

Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products

J.S.J. van Deventer*, J.L. Provis, P. Duxson, G.C. Lukey

Department of Chemical and Biomolecular Engineering, The University of Melbourne, Vic. 3010, Australia

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Abstract

High-performance materials for construction, waste immobilisation and an ever-growing range of niche applications are produced by the reaction sequence known as ‘geopolymerisation’. In this process, an alkaline activating solution reacts with a solid aluminosilicate source, with solidification possible within minutes and very rapid early strength development. Geopolymers have been observed to display remarkable chemical and thermal stability, but due to their largely X-ray amorphous nature have only recently been accurately characterised. It has previously been shown that both fly ash and ground granulated blast furnace slag are highly effective as solid constituents of geopolymer reaction slurries, providing readily soluble alumina and silica that undergo a dissolution–reorientation–solidification process to form a geopolymeric material. Here a conceptual model for geopolymerisation is presented, allowing elucidation of the individual mechanistic steps involved in this complex and rapid process. The model is based on the reactions known to occur in the weathering of aluminosilicate minerals under alkaline conditions, which occur in a highly accelerated manner under the conditions required for geopolymerisation. Transformation of the waste materials to the mixture of gel and nanocrystalline/semicrystalline phases comprising the geopolymeric product is described. Presence of calcium in the solid waste materials affects the process of geopolymerisation by providing extra nucleation sites for precipitation of dissolved species, which may be used to tailor setting times and material properties if desired. Application of geopolymer technology in remediation of toxic or radioactive contaminants will depend on the ability to analyse and predict long-term durability and stability based on initial mix formulation. The model presented here provides a framework by which this will be made possible.

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1. Introduction

Geopolymers are a class of largely X-ray amorphous aluminosilicate materials, generally synthesised at ambient or slightly elevated temperature by reaction of a solid aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution [1,2]. As a means of converting waste materials to useful products, the value of geopolymer technology lies primarily in its ability to produce a high-performance binder from materials such as fly ash or blast furnace slag. Alkali-activation of high-calcium slags has been the focus of much research over the past 65 years [3,4], and these products have in fact seen large-scale use in construction in Eastern Europe [5], but significant interest in alkali-activated fly ashes as a means of waste utilisation and/or immobilisation has only developed more recently [6]. It must

also be noted that the use of fly ash as an aluminosilicate source for synthesis of geopolymers is entirely distinct from its alternative use as a filler in concrete [7], as the major geopolymeric binder phase is an aluminosilicate gel, as opposed to the calcium silicates formed in fly ash-blended cements. Low-calcium (Class F) fly ash is currently most commonly used in geopolymer synthesis [8,9], although there seems to be no reason why Class C fly ash could not also be used. Brown coal fly ash has also been used in combination with metakaolin (calcined kaolinite clay) to produce geopolymeric materials [10], but it appears that the role of this fly ash in producing a geopolymeric binder is limited due to its very low reactive silica and alumina levels.

Applications for geopolymeric products made from waste materials are primarily centred in, but by no means limited to, the construction industry, where the durability, strength and fire resistance of geopolymers provide many advantages over more traditional materials. The performance of waste-based geopolymers is comparable to or better than that of ordinary Portland cement in many respects, and development of the ability to tai-

* Corresponding author. Tel.: +61 3 8344 6619; fax: +61 3 8344 7707.
E-mail address: jannie@unimelb.edu.au (J.S.J. van Deventer).

lor geopolymer formulations for desired properties will further enhance this advantage.

The other primary use of geopolymer technology in waste management is as a matrix for the immobilisation of cationic radioactive and/or toxic contaminants [6,11,12]. The low permeability, resistance to acid attack and inherent durability of the geopolymeric binder makes it an ideal solution in both landfill-based and non-landfill-based immobilisation methods. Both fly ash-based and metakaolin-based geopolymers have been tested in these applications, and with significant success. However, as this paper is primarily focused on waste utilisation techniques, the use of fly-ash based geopolymers is of primary interest here.

2. Reaction mechanisms in geopolymerisation

2.1. Metakaolin as a model system

The reaction mechanisms involved in the geopolymerisation of metakaolin and fly ash are believed to be similar, and so the relatively simpler chemistry of metakaolin makes it valuable as a model system by which the geopolymerisation of fly ash may be better understood. The very high level of calcium present in blast furnace slag complicates matters greatly, as the solid product formed by its alkali-activation has been shown to be pH dependent and a mixture of geopolymeric gel, calcium silicate hydrate phases and calcium hydroxide precipitate [13]. A conceptual model for geopolymerisation should therefore be applicable in the general sense to both metakaolin and fly ash-based systems, while being capable of extension to the very different chemistry of alkali-activated slags. The obvious means of developing such a model is to start by analysing the metakaolin system, and then extending the model to the more

complex processes occurring in the fly ash and slag systems by incorporation of effects due to the more complex chemistry of these materials.

A basic conceptual model for geopolymerisation was presented by Provis et al. [14], and may be briefly summarised by Fig. 1. This model was originally applied to the geopolymerisation of metakaolin, but its extensibility and therefore applicability in a wider sense will be demonstrated in this paper.

It is clear that a diagram such as Fig. 1 will necessarily oversimplify the reaction process, for example by not explicitly showing the potential combination of polymeric silicate species with aluminate monomers or the direct participation of monomeric species in the later polymerisation/crystallisation reactions. However, as a tool for understanding the influence of various different synthesis parameters on the process of geopolymerisation, such a model will prove to be invaluable. For example, a reaction kinetic model using a sequence of reactions based on the process shown in Fig. 1 has been shown to provide a quantitatively accurate description of the measured heat evolution during the early stages of the geopolymerisation of metakaolin [14]. Such quantitative analysis has not yet been possible in the case of fly ash-based geopolymers due to the difficulties inherent in analysis and description of the nature and relative reactivities of all the phases present within the raw material. However, an understanding of the chemistry of geopolymerisation may be used in conjunction with the reaction process presented in Fig. 1 to qualitatively analyse and explain a range of previous experimental results in this field. This is critical for the acceptance of geopolymers in waste encapsulation, as the long-term performance of encapsulants cannot always be adequately studied under laboratory conditions, and so modelling of the performance of geopolymeric materials is expected to play a significant role in determining their utilisation in different applications.

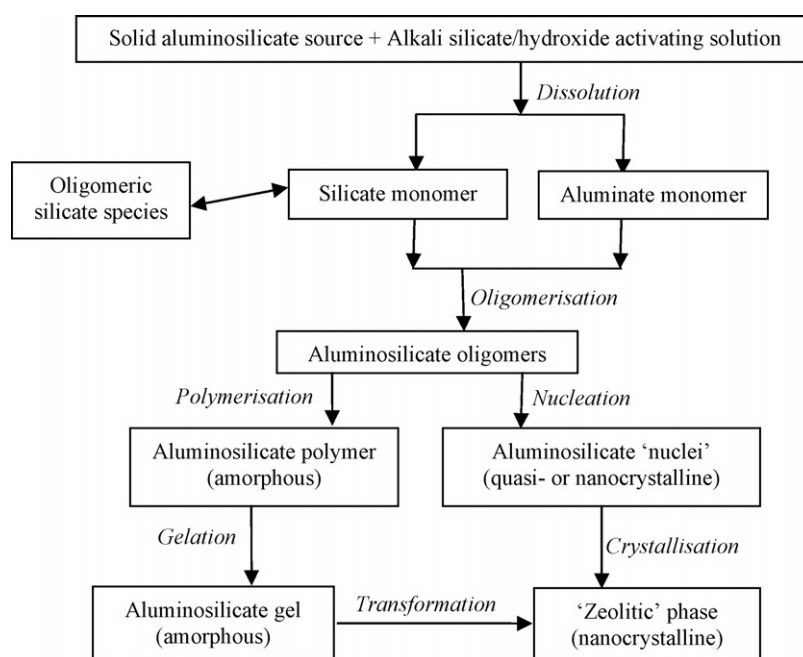


Fig. 1. Schematic outline of the reaction processes involved in geopolymerisation.

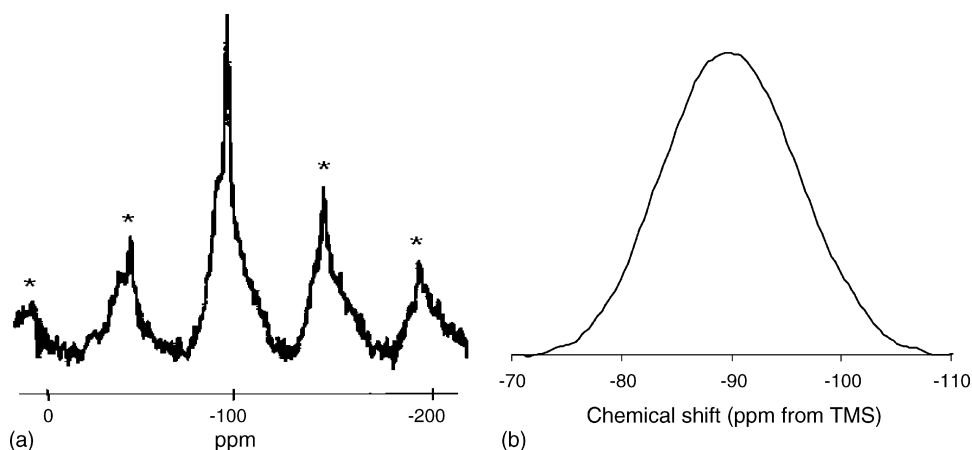


Fig. 2. ^{29}Si MAS-NMR spectra of (a) a geopolymer made by activation of Gladstone fly ash (adapted from [20]), and (b) a geopolymer made by activation of metakaolin (Metastar 402, Imerys, Bristol UK) with a solution of composition $\text{Na}_2\text{O}\cdot 1.5\text{SiO}_2\cdot 11\text{H}_2\text{O}$.

It must also be noted that the reaction process denoted ‘Transformation’ in Fig. 1 will in most cases be quite slow, depending on post-synthesis treatment and the composition of the samples. Samples stored in gently aggressive media have been observed to crystallise noticeably inside 9 months [15], and the extent of crystallinity generally decreases with increasing Si/Al ratio [2,16]. It is not clear whether the compositional dependence of the degree of crystallisation is due simply to the higher pH of the low-silica activating solutions, or whether the particular zeolite framework types being formed have a significant influence. Two zeolite structures commonly observed in low-Si/Al ratio sodium-containing geopolymers, hydroxysodalite (SOD framework) and Linde Type A (LTA framework), have been observed to show a distinct preference for formation at Si/Al ratios equal or very close to 1 [17]. It is therefore plausible to suggest that the tendency towards greater crystallisation at low Si/Al ratios may be due to differences in the crystal structures that will form under different compositional conditions, and is therefore not an inherent property of the actual amorphous geopolymeric gel. Control of the crystallisation behaviour of geopolymers will be of significant benefit in the use of these materials in immobilisation of wastes containing high levels of alkali or alkaline earth metals, which are known to participate selectively in ion exchange reactions on particular zeolites. Tailoring of the particular zeolite crystal structures formed within a geopolymeric binder to ensure optimal immobilisation of the desired contaminant may therefore be possible, and work in this area is ongoing.

2.2. Comparison of metakaolin- and fly ash-based geopolymers

^{29}Si MAS-NMR spectra of fly ash- and metakaolin-based geopolymers have recently been published, and are reproduced as Fig. 2. Although the Si/Al ratios of these specimens are different, it is observed that both spectra exhibit the same broad resonance between 80 and 100 ppm, typical of an amorphous tetrahedral silicate centres surrounded by varying numbers of aluminium atoms. However, the presence of crystalline materials such as quartz and mullite in fly ash causes sharp res-

onances to appear in the fly ash-based geopolymer spectrum. These may be subtracted from the overall spectrum since they do not participate in geopolymerisation. Once resonances from non-participating phases are removed, the spectra of fly ash- and metakaolin-based geopolymers appear remarkably similar. Analysis of ^{29}Si NMR has shown that the resonance position and shape can be predicted by knowledge of the Si/Al ratio of the specimen [18,19], and it is hoped in future to be able to extend a similar method of quantitative analysis to fly ash-based systems.

Despite these similarities on the molecular structure level, the differences in the properties of geopolymers derived from different raw materials are clearly evident. Fly ash-based geopolymers are generally more durable and stronger. SEM micrographs of typical microstructures of metakaolin- and fly ash-based geopolymers are presented in Fig. 3. It can be observed that the microstructure of the metakaolin-based specimen in Fig. 3b is homogeneous, containing little evidence of unreacted raw material. In contrast, the microstructure of the fly ash specimen in Fig. 3a can be observed to contain large amounts of unreacted material bound together by geopolymeric gel that appears identical to that in Fig. 3b. Despite the large differences in the physical behaviour of these two specimens it appears that the binder phase responsible for mechanical strength has similar molecular structure and microstructure in both cases.

The microstructure and performance of metakaolin- and fly ash-based derived geopolymers are both known to be dependent on the amount of soluble silicon in the activating solution [21,22]. Fig. 3c and d show the similarity of the appearance of geopolymer specimens synthesised with small concentrations of soluble silicon in the activating solution. The highly porous appearance of these specimens compared to specimens synthesised with greater amounts of soluble silicon in Fig. 3a and b signifies analogous effects of system parameters on the microstructural development and properties of both systems. Though the inherent differences in the dissolution properties and phase composition of fly ash result in geopolymers that exhibit vastly different properties, it is observed both in molecular structure (Fig. 2) and in microstructure (Fig. 3) that the same Al/Si bonding and gel-phase binder is present in both systems.

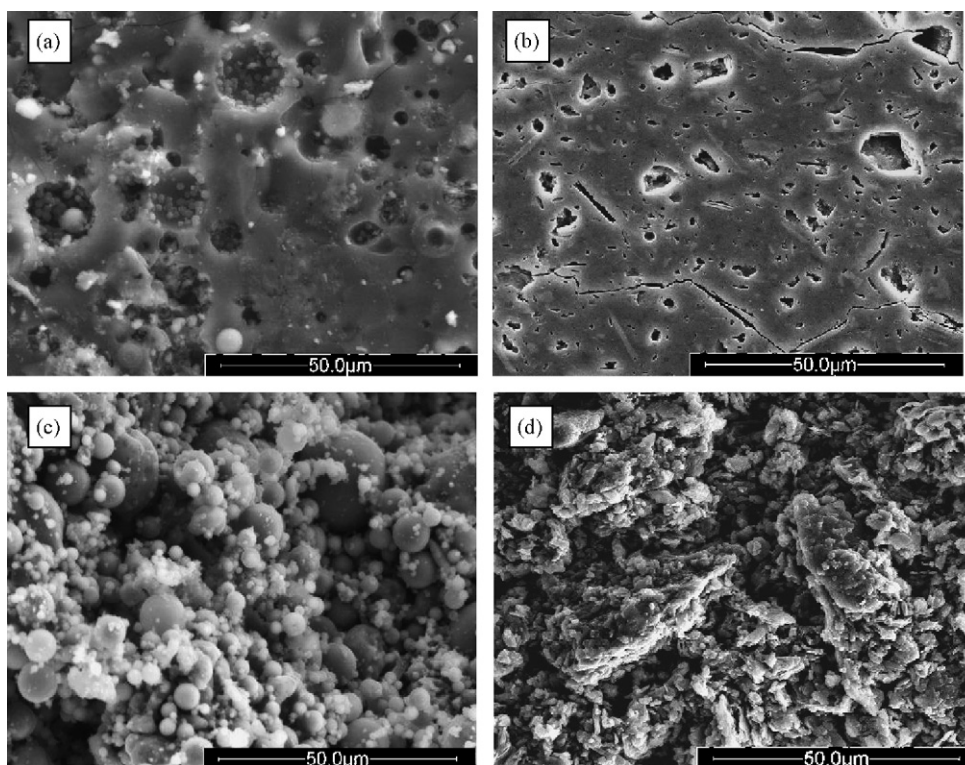


Fig. 3. SEM micrographs of (a) fly ash- and (b) metakaolin-based geopolymers activated with sodium silicate solution with $\text{SiO}_2/\text{Na}_2\text{O}$ of 2, and (c) fly ash- and (d) metakaolin-based geopolymers activated with sodium hydroxide solution. (a and c) courtesy of Redmond Lloyd.

3. The use of fly ash in geopolymers

The development of processing techniques by which the complex and challenging rheology of fly ash-based geopolymerisation slurries may be controlled and utilised in the production of large volumes of geopolymeric product is seen as the key to widespread acceptance of this technology. Rheological characterisation of geopolymers has provided some insight into their setting behaviour [23–25], and these known relationships may therefore be used in conjunction with the conceptual model outlined in Fig. 1 to provide a means of controlling setting behaviour as is required for a commercial concrete-replacement product. The later stages of the reaction process continue well past the point at which the geopolymer is observed to harden and significant improvements in strength over a period of many years have been observed, particularly in the case of blast furnace slag-based geopolymeric materials [5]. This may be related to the transformation of the metastable amorphous gel phase to more stable crystalline phases, or may be due to other factors entirely. Further work in the analysis of aged samples is ongoing, but is currently hampered by the fact that the study of geopolymers has become widespread only relatively recently, and the use of fly ash in geopolymers is also quite a recent development. Therefore, samples of sufficiently aged fly ash-based geopolymer for analysis of behaviour on timescales of decades or more are not yet available. This issue will obviously be remedied in the fullness of time, but its resolution will be critical to widespread use of geopolymers in the construction industry, where the lifespan of products must generally be measured in decades or more.

A given fly ash sample will contain particles of wildly varying size, morphology, composition and reactivity [26], and the relative proportions of different classes of particle vary significantly depending on the conditions under which the ash was formed and the composition of the feedstock to the furnace generating the ash. The ability to produce a geopolymer with consistent physical properties despite this variability in the raw materials used will play a significant role in determining the usefulness of geopolymerisation as a means of recovering value from fly ash waste streams [27]. The use of fly ashes of superficially similar composition but from different sources, as well as different batches of ash from the same source, has been observed to result in geopolymers with significantly differing strengths [8,9]. As an additional complication, the trends in early strength across a particular group of fly ashes do not match the trends in final strength for the same ashes [8]. Therefore, production of a consistent geopolymeric product from a raw material (fly ash) stream with fluctuating physicochemical characteristics will require a deeper understanding of the effects of a variety of synthesis parameters on the properties of the geopolymer formed, so these parameters may be manipulated accurately to ensure product specifications are met.

The conceptual reaction mechanism outlined in Fig. 1 provides a means by which some of the effects of the inhomogeneous nature of fly ash on geopolymerisation may be predicted, at least qualitatively if not yet quantitatively. No clear correlation between fly ash composition and reactivity has been established, as the overall fly ash composition is a relatively poor measure of the properties of the individual particles comprising

the ash, and so different methods of ash classification are currently being developed [27]. However, conceptually analysing the behaviour of each type of particle, without necessarily developing a system for categorising actual fly ash particles, still provides useful information regarding both the process of geopolymerisation and also the nature of the geopolymeric product.

For example, the work of Oelkers and co-workers [28–31] provides a wealth of information regarding the dissolution rates of various aluminosilicate glasses under different conditions, which may be applied directly to the behaviour of individual glass particles within a fly ash undergoing geopolymerisation. It is known that Al is preferentially leached in the early stages of aluminosilicate glass dissolution [28] prior to the establishment of a roughly stoichiometric steady-state dissolution process. This burst of rapid Al release into solution in the early stages of geopolymerisation will mean that the initial regions of geopolymer gel-phase binder formed, particularly if relatively low levels of soluble silicate are present in the activating solution, will have a lower Si/Al ratio than the regions of gel formed in the later stages of the dissolution/reprecipitation process. This is in agreement with the observations of Palomo et al. [32], who found that an Al-rich geopolymeric binder phase was initially formed upon activation of fly ash by NaOH. This phase was then gradually replaced by a relatively Si-rich and more crystalline phase as the reaction progressed, corresponding to the expected rates of release of each of the network-forming cations from the glassy fly ash phases.

4. The effect of cationic contaminants on fly ash geopolymers

4.1. The effects of Ca^{2+}

The effect of the presence of Ca^{2+} on geopolymerisation has recently been the subject of a number of detailed investigations [33,34], with segregation of high- and low-calcium regions within the product as was noted earlier. The amount of Ca^{2+} added and the form in which it is added both play a significant role in determining the physical properties of the final geopolymer. The level of dissolved silicate in the activating solution also plays a highly significant role in determining the effects of calcium on the final reaction product by controlling the pH of the activating solution and therefore influencing the relative stabilities of the different calcium-containing precipitates [34]. In particular, the addition of highly alkaline activating solutions to a fly ash containing any calcium leads to rapid dissolution of calcium from the ash followed by precipitation of $Ca(OH)_2$. This has the net effect of lowering the pH of the activating solution due to the removal of the OH^- ions, which will then significantly affect the rate of further dissolution/precipitation processes. Lee and van Deventer [24] observed that the addition of even a small amount of calcium as a soluble salt to a Class F fly ash-based geopolymer formulation drastically increases its solidification rate and early yield stress.

It has also been observed that CaO if present at levels above 3% by mass interferes with crystallisation during synthesis of

zeolites from fly ash [35]. The formation of Ca-containing precipitates in the initial stages of geopolymerisation will provide a large number of potential nucleation sites at the solid–liquid boundaries thus formed [24]. Nucleation at any of these additional sites will then cause the total number of nuclei present to be higher than would be possible in the absence of calcium. Competition for growth nutrients between the nuclei will then reduce the likelihood of formation of observable zeolitic crystallites. However, the formation of calcium silicate hydrates will also remove a proportion of the excess silicate from solution [35], thereby reducing the supersaturation levels which are the primary driving force for nucleation and crystal growth. This will therefore compete with the accelerating effects of added nucleation to further complicate description of kinetic effects. Understanding the behaviour of calcium, even at the relatively low levels (<10%) present in Class F fly ash but more critically in the case of Class C fly ash or blast furnace slag, is central to the industrial and commercial application of geopolymeric materials. Extension of the reaction kinetic model of Provis et al. [14], based on the process described in Fig. 1, to include a description of these effects should therefore be a focus of future work.

4.2. The effects of $Fe^{2+/3+}$

Most Class F fly ashes will contain appreciable levels of Fe in various forms, either as a network former or network modifier in the glassy phases, or as discrete oxide phases such as maghemite or magnetite [27]. Daux et al. [36] showed that, in the dissolution of basaltic glasses containing significant levels of network-forming Fe^{3+} under slightly alkaline conditions, reprecipitation of dissolved Fe was much faster than the reprecipitation of Si and Al. It is therefore most likely that any reactive Fe present during geopolymerisation of fly ash behaves similarly, and reprecipitates very rapidly as hydroxide or oxyhydroxide phases. This is then likely to have a similar effect to those discussed above with regard to precipitation of $Ca(OH)_2$, removing OH^- ions from the solution phase and therefore slowing the dissolution of the remaining fly ash particles as well as providing nucleation sites.

The role of iron within a fly ash-based geopolymeric structure is also currently receiving attention with respect to the immobilisation of arsenic. It has been observed that arsenic, when immobilised within a fly ash-based geopolymer, appears to become associated with iron-rich components of the fly ash [37]. However, similar association was not observed with iron added to the geopolymer mixture in the form of Fe_2O_3 , suggesting that the association with arsenic is primarily limited to the iron hydroxide or oxyhydroxide species produced when the relatively soluble iron compounds present in the glassy fly ash particles react with the alkaline activating solutions. This further emphasises the importance of the correct choice of activating solution for a particular application, as the alkalinity of the system will determine the relative stabilities of the different iron-containing species, and will therefore play a significant role in determining the arsenic immobilisation efficiency.

Table 1
Summary of the leaching results of Bankowski et al. [10]

Element	Performance ^a
As	I
Ba	I
Cr	N
Cu	N
Mn	+
Mo	N
Ni	+
Se	I
Sr	I
V	+
Zn	+

^a I denotes immobilisation, N denotes little or no effect, + denotes increased leachability.

4.3. The effect of geopolymerisation on cation leachability

Bankowski et al. [10] investigated leaching of a variety of cationic contaminants from a mixed brown coal fly ash/metakaolin geopolymer via the TLCP procedure, and found that some were very effectively immobilised by geopolymerisation, some showed little or no immobilisation, and others actually leached more from the geopolymerised fly ash than from untreated fly ash. The results of these experiments are summarised in Table 1.

It must be noted that brown coal fly ash is largely unreactive as a source of Si and/or Al in geopolymerisation, and so these experiments are essentially representing the addition of a large quantity (up to 60% by mass) of contaminated waste to a metakaolin-based geopolymer. From Table 1, a clear distinction in immobilisation efficiency is visible between the main group elements and the transition metals. Every s- or p-group element listed is effectively immobilised by the geopolymerisation process, while every transition metal either shows no immobilisation or increased leachability. This fact, which was not noted by the authors of the original study from which the data were obtained, shows further that the utility of the process of geopolymerisation as a means of waste treatment is highly dependent on the development of an understanding of the chemistry of the waste materials being treated when exposed to the highly alkaline conditions prevalent during geopolymerisation. Upon exposure to conditions of very high pH, the speciation of transition metal oxides will often change to favour much more soluble oxide or hydroxide compounds [38]. The formation of these compounds may also interfere with the setting of the geopolymeric binder, as was observed by Palomo and Palacios [39] in the case of Cr. In contrast, the main group elements do not have the same degree of flexibility with regard to their oxidation state, but rather in some cases will tend to form relatively insoluble compounds. These will then be expected to interfere with the setting process to a lesser or minimal extent, as was observed by Palomo and de la Fuente [40] in addition of B to fly ash-based geopolymers.

It is therefore clear that chemical immobilisation by geopolymerisation is not a method that is able to be applied blindly, and that care must be taken in formulating the geopolymeric matrix

to ensure appropriate processing conditions and waste loadings. In particular, geopolymerisation is most effective as a means of treating waste stream components that do not significantly increase in solubility at high pH. Alternative means of immobilisation, such as physical encapsulation or treatment under less alkaline conditions, must be sought particularly for waste streams rich in transition metal oxides. Appropriately designed geopolymeric matrices have been shown to immobilise both Cu^{2+} and Pb^{2+} added in nitrate form [41–43]. Interestingly, Pb^{2+} was seen to be immobilised more effectively than Cu^{2+} at very low levels (0.1–0.2% by mass) [41], while the reverse was true at higher loadings (0.5% by mass) [42]. Also, the leachability of both Cu^{2+} and Pb^{2+} from the geopolymer matrix decreased dramatically with an increase in the pH of the activating solution [42]. It is believed that Pb is immobilised within a geopolymer as an insoluble lead silicate compound, possibly Pb_3SiO_5 [39], whereas Cu is observed to be more or less distributed throughout the aluminosilicate gel binder phase [41]. Different immobilisation mechanisms have been observed for other immobilised cations, for example Cs^+ acting as a charge-balancing cation within zeolitic phases in a geopolymeric binder [44] or Sr^{2+} being chemically trapped (maybe similarly to Cu^{2+}) in the aluminosilicate phase [45].

Due to this wide variety of possible encapsulation mechanisms within geopolymers, the exact details of the geopolymerisation process to be used to immobilise a particular waste stream must be carefully tailored. This requires an understanding of the mechanisms by which chemical immobilisation is occurring, for which the model presented in Fig. 1 is intended to provide a basis. Development of this model, by both qualitative and quantitative means and by comparison to the ever-growing body of experimental data relating to both metakaolin- and fly ash-based geopolymers, will provide an enhanced understanding of the immobilisation capabilities of geopolymers. Commercialisation and development of geopolymerisation technology will therefore provide not only an environmentally sustainable and effective means of treating heavy metal-contaminated waste streams, but also provide a valuable use for much of the fly ash that is currently being sent to landfills around the world. As with any waste containment strategy the risk of failure must be absolutely minimised, and the most effective means of ensuring success is to build a solid foundation of fundamental understanding. The link between reaction mechanisms and immobilisation effectiveness must be fully investigated, and the conceptual model laid out in this paper provides a significant step towards developing the necessary understanding.

5. Conclusion

The use of fly ash as a raw material for geopolymerisation has been the subject of significant research and commercial interest over the past decade. Geopolymerisation provides an opportunity whereby a valuable product may be derived from a currently under-utilised waste stream. However, the variability in fly ash properties and reactivity between sources and even between batches from the same source necessitates the development of a fully quantitative understanding of the effects of

different compositional, synthesis, and post-synthesis parameters on the nature and performance of the geopolymeric product. A conceptual model which goes some way towards providing at least a qualitative means of describing the effects of a number of these parameters has been presented. The observed effect of process chemistry on the relative immobilisation efficiencies of different cationic species is able to be explained by reference to this model. Further work in this area will involve development of the conceptual model into a quantitatively accurate model for the geopolymerisation of fly ash, similar to work that has already been carried out for the simpler case of metakaolin-based geopolymers.

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