

THE POTENTIAL USE OF GEOPOLYMERIC MATERIALS TO IMMOBILISE TOXIC METALS

PART I. THEORY AND APPLICATIONS

J.G.S. van Jaarsveld and J.S.J. van Deventer

Department of Chemical Engineering, The University of Melbourne, Parkville,
Victoria 3052, Australia. Email: jsj.van_deventer@chemeng.unimelb.edu.au

L. Lorenzen

Department of Chemical Engineering, University of Stellenbosch,
Stellenbosch 7600, South Africa.

Published in: *Minerals Engineering* vol 10, no. 7 pp. 659-669 (1996)

UniNEWS, Melbourne, Australia, April 1997

Best Student Research Paper award for geopolymer research, in Australia

A report by Mr van Jaarsveld on his geopolymer research won the prize for Best Student Paper at the 1997 Australian Institute of Mining and Metallurgy Students and Young Professionals Conference: Resourcing the 21st Century, in Canberra recently.

Amazing World of Science

A display featuring geopolymer research at the University of Melbourne was presented at the Amazing World of Science Exhibition during the Australian Science Festival in Canberra this week.

THE POTENTIAL USE OF GEOPOLYMERIC MATERIALS TO IMMOBILISE TOXIC METALS: PART I. THEORY AND APPLICATIONS

J.G.S. van Jaarsveld and J.S.J. van Deventer

Department of Chemical Engineering, The University of Melbourne, Parkville,
Victoria 3052, Australia. Email: jsj.van_deventer@chemeng.unimelb.edu.au

L. Lorenzen

Department of Chemical Engineering, University of Stellenbosch,
Stellenbosch 7600, South Africa.

During the last decade geopolymerisation has emerged as a possible technological solution for the effective stabilisation and immobilisation of toxic materials. Despite the fact that this technology is based on a very old principle, surprisingly little is known about the nature of these reactions or their products. It is only in the last fifteen years that it has been rediscovered and attention has been drawn to its useful chemical and physical properties. This paper will therefore attempt to briefly discuss the available literature on geopolymerisation in terms of its history, reaction kinetics and structure as well as investigations into the application of geopolymerisation to various waste forms. It is evident from the literature that factors governing the formation of geopolymers are still not completely understood, although the physical and chemical properties suggest that these matrices are well suited for the immobilisation of toxic materials and specifically toxic metals. It is finally concluded that geopolymers offer attractive options towards simple industrial applications where large volumes of waste materials need to be stabilised. It must also be acknowledged that these advantages can only be applied optimally once all relevant interactions regarding the formation of geopolymers from waste materials have been quantified scientifically. Hence, further research is required regarding the formation of geopolymers and their application in industry.

Keywords geopolymer, waste processing, zeolites, immobilisation, landfill, fly ash

INTRODUCTION

Landfilling is currently the most widely used technique for processing of wastes associated with the mining industry and the problems associated with this are well known and well studied throughout the scientific literature. The increasing toxic metal threat to limited natural freshwater resources constitutes only a fraction of the real problem. Physical stabilisation of large amounts of mineralogical wastes, in particular tailings and fly ash, is increasingly becoming an environmental, social and political necessity. It is clear that a need exists for a technology that can easily and cheaply handle large quantities of waste materials, including contaminated top soil, fly ash, landfill leachate and mine tailings containing heavy metals. Economic factors also increasingly dictate that industry should look towards recycling or value addition to waste materials as opposed to landfilling and discarding.

It has been shown by the authors [1] and others [2] that geopolymerisation seems to meet the above requirements and can make a profitable contribution towards recycling and utilisation of previously unused waste materials. This technology is, however, still fairly unknown and predictably viewed with scepticism by most workers in the field of traditional waste processing techniques. In order to familiarise the reader with the concept of geopolymerisation as well as to create a better understanding of its possible applications in the mining industry, the aim of this paper is to provide a literature review and to explain the underlying theory.

HISTORICAL BACKGROUND

The phenomenal durability of ancient concretes and mortars compared to those being used in modern time prompted research into the nature of these ancient compounds. Results from various studies, summarised by Davidovits [3], proved that there is in fact a very distinct differ-

ence between ancient mortars and the Portland cement-based building materials in use today. The ancient products seem to be not only physically more durable, but also more resistant to acid attack and freeze-thaw-cycles. Initially [4] it was thought that this difference is the consequence of Calcium Silicate Hydrates (of the C-S-H-gel type) which constitute the main part of Portland cement. Later [5], however, it was discovered that these ancient concretes also contain amounts of C-S-H-gel and consequently researchers [3] turned their attention to the large amounts of zeolitic phases also found in the ancient products. It was later [6] concluded that the long-term durability of ancient mortars is the result of high levels of zeolitic and amorphous compounds in their compositional make-up.

As a result of this Davidovits, in the mid 1970's, proposed a controversial theory which culminated in a book [7] and has since gained widespread support and acceptance. He postulated that the Pyramids in Egypt were not built by the means previously thought but that the blocks were cast in place and allowed to set, creating an artificial zeolitic rock. Experimental programs conducted with the purpose of proving this theory partly resulted in the rediscovery of a new family of mineral binders, named "geopolymers" because of similarities with organic condensation polymers as far as their hydrothermal synthesis conditions were concerned [8].

Terminology

Geopolymers can best be viewed as the amorphous equivalent of certain synthetic zeolites and would generally have more or less the same chemical composition although the distinctive zeolitic structure is absent which makes them amorphous to X-rays. Davidovits [2] proposed that geopolymers consist of a polymeric silicon-oxygen-aluminium framework, not unlike that found in zeolites, with alternating silicon and aluminium tetrahedra joined together in three directions by sharing all the oxygen atoms. This is of course a very simplified representation of the real structure although it aids in discussing the basic principles involved. The fact that aluminium is four co-ordinated with respect to oxygen creates a negative charge imbalance and therefore the presence of cations such as K^+ and Na^+ is essential to maintain electric neutrality

in the matrix. In order to better describe the three dimensional geopolymeric structures, a new terminology was proposed [8] whereby structures are described as: (1) Poly(sialate) with [-Si-O-Al-O-] as repeating unit, (2) Poly(sialate-siloxo) with [-Si-O-Al-O-Si-O-] as repeating unit and (3). Poly(sialate-disiloxo) with [-Si-O-Al-O-Si-O-Si-O-] as repeating unit.

What is today known as geopolymers are also sometimes referred to as alkali-activated alumino-silicate binders and Malone et al. compiled an extensive [9] list of references relating to the early applications of the reaction between reactive silica sources and alkaline metal solutions.

In order to prevent confusion with ordinary cement forming reactions, it is necessary to briefly explain the differences between geopolymerisation and the hardening of ordinary Portland cement [OPC].

Portland Cement and the Pozzolanic Reaction

The main reactions associated with cement hydration involve the formation of calcium silicate hydrate $[(CaO)_3(SiO_2)_2(H_2O)_3]$ and $Ca(OH)_2$. Other reactions [10] include the formation of ettringite $[(CaO)_3(Al_2O_3)(CaSO_4)_3(H_2O)_{32}]$ from gypsum as well as various calcium aluminate hydrates $[(CaO)_4(Al_2O_3)(H_2O)_{19}]$ and hydrogarnet $[(CaO)_6(Al_2O_3)(Fe_2O_3)(H_2O)_{12}]$. Pozzolans, such as fly ash, are sometimes added to cement mixtures in order to increase durability and decrease shrinkage. These materials react with the lime produced by the cement hydration reactions to also produce C-S-H-compounds as well as calcium aluminate hydrates. The main difference between cement forming reactions and pozzolanic reactions is that the latter are accelerated by temperature increases and in particular the presence of an alkali metal hydroxide. Pozzolanic reactions therefore generally proceed faster than normal cement hydration reactions and the products may or may not have the same composition as those found in Portland cements. Pozzolans can also serve as reagents for the synthesis of geopolymers although the reaction path is different as it does not utilise the reaction between lime and pozzolanic material but rather the interaction of the latter with alkaline media and specifically aqueous solutions of polysilicates. This aspect will be discussed in more detail later. Portland

cement as we know it is also sometimes referred to as alkali-activated calcium-silicate [2].

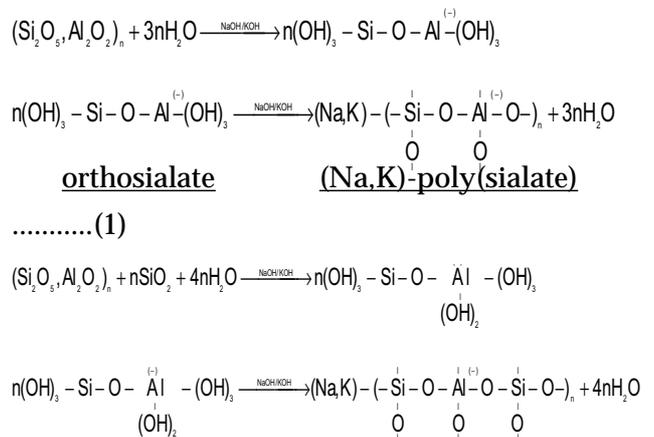
Chemistry, Reaction Mechanism and Structure Formation

In ancient times synthetic rocks were formed by mixing kaolinite, dolomite or limestone with Na₂CO₃ or K₂CO₃ (obtained from plant ashes or salt lakes) and silica [3]. This mixture produces NaOH and KOH when mixed with water which dissolves some of the silica and reacts strongly with the other additives to form a geopolymeric binder. Purdon [11] investigated the action of sodium hydroxide on a variety of minerals and glasses containing silicon and/or aluminium and summarised it as consisting of two steps: (1) Liberation of silica, alumina and lime and (2) Formation of hydrated calcium silicates and aluminates as well as regeneration of the caustic solution. These results let Purdon [11] to believe that the alkali-metal hydroxide acts as a catalyst and he proved his theory by leaching the metal from the hardened alkali-activated binder in more or less the same amounts as what was added during synthesis. He also proposed a mechanism for hardening of alkali-activated aluminosilicate binders that involved: (1) Dissolution of either Si or Al in association with sodium hydroxide and (2) Precipitation of Calcium Silicate or Aluminate Hydrate with regeneration of the sodium hydroxide.

In the 1970's Glukhovsky [12] investigated alkali-activated slag binders and made major contributions in: 1. Identifying both calcium silicate hydrates, and calcium and sodium aluminosilicate hydrates as solidification products and 2. Noting that clay minerals react during alkali-treatment to form aluminium silicate hydrates (zeolites). Further Russian research during the 1980's [9] resulted in a better understanding of the setting reactions of alkali-activated slag cement and the hardening process was found to be more complex than that proposed by Purdon [11]: (1) Dissolution of alkali and alkali-earth cations into solution, (2) Formation of a colloidal sodium silicate layer on the slag particles, (3) Dissolution of aluminium oxides directly in the sodium silicate, (4) Formation of semi-crystalline tobermorites [(Ca₁₀(Si₁₂O₃₁)(OH)₆·8H₂O)], (5) Appearance of calcium aluminosilicate hydrates with expulsion of water and (6) Formation of zeolite and zeolite-like products of various compositions.

The resultant solid will therefore consist of various amounts of a variety of minerals.

According to Davidovits the hardening mechanism for geopolymerisation essentially involves the polycondensation reaction of geopolymeric precursors, usually aluminosilicate oxides, with alkali polysilicates yielding polymeric Si-O-Al bonds [8] as is depicted:



.....(2)

In view of the above discussion it is clear, however, that for mine tailings this description is a simplification and a whole range of related materials can be expected to form in practice where temperature control is not exact and trace amounts of most metals are present in the reaction mixture.

Any pozzolanic compound or source of silica and alumina that is readily dissolved in alkaline solution will suffice as a source of geopolymer precursor species and thus lend itself to geopolymerisation. Conceptually, the formation of geopolymers follow much the same route as that for most zeolites [13] i.e. three main steps: (1) Dissolution, with the formation of mobile precursors through the complexing action of hydroxide ions, (2) Partial orientation of mobile precursors as well as the partial internal restructuring of the alkali polysilicates and (3) Reprecipitation where the whole system hardens into an inorganic polymeric structure. There are, however, some marked differences between zeolite formation and geopolymerisation and most of these are related to the composition of the initial reaction mixture.

Davidovits and co-workers [14, 15] indicated that certain compositional criteria have to be met for geopolymerisation to occur. These include:

(1) The molar ratio $\text{SiO}_2:\text{M}_2\text{O}$ must be between 4.0:1 and 6.6:1 in the aqueous soluble silicate solution where M is an alkali metal cation, (2) The alumino-silicate oxide must contain Al which is readily soluble and (3) The overall molar ratio $\text{Al}_2\text{O}_3:\text{SiO}_2$ must be between 1:5.5 and 1:6.5. Our research [1] has shown, however, that these ratios are not very critical when dealing with waste materials and are for the most part only an indication of approximate composition. The reason for this is the fact that these compositional ratios are based on chemical analysis although it is highly unlikely that all of the silica or alumina actually takes part in the synthesis reaction.

As far as synthesis of geopolymers is concerned, the most important differences between zeolite formation and geopolymerisation are in the concentration of the precursor species as well as the fact that zeolites usually form in closed hydrothermal systems and geopolymers not. Zeolites usually crystallise from fairly dilute aqueous solutions where precursor species have mobility as well as enough time to undergo proper orientation and alignment before bonding into a crystal structure. In contrast, setting of the geopolymeric reagent mixture occurs fairly quickly, without enough time for the formation of a proper crystal structure resulting in a microcrystalline, amorphous or semi-amorphous structure depending on the exact reaction conditions.

It is a well known fact that in zeolite synthesis the compositional ratios, $\text{SiO}_2/\text{Al}_2\text{O}_3$ and $(\text{Na}_2\text{O}+\text{K}_2\text{O})/\text{SiO}_2$, determine the resultant crystal structure and are, together with X-ray diffraction, used in characterising different zeolites [13]. Apparently these ratios also influence structure formation in geopolymers [14], although this has not been scientifically proven and would certainly not be the case where geopolymers are synthesised from waste materials, mainly because total dissolution of the waste materials is not achieved as will be explained in more detail later. The amorphous nature of geopolymers makes structural investigations by X-ray powder diffraction inconclusive and other techniques such as Infrared Spectroscopy [13] and Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR), developed for studies of zeolitic structures [16, 17], have been employed with varying degrees of success [2, 8]. The proposed structure deter-

mined for pure geopolymers remains, however, fairly inconclusive for toxic metals stabilisation, to a certain extent.

PROPERTIES OF GEOPOLYMERIC BINDERS

From a waste processing point of view the physical and chemical properties of geopolymers as well as the conditions needed for synthesis make it one of the best prospects for future waste processing techniques and therefore merit further discussion.

The synthesis temperature required for geopolymerisation vary between 25 and 80 °C [18] while the use of pressure [19] is not essential, but sometimes preferred when the porosity of the final product is required to be lower than normal. Depending on the synthesis conditions, structural integrity and reasonable strength are attained in a very short time, sometimes in as little as sixty minutes. In most cases 70% of the final compressive strength is developed in the first 4 hours of setting [2, 20]. As can be seen from Table 1, low permeability is another property that favours the use of these materials as immobilisation systems for toxic metals [2]

Table 1: Permeability values in cm/s [2]

Sand	10^{-1} to 10^{-3}
Clay	10^{-7}
Granite	10^{-10}
Fly ash cement	10^{-6}
Portland cement	10^{-10}
Geopolymer binders	10^{-9}

Geopolymeric matrices also have a reported [3, 21, 22] resistance to acid attack that surpasses that of Portland cement as can be inferred from Fig. 1.

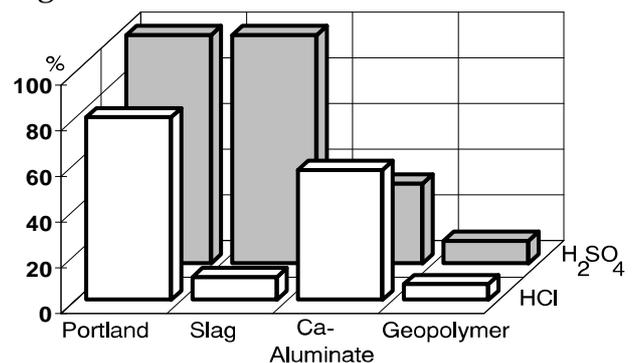


Figure 1: Break up in 5% acid solutions (% of matrix dissolved under identical conditions) [21,

Apart from their short setting times and low permeability compared to concrete, they also attain higher unconfined compressive strengths [9] and shrink much less on setting as can be seen from Table 2.

Table 2: Percentage shrinkage of Geopolymeric cement compared to Portland cement [23]

Matrix	7 days	28 days
Portland cement type I	1.0	3.3
Portland cement type III	1.5	4.6
Geopolymer cement	0.2	0.5

As was discussed earlier one of the main differences between geopolymers and zeolitic structures is the fact that geopolymers are amorphous to X-rays. The exact nature of this amorphicity is still not fully quantified, mainly because of different definitions of the term "amorphous". It must also be mentioned that although the product seems amorphous to X-rays, this does not guarantee the absence of very small disordered crystals and therefore some or total crystallinity could well be present to a certain extent. Malone et al. [9] attributed much of the physical strength of these matrices to this mixture of structural phases because of increased crystallisation contacts between the more crystalline and more amorphous regions.

Other documented properties include good resistance to freeze-thaw cycles [2] as well as a tendency to drastically decrease the mobility of most heavy metal ions contained within the geopolymeric structure [1, 24]. Experimental evidence as to this claim is presented in Table 3 while this aspect will be discussed in more detail in the following section.

Application to waste processing

The technology of geopolymerisation has been applied [22] to the manufacture of some cement-related products that can be bought commercially, mixed with toxic waste and allowed to set. The result is a very hard, impermeable solid containing the toxic waste in immobilised form. Similar processes utilise ordinary Portland cement for the same purpose, and mainly because of monetary reasons geopolymeric binders have not been used widely despite their superior physical properties. Although this discussion will also focus on the advantages of

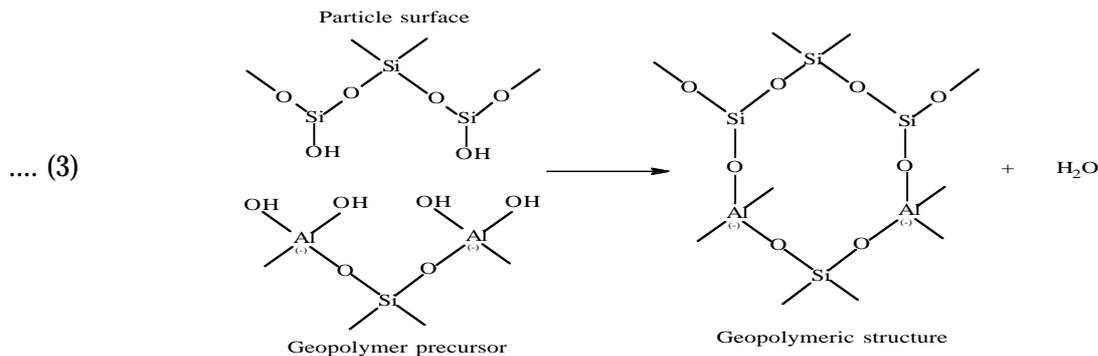
geopolymers towards toxic metal immobilisation, it must be kept in mind that because of their physical properties these products can also be utilised as replacements for concrete in most instances. If the physical properties can be conserved while the product is still acting as an immobilisation system a novel process of toxic waste utilisation will have been developed.

Research into this field with the purpose of finding a practical solution to toxic waste processing in the mining industry should therefore have two main objectives, i.e. (a) the immobilisation efficiency and mechanism should be determined, and (b) the physical properties should be stable, not only to encapsulate toxic metals, but also to make the product suitable for further building applications. Some research has already been conducted into the potential application of geopolymer technologies towards solving practical, building related problems, as summarised by Malone et al. [9]. Research into the utilisation of metallurgical slags by geopolymerisation has also been dealt with by Glukhovskiy et al. [12], albeit not extensively. Comrie et al. [22, 24] investigated the possibilities of heavy metal immobilisation by commercial geopolymeric products. Most research conducted to date, however, has focused on either the immobilisation efficiency or strength aspect of geopolymers and in most cases commercially available products were involved. No one has yet investigated the integration of the two aspects into one product as well as utilising silica and aluminium containing waste materials to their maximum.

Most waste materials, such as fly-ash (from various sources), contaminated soil, mine tailings and even building waste, contain large amounts of silica and alumina that can be used as reagents for in situ geopolymerisation reactions. In most cases only a small amount of the silica and alumina present on particle surfaces need to dissolve and take part in the reaction for the whole mixture to solidify with the resultant immobilisation of any heavy metals contained within. The difference between this system and Portland cement systems therefore lies in the fact that almost no additional additives need to be added as the reactive properties of silica and alumina in the waste materials are utilised for the geopolymeric synthesis reactions.

For geopolymerisation of waste materials to occur an alkali medium is needed that can dis-

solve some of the silicon and aluminium as well as hydrolyse the surfaces of the waste particles. The concentration of dissolved silicon can be artificially increased by addition of soluble silicates if dissolution does not proceed fast enough. The presence of K^+ , Na^+ and Ca^{2+} is also needed because of their charge balancing and catalytic roles. Reaction between the amorphous matrix and the particle surfaces will then proceed along the path described by equation 3, see in [15].



It is apparent that this surface reaction is the one responsible for binding the waste particles as well as immobilising any toxic metals that they might contain. The eventual strength development therefore greatly depends on the extent to which this surface reaction proceeds.

The nature of the surface bond between the amorphous phase and the waste particles is one of the reasons why characterisation of geopolymer structures by X-ray diffraction is not conclusive as the undissolved part of the original particle becomes part of the overall structure. The surface reaction on waste particles, as well as their overall involvement in the synthesis reaction, depend on four main factors [10]: (1) Their mineralogy, (2) Silica and Alumina content, (3) Fineness or reactive surface area and (4) Morphology. These properties can also be expected to vary from particle to particle and therefore the structure as a whole will rarely be homogeneous.

Heavy metal immobilisation in geopolymeric structures is not thought to be caused by physical encapsulation alone, but also through adsorption of the metal ions onto the geopolymer structure and possibly even bonding of the metal ions into the structure [1]. Whether the included heavy metal will also fulfil a charge balancing role is still unsure but they are bonded into the structure in some instances although the mechanism by which this occurs is still un-

known [1]. One of the only methods available for determining the efficiency of heavy metal immobilisation is by conducting leaching tests with various solvents and by characterising the respective kinetic leaching curves in terms of the metal being immobilised and other factors that could ultimately affect the immobilisation efficiency such as the starting materials as well as alkali-metal cations used as reagents. Interpretation of leaching data should take physical properties into account and could ultimately

lead to a better understanding of the mechanism by which heavy metal immobilisation occurs. Apart from our own work and that conducted by Comrie et al. [24], no other investigations have been conducted in this regard and much still needs to be done.

Table 3: Concentration of cations in leachate from Kam-Kotia mine tailings and paint sludge, ppm [24]

	<u>As</u>	<u>Fe</u>	<u>Zn</u>	<u>Cu</u>	<u>Ni</u>	<u>Ti</u>
Untreated tailings	42	9726	1858	510	5	20
Geopolymerised tailings	2	123	1115	4	3	7

	<u>Mg</u>	<u>Cr</u>	<u>Zn</u>	<u>Mn</u>	<u>Co</u>	<u>Ti</u>	<u>V</u>
Untreated sludge	1024	55	384	64	84	6	9
Geopolymerised sludge	512	7	7	6	9	3	1

From a practical point of view implementation of this technology will not require complicated control systems or equipment as the process is simply one of mixing various waste forms with small amounts of readily available chemicals depending on which compounds are not supplied by the waste materials in large enough

quantities [9]. A fairly accurate idea of the silica and alumina contained in the waste materials is therefore essential, although not enough is currently understood regarding the effect of their respective crystal structures on the final product. Other uncertain factors affecting geopolymeric structure formation from waste materials include those regarding the alkali metal cation, the exact coordination number of Al^{3+} as well as the effect of the heavy metal ions. As was discussed earlier, setting temperatures are quite low and could even be met by atmospheric conditions. Usually mouldability is very good although pressure might be needed in certain instances to reduce pore volumes or the amount of entrapped air.

Potential practical applications

A cementitious product with properties such as high early strength, fast setting, low permeability, acid resistance as well as low cost will have numerous obvious possibilities of application and the most important ones are listed below:

1. Surface capping of waste dumps and landfill sites where a rigid high strength structure is needed to prevent contact by rain-water and provide a solid and safe cover which can also assist in utilising the area for building purposes.
2. Low permeability base liners of landfill sites where minimum leakage of contaminants into the groundwater is desired or where fresh water reservoirs need a lining to prevent water from seeping away as in regions where not enough clay is present in the soil.
3. Vertical barriers and water control structures where water deflection is needed, both above and below the surface.
4. Dam construction as well as the stabilising of tailings dams, the latter being a large problem in countries with high humidity. The in situ treatment of tailings in order to increase their solidification potential will also enable mining in environmentally sensitive areas where it might not be possible to mine at the moment due to the threat of not only physically unstable tailings dams but also of leaching of toxic metals into fresh water drainage systems.
5. Heap leach pads are another possible application where a large, cheap, non-porous, non-permeable and non-reactive surface is needed for the leaching of ores and collection of leachate.
6. Structural surfaces like floor and storage areas as well as runways have also been proposed and the feasibility of the latter was investigated by Malone et al. [9].
7. Intermittent horizontal barriers in waste masses, used to keep waste masses stable and prevent contact between various layers stacked on top of one another. In this case the properties required include low-permeability and intermediate strength.
8. Back fill for cut-and-fill and under-cut-and-fill type mining methods. Fast setting and high early strength are required for this application, both of which can be met by geopolymerisation. The abundance of mine tailings as well as the relatively high temperatures found in most mines should favour the application of geopolymerisation and definitely merits a thorough investigation.
9. Pre-casting of simple structures used in non-specialist applications such as fences, paving materials and low cost pipes. In general the mouldability of geopolymeric pastes is very good and together with their relatively low shrinkage compared to Portland cement, any such non-specialist application should be suitable.
10. Immobilisation of toxic waste such as arsenic, mercury and lead [22]. This is possibly one of the major areas where geopolymerisation can impact heavily on the status quo. As has been mentioned earlier, the advantages of heavy metal immobilisation by geopolymerisation have only had limited attention as far as research is concerned and apart from this study, only one other program [24] sought to investigate the issue. The results have been very favourable and although little is understood about the mechanism of immobilisation, the efficiency of these matrices seems promising.
11. Inexpensive but durable encapsulation of hazardous waste such as asbestos and radioactive wastes [21]. Manufacturing geopolymeric materials from waste should provide cheap encapsulation media for a variety of applications where Portland cement might be too expensive or not sufficiently durable.
12. Any current building component such as bricks, ceramic tiles and cement could be replaced by geopolymers.

CONCLUSIONS AND SIGNIFICANCE

It is obvious that some progress has been made towards creating a better understanding of geopolymerisation and its potential. There are, however, certain factors that hamper the further development and even industrial implementation of this technology, and although some of them constitute a lack of fundamental knowledge, others involve the usual apprehension by which new technologies are greeted, both by researchers as well as by industry. There also exists some confusion regarding geopolymers and especially regarding the terminology associated with it, and although Davidovits proposed a new terminology, there are still doubts regarding the novelty of these matrices. It is possible that these reactions, being closely related to zeolite synthesis, have been known all along but have been overlooked because of the fact that the main thrust in zeolite related research has focused on the opposite to what geopolymers is trying to achieve, namely a well-formed, homogeneous, crystal structure where pore sizes are uniform and well-structured [13, 25]. It is evident that a fair amount of research still needs to be conducted, both in characterising these matrices as well as in determining not only the mechanism of formation, but also the mechanism by which metal immobilisation proceeds.

Adequate characterisation of the solid state includes the development of new analytical techniques and methods by which differences in structure can easily be identified. The solid state analytical techniques currently available are both expensive and time consuming while they only provide limited and inconclusive results as far as structural analysis is concerned.

Investigations into the mechanism of synthesis as well as that of immobilisation of metals will rely heavily on the efficiency of appropriate structural analysis techniques as well as information collected through kinetic leaching tests or even the use of selective resins for the extraction of certain cations. A related paper on the topic of leaching from geopolymeric matrices will be published as a second part to the present one [26].

From an application and engineering point of view, research into the utilisation of waste ma-

terials, and in particular those from the minerals industry, requires urgent attention. Although fundamental research would provide a better understanding of the bonding mechanism and subsequent leaching behaviour of immobilised metals from these structures, there is a need for immediate application orientated research in order to consolidate and practically evaluate the progress that has been made up to now. A system of waste classification based on the suitability of various waste forms to take part in the geopolymerisation reaction needs to be developed and will be pivotal in developing a knowledge base for allowing the creation of geopolymeric matrices tailor-made for specific metal ions and manufactured from waste materials. Although some references exist in the patent literature [27-32] that describe applications of this technology, none of them contributes to an overall understanding of these processes, and indicates that not enough is known about geopolymers to be able to fully assess their application possibilities.

By utilising certain waste materials and their reactive properties, it is supposedly possible to create various geopolymeric matrices that are not only strong enough to be used as building materials, but also as immobilisation systems for toxic metal containment. In addition, these matrices can be synthesised almost entirely from waste materials that are currently posing a threat to the environment. In order to optimise the advantages offered by geopolymers derived from waste materials, it is imperative to identify as well as quantify critical parameters that affect the eventual structural stability of the finished product. This has to be done by the techniques currently available and of these, leaching analysis seems to be the most powerful as will be discussed in a subsequent paper [26].

REFERENCES

1. Van Jaarsveld, J.G.S., Van Deventer, J.S.J. and Lorenzen, L., Factors affecting the immobilisation of metals in geopolymerised fly ash, Research Report, Department of Chemical Engineering, University of Stellenbosch, South Africa, 1995.
2. Davidovits, J., Properties of geopolymer cements, *Proceedings First International Conference on Alkaline Cements and Concretes*, 1994, pp. 131-149.
3. Davidovits, J., Ancient and modern concretes: What is the real difference?, *Concrete Interna-*

- tional, vol. 9, nr 12, December 1987, pp. 23-35.
4. Langton, C.A. and Roy, D.A., Longevity of borehole and shaft sealing materials: Characterisation of ancient cement-based building materials, Symposium Proceedings no.26, Materials Research Society, Pittsburgh, 1984, pp. 543-549.
 5. Eitel, W., Silicate science: vol.5, Ceramics and hydraulic binders, Academic Press, new York, 1966, pp. 488-510.
 6. Campbell, D.H. and Folk, R.L., The ancient Egyptian pyramids - concrete of rock?, *Concrete International*, August 1991, pp. 29-44.
 7. Davidovits, J. and Morris, M., The pyramids: An enigma solved, Hippocrene Books, Inc., New York, 1988, 263 pp.
 8. Davidovits, J., Geopolymers: Inorganic polymeric new materials, *J. Materials Education*, vol. 16, 1994, pp. 91-139.
 9. Malone, P.G., Kirkpatrick, T. and Randall, C.A., Potential applications of alkali-activated aluminosilicate binders in military operations, Report WES/MP/GL-85-15, U.S. Army, Corps of Engineers, Vicksburg, Mississippi, 1986.
 10. Kruger, R.A., The chemistry of fly ash and the pozzolanic reaction, *ChemSA*, Nov 1990, pp. 301-303.
 11. Purdon, A.O., The action of alkalis on blast-furnace slag, *J. Soc. Chem. Ind.*, vol. 59, 1940, pp. 191-202.
 12. Glukhovskiy, V.D., Rostovskaja, G.S. and Rumyna, G.V., High strength slag-alkaline cements, Communications of the 7th International Congress on the Chemistry of Cement, vol. 3, 1980, pp. 164-168.
 13. Breck, D.W., Zeolite Molecular Sieves, John Wiley and Sons, London, 1974, 771p.
 14. Davidovits, J., Davidovics, M. and Davidovits, N., Process for obtaining a geopolymeric aluminosilicate and products thus obtained, U.S. Patent no. 5,342,595, 1994.
 15. Davidovits, J., Geopolymers of the first generation: SILIFACE-Process, Geopolymer '88, First European Conference on Soft Mineralogy, vol. 1., Compiègne, France, 1988, pp. 49-67.
 16. Klinowski, J., Nuclear magnetic resonance studies of zeolites, *Progress in NMR Spectroscopy*, vol. 16, 1984, pp. 237-309.
 17. Lipmaa, E., Samoson, A., Magi, M., Tarmak, M. and Engelhardt, G., Investigation of the structure of zeolites by solid-state high resolution ^{29}Si NMR spectroscopy, *J. Am. Chem. Soc.*, vol. 103, 1981, pp. 4992-4996.
 18. Davidovits, J. and Davidovics, M., Geopolymer room temperature ceramic matrix for composites, *Ceram. Eng. Sci. Proc.*, vol. 9, 1988, pp. 835-842.
 19. Davidovits, J. and Davidovics, M., Geopolymer: Ultra-high temperature tooling material for the manufacture of advanced composites, 36th International SAMPE Symposium, vol. 36, 1991, pp. 1939-1949.
 20. Palomo, A., Macias, A., Blanco, M.T. and Puertas, F., Physical, chemical and mechanical characterisation of geopolymers, Proceedings of the 9th International Congress on the Chemistry of Cement, Nov 1992, pp. 505-511.
 21. Comrie, D.C. and Davidovits, J., Long term durability of hazardous toxic and nuclear waste disposals, Geopolymer '88, First European Conference on Soft Mineralogy, vol. 1., Compiègne, France, 1988, pp. 125-134.
 22. Davidovits, J., Comrie, D.C., Paterson, J.H. and Ritcey, D.J., Geopolymeric concretes for environmental protection, *Concrete International*, Vol. 12, nr 7, July 1990, pp.30-40.
 23. Davidovits, J., Geopolymer chemistry and properties, Geopolymer '88, First European Conference on Soft Mineralogy, vol. 1., Compiègne, France, 1988, pp. 25-48.
 24. CANMET Canada, DSS Contract #234406-9195/01SQ, 1988.
 25. Barrer, R.M., Hydrothermal Chemistry of Zeolites, Academic Press, 1982, 360p.
 26. Van Jaarsveld, J.G.S., Van Deventer, J.S.J. and Lorenzen, L., The potential use of geopolymeric materials to immobilise toxic metals: Part II. Material and leaching characteristics, submitted to *Minerals Engineering*, 1996.
 27. Davidovits, J. and Sawyer, J.L., Early high-strength mineral polymer, U.S. Patent no. 4,509,985, 1985.
 28. Helferich, R.L. and Shook, W.B., Aluminosilicate hydrogel bonded aggregate articles, U.S. Patent no. 4,432,798, 1984.
 29. Laney, B.E., Geopolymer-modified gypsum-based construction materials, U.S. Patent no. 5,194,091, 1993.
 30. Neuschaeffer, K.H., Aqueous curable moulding compositions based on inorganic ingredients and process for the production of moulded parts, U.S. Patent no. 4,533,393, 1985.
 31. Davidovits, J., Waste solidification and disposal method, U.S. Patent no. 4,859,367, 1989; EP no 0 338 060, 1991.
 32. Forss, B., Process for producing a binder for slurry, mortar, and concrete, U.S. Patent no. 4,306,912, 1981.