool with formaldehyde which increased its resistance to the alkaline environment and produce a 40% improvement in the flexural strength of the geopolymer [A number of our geopolymer studies exploited their ability to support photoactive species, including Cu_2O nanoparticles [25] and a composite of $\text{TiO}_2+\text{Cu}_2\text{O}$ [26]. The latter was shown to efficiently destroy hazardous organic pollutants in wastewater [27]. The catalytic properties of geopolymers were also extensively investigated, and these materials were shown to act as environmentally benign solid acid catalysts in heterogeneous organic reactions such as the Beckmann rearrangement of cyclohexanone [28] and Friedel-Crafts alkylation reactions [29]. These model reactions were carried out using metakaolin-based geopolymers, but in view of the fact that fly ash geopolymers are cheaper and more practical starting materials, a series of Friedel-Crafts benzoylation reactions was carried out using fly ash geopolymers, with excellent yields [30]A number of other potential applications for geopolymers were investigated by our group. These included their possible use as colour-change humidity indicators by incorporating the acid-base indicator thymol blue which showed a promising reversible colour change from light tan (in the dry state) to deep blue in the damp state, reflecting the change in pH of the geopolymer as it lost or gained moisture [31].

Since the porosity of a metakaolinite-based geopolymer can be controlled by controlling its composition, especially its H_2O/Al_2O_3 ratio, a potential application for porous geopolymers produced in this way was proposed as a means of counteracting heat island effects in hot climates. These porous materials were developed to act as passive cooling systems by exploiting the latent heat of evaporation of water [32]. Another method for generating porous metakaolin-based geopolymers developed by our group involved incorporating polylactic acid fibres in the uncured geopolymer. The aligned PLA fibres were decomposed under the alkaline conditions during curing and drying of the matrix, producing an aligned pore structure [33].

The group also investigated the possibility of using geopolymers as stationary phase media for column chromatography. These materials were found to produce excellent separation of three model aromatic compounds, and their performance compared very favourably to other commonly used chromatography media. Furthermore, they were chemically stable to strong column-cleaning solvents and could be re-used [34].

Another interesting geopolymer application developed by our group was their use as precursors for the carbothermal reduction and nitridation (CRN) synthesis of advanced SiAlON ceramics. A mixture of kaolinite-based geopolymer and carbon was heated to $1400^{\circ}C$ under a nitrogen atmosphere, and the presence of the charge-balancing cations in the geopolymer produces a mixture of β -SiAlONs of low and high z-value [35].

In a study of potassium aluminosilicate geopolymers containing 10 wt% of calcium hydroxide, calcium phosphate or calcium silicate, these calcium-containing samples were exposed to simulated body fluid (SBF) to determine their behaviour as potential bioactive materials for bone repair. The alkalinity of the samples was lowered by heating to $600^{\circ}C$, but they were otherwise unchanged, as shown by ^{29}Si and ^{43}Ca MAS NMR spectroscopy. All these samples formed calcium phosphate upon reaction with SBF, and the concentrations of Al leached from the samples were acceptable for use as biomaterials. The strengths of all the samples was adequate for biomedical applications, but that of the $Ca_3(PO_4)_2$ sample was slightly greater, making it the more promising material [36]. This brief summary covers only a small part of the work of the New Zealand geopolymer group over the last 20 years, but more extensive details of our work in several of these research areas can be found in the book chapters [37-43] and summarised in Figure 2.

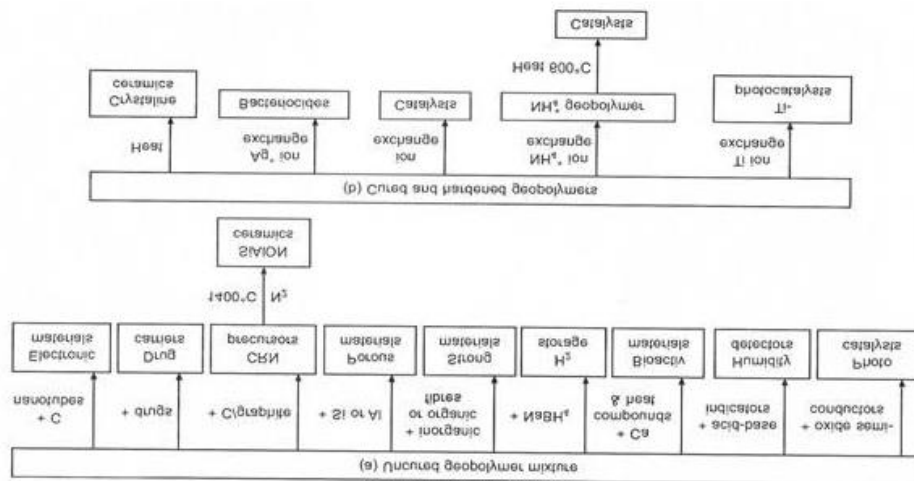


Fig.2. A brief summary of geopolymers application.

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