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Reduction of metal leaching in brown coal fly ash using geopolymers

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Abstract

Current regulations classify fly ash as a prescribed waste and prohibit its disposal in regular landfill. Treatment of the fly ash can reduce the leach rate of metals, and allow it to be disposed in less prescribed landfill. A geopolymer matrix was investigated as a potential stabilisation method for brown coal fly ash. Precipitator fly ash was obtained from electrostatic precipitators and leached fly ash was collected from ash disposal ponds, and leaching tests were conducted on both types of geopolymer stabilised fly ashes. The ratio of fly ash to geopolymer was varied to determine the effects of different compositions on leaching rates. Fourteen metals and heavy metals were targeted during the leaching tests and the results indicate that a geopolymer is effective at reducing the leach rates of many metals from the fly ash, such as calcium, arsenic, selenium, strontium and barium. The major element leachate concentrations obtained from leached fly ash were in general lower than that of precipitator fly ash. Conversely, heavy metal leachate concentrations were lower in precipitator fly ash than leached pond fly ash. The maximum addition of fly ash to this geopolymer was found to be 60 wt% for fly ash obtained from the electrostatic precipitators and 70 wt% for fly ash obtained from ash disposal ponds. The formation of geopolymer in the presence of fly ash was studied using 29Si MAS-NMR and showed that a geopolymer matrix was formed. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) imaging showed the interaction of the fly ash with the geopolymer, which was related to the leachate data and also the maximum percentage fly ash addition.

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Keywords: Fly ash; Geopolymer; Metal leaching; Waste management; Stabilisation

1. Introduction

The generation of electricity by combustion of pulverised coal produces many waste products, one of which is fly ash. The Latrobe Valley in Victoria, Australia, has thousands of tonnes of brown coal deposits used for the generation of electricity; however, the coal varies in composition by deposit and seam. Consequently, the composition of the fly ash also varies. The brown coal fly ash (BCFA) used in this study cannot be assumed as a typical Latrobe Valley ash. It is characterised as having high calcium and magnesium contents, low silica and alumina contents [1] and low heavy metal content [2].

Stabilisation of the brown coal fly ash by using geopolymers was studied to determine the effectiveness of this material for waste stabilisation. Calcium content plays a large role in the suitability of coal fly ash to specific applications [3,4]. This inevitably leads to tonnes of waste remaining for disposal in ash ponds. Stabilisation by geopolymers provides an alternative method, which could be used to reduce the leaching of metals from the fly ash. Despite heavy metals in this fly ash being below the Victorian EPA guidelines [5], there are also heavy metals which are not listed and require attention, such as strontium and barium. Currently, it is still classified as a prescribed industrial waste and direct landfill

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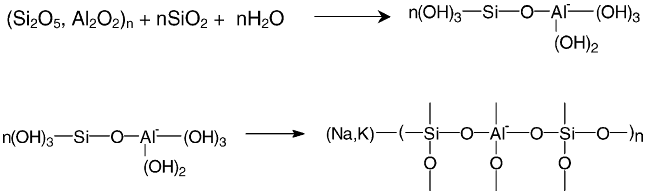
disposal is not permitted without treatment. The role of the geopolymer and indeed the aim of this research are to reduce the leaching of heavy metals in the fly ash as far as possible to eliminate any environmental concerns once it is disposed in landfill.

2. Background

Geopolymers are an old technology that has recently received attention in various forms one of which is waste stabilisation. They function similarly to cement binders in terms of encapsulation however have improved chemical and physical properties, such as acid resistance, compressive strength [6], durability [7] and thermal resistance [8,9]. The mechanisms of encapsulation are believed to be either physical or chemical where metals are taken into the geopolymer network and possibly bound into the structure for charge balancing roles [10]. Synthesis of geopolymers involves using materials with silica and alumina in the correct ratios and activated by an alkali metal hydroxide to produce a three-dimensional inorganic amorphous structure. The principles of geopolymers are simple and involve the synthesis of aluminosilicate oxides (Al^{3+} in four-fold coordination) with alkali polysilicates to give polymeric Si–O–Al bonds [11] according to the reaction:



$$(Si_2O_5, Al_2O_2)_n + nSiO_2 + nH_2O \longrightarrow n(OH)_3\text{—Si—O—}\underset{(OH)_2}{Al^-}\text{—}(OH)_3$$

$$n(OH)_3\text{—Si—O—}\underset{(OH)_2}{Al^-}\text{—}(OH)_3 \longrightarrow (Na,K)\text{—}(\text{—}\underset{O}{Si}\text{—O—}\underset{O}{Al^-}\text{—O—}\underset{O}{Si}\text{—O—})_n$$

Geopolymerisation can be carried out with a clay or pozzolanic material that partially dissolves in alkali solution and is therefore a source of geopolymeric precursors. The alkali solution not only dissolves alumina and silica precursors but also hydrolyses the surface of particles allowing reactions to occur between already dissolved silicate species and the particle surface [12]. The presence of cations (Na^+, K^+ and Ca^{2+}) is important due to charge balancing and catalytic properties. It has been proven that apart from pure materials such as kaolinite, other raw materials can be used to synthesise geopolymers. Previous studies have used black coal fly ash and builders' waste [6,10], slags [13] and alumino–silicate minerals [14] as a basis for geopolymerisation.

Geopolymers as a means of stabilising waste have shown great potential. Radioactive waste encapsulation by geopolymers has received attention as an alternative to ordinary Portland cement. Khalil and Merz [15] studied intermediate level wastes and found that waste loading should be below 50 wt% of the reactive components or the geopolymer will fail to cure [15]. The aim of this paper is to determine the effectiveness of stabilising brown coal fly ash by using a geopolymer material.

Table 1
Composition of raw materials (mass%)

Element	Precipitator fly ash	Leached fly ash	Kaolin clay
SiO_2	2.4	21.2	49.3
Al_2O_3	1.2	4.3	35.0
CaO	30.6	14.9	0.1
MgO	16.4	11.6	0.3
Na_2O	4.3	0.5	0.2
Fe_2O_3	8.2	6.4	1.1
K_2O	0.3	0.2	0.2
TiO_2	–	–	1.1
SO_3	14.0	4.7	–
Loss on ignition (L.O.I.)	22.6	36.3	12.9 (1000 °C)

3. Experimental

3.1. Materials

Fly ash used for synthesis of geopolymer structures was obtained from Latrobe Valley, Victoria, Australia, and is of brown coal origin. Precipitator fly ash (PFA) was collected from the hoppers of electrostatic precipitators while leached fly ash (LFA) was collected from ash disposal ponds. LFA is the disposed form of PFA after it has been sluiced, transported and stored in ash disposal ponds. It has been in contact with water and is of a moist consistency. Kaolin clay, a product of Unimin Aust. Pty Ltd., is HR1 grade. The major chemical composition of the precipitator fly ash, leached fly ash and kaolin are shown in Table 1 and were obtained using X-ray fluorescence (Phillips PW1660). Analytical grade sodium hydroxide was used in pellet form. Sodium silicate solution was obtained from PQ Australia and consists of a 2:1 molar ratio of silica to sodium oxide. The same batch materials were used for all experiments and distilled water was used throughout.

3.2. Sample preparation

Thirteen 750 g samples were prepared ranging from 100% geopolymer, 10–60 wt% PFA–geopolymer composite and 10–70 wt% LFA–geopolymer composites in 10% increments (Table 2). LFA, obtained in moist form, was oven dried at 105 °C overnight to remove moisture. Metakaolin clay was prepared by calcining kaolin at 750 °C for 10 h.

Table 2
Fly ash and water content of samples (mass%)

Sample name	Fly ash	Water content
Geo100	0	46.0
PFA10/LFA10	10	41.4
PFA20/LFA20	20	36.8
PFA30/LFA30	30	32.2
PFA40/LFA40	40	27.6
PFA50/LFA50	50	23.0
PFA60/LFA60	60	18.6
LFA70	70	15.2

Each geopolymer had a molar silica to alumina ratio of 2:1 and the effect of the fly ash on this ratio was ignored. An activator solution of sodium silicate, sodium hydroxide and water was prepared. The sodium hydroxide concentration in the solution was 0.76 M and the sodium silicate concentration was 4.25 M. Upon dissolution of the sodium hydroxide pellets in the activator solution, the metakaolin clay was added slowly to ensure uniformity. Once the required mass of clay had been added the mixture was allowed to mix for a further 10 min to dissolve the metakaolin and produce a geopolymeric paste. Then fly ash was blended in the required percentages, homogenised, and the mixture was transferred to moulds and cured. Polypropylene labware was used throughout the experiments to avoid silica contamination.

Addition of the fly ash into the geopolymer paste caused the mixture to become dry as the percentage of fly ash was increased in each sample. The water content of each sample is shown in Table 2. Sample containing more than 40 wt% fly ash (less than 32.2 wt% water) were no longer a paste, but a semi-dry powder and required pressing to consolidate. For this reason, two different methods of curing were used once the fly ash–geopolymer mix was prepared. Samples in slurry form were transferred to polypropylene moulds and cured at 65 °C for 24 h; otherwise the semi-dry form of the mixture was transferred to a die and compressed to 10 MPa, removed and allowed to set at the same conditions. After oven curing, the fly ash–geopolymer composite material was removed from the moulds and allowed to cure for a further six days at room temperature, giving a total preparation to testing time of seven days.

3.3. *Leaching tests*

Each sample was prepared and leached according to the standard USEPA TCLP Method 1311 [16] leaching test. Total sample mass of 750 g were prepared for each combination. Every sample was mixed well to achieve maximum homogeneity. From the 750 g sample, two 100 g sub-samples were taken and leached in duplicate, and the average leachate concentration was calculated after analysis. After the test, the solid and liquid phase were separated by centrifuging for 5 min at 6000 rpm. Two hundred and fifty millilitres of supernatant were filtered and acidified with 4 mL of concentrated nitric acid to give a pH less than two for all samples. Glassware, filters, extraction vessels and other equipment were acid washed to avoid metal contamination.

Analysis of the major elements in the leachate solutions was conducted using ICP-OES (Varian Liberty 200). The trace elements were analysed by ICP-MS due to its lower detection limit, particularly for heavy metals. A small quantity of each sample was initially analysed by ICP-MS to give an indication of the typical concentrations of heavy metals in the untreated fly ash and in stabilised fly ash. Some elements were omitted from further study due to their concentrations being below the detection limits. ICP-OES samples were analysed in batches with standards repeated no more than every 15 samples. This allowed for the determination of machine drift and correction for errors.

3.4. *SEM analysis*

Scanning electron microscopy (SEM) was carried out using a Leo 1530 microscope. Samples were mounted in low viscosity SPURR resin under vacuum for 8 h. Each mounted sample was ground beginning with 220 grit silicon carbide paper then progressively through 500 grit, 800 grit and 1200 grit and polishing with 6 μm, 3 μm and 1 μm diamond suspension. Ultrasonic cleaning was performed before polishing and between each stage of polishing to remove contamination. Mounts were carbon coated for imaging.

4. Results

4.1. *MAS-NMR*

The formation of geopolymer was confirmed by NMR analysis (Fig. 1) and typical 29Si MAS-NMR features were observed that agree with other published information on the structure of geopolymers [12,17]. Broad resonance, associated with disordered structure, was observed at −99.6 ppm and smaller resonance at −81.5 ppm for geopolymer without fly ash addition. The peaks correspond to SiQ_4(3Al), SiQ_4(2Al) and SiQ_4(1Al).

The introduction of fly ash into the geopolymer caused a slight shift up-field in the spectrum from that observed in the pure geopolymer. The broad resonance peak for 29Si MAS-NMR is observed at −94.4 ppm instead of −99.6 ppm, although a change in shape of the spectrum was not observed. Peaks that corresponded to SiQ_4(3Al), SiQ_4(2Al) and SiQ_4(1Al) have become less resolved in the fly ash–geopolymer sample indicating that perhaps the structure is more disordered, due to the presence of fly ash, than that observed in pure geopolymer.

4.2. *X-ray diffraction*

The composition of BCFA greatly differs in comparison to black coal fly ash. PFA contains only 2.4 wt% SiO_2 and 1.2 wt% Al_2O_3 and without another added source of silica and alumina a geopolymeric material could not be formed. The major inorganic oxide constituents in BCFA are calcium oxide, magnesium oxide, sodium oxide and iron oxide that make approximately 60% of total mass (Table 1). Presence of some crystalline phases in unstabilised PFA such as, quartz, calcium sulphate (anhydrite), calcium oxide (lime), magnesium oxide (periclase) and sodium silicate (Na_2SiO_3) are reflected in X-ray diffraction (XRD), though high noise to background ratio indicates the presence of non-crystalline phases (Fig. 2).

XRD analysis of two fly ash–geopolymer samples is shown in Figs. 3 and 4. The low fly ash sample containing

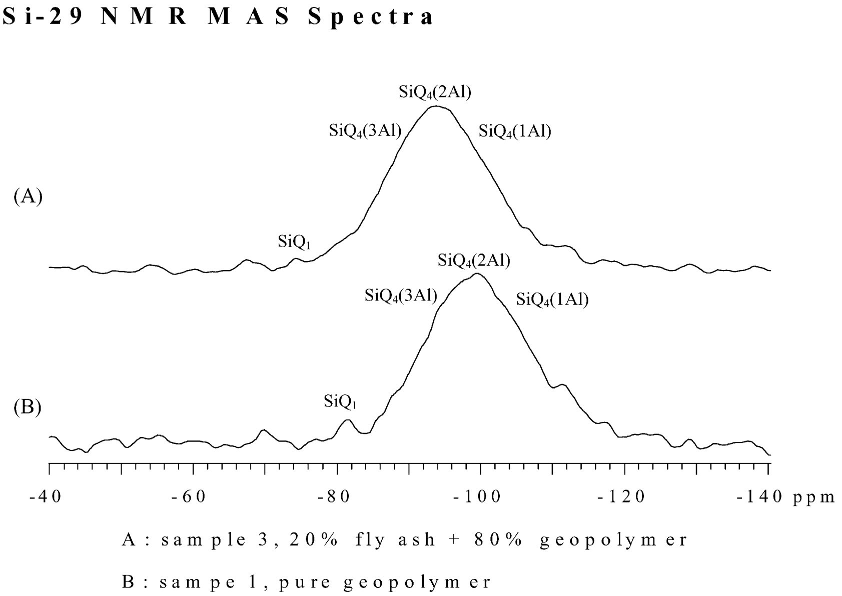


Fig. 1. MAS-NMR spectrum of 20 wt% PFA–80 wt% geopolymer (A) and pure geopolymer (B).

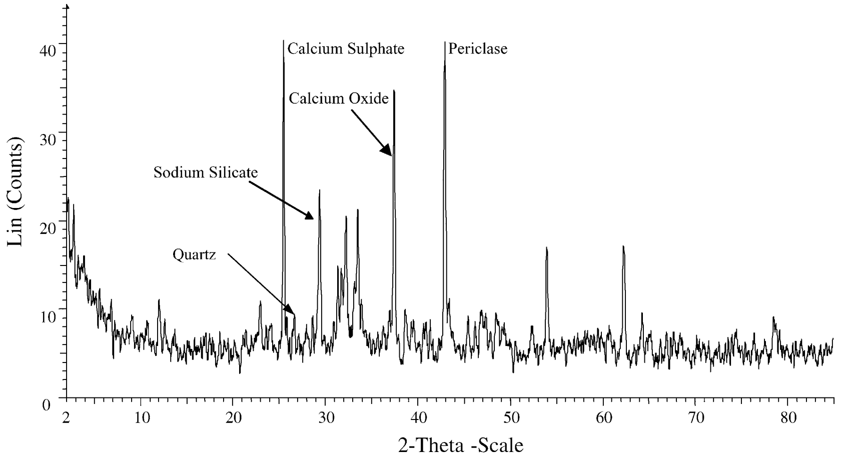


Fig. 2. X-ray diffraction spectrum of untreated brown coal fly ash.

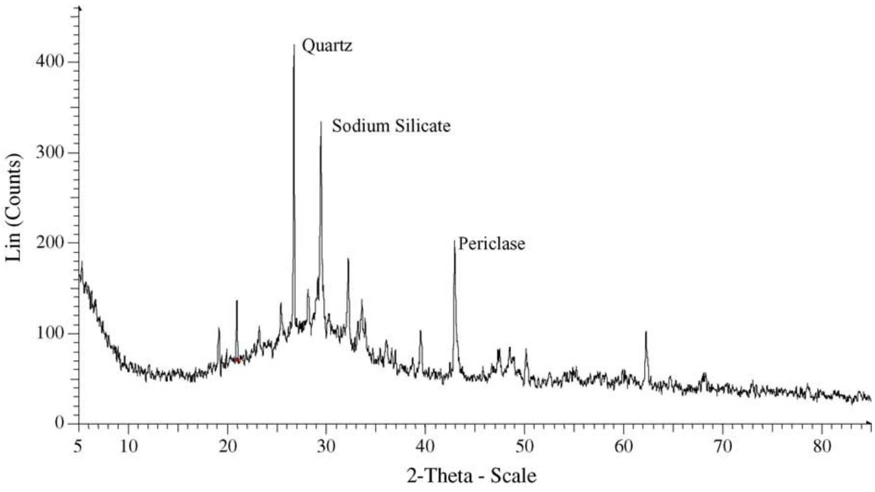


Fig. 3. X-ray diffraction spectrum of sample containing 20 wt% PFA.

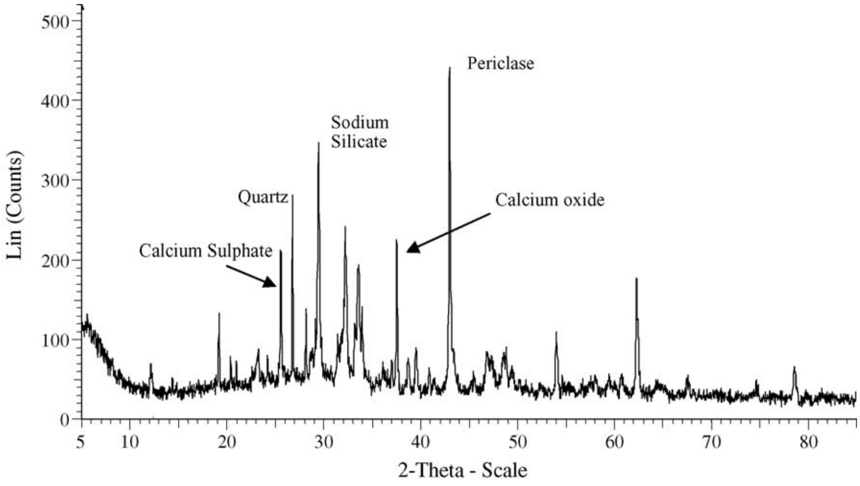


Fig. 4. X-ray diffraction spectrum of sample containing 60 wt% PFA.

20 wt% PFA (Fig. 3) shows the typical curve associated with amorphous and geopolymer materials. The increase in fly ash addition (Fig. 4, 60 wt% PFA sample) shows that the amorphous curve becomes less noticeable. The cause of this is the reduction in amorphous material, mainly metakaolin, and does not reflect on the amount of geopolymer present in the sample, since metakaolin could remain unreacted.

In Fig. 3, 20 wt% PFA, the three main crystalline mineral phases detected were quartz, sodium silicate and magnesium oxide. Calcium oxide and calcium sulphate have not been detected. Either the percentage of these calcium compounds has fallen below the detection limit or they have been consumed by reactions with the geopolymer phase or other fly ash constituents. Detection becomes possible again when larger percentages of fly ash are added to the geopolymer. From this data alone, it is difficult to determine the fate of calcium. However, since PFA contains 30.6 wt% calcium, there is still approximately 6 wt% in the 20 wt% PFA sample analysed in Fig. 3 and is within detection limits of the XRD. Therefore, it is likely that calcium compounds have been reacted rather than not detected.

Figs. 2 and 4 appear similar suggesting that a large percentage of the fly ash in samples with 60 wt% PFA is unreacted. This was expected since matrices containing 40 wt% or more fly ash were no longer a paste when synthesised, making the transport and reaction of constituents difficult. In terms of water content (Table 2), this means that less than 32.2 wt% total moisture changes the consistency of the sample and inhibits dissolution and transportation of fly ash constituents. Magnesium oxide, with a low solubility, is detectable in 20 wt% PFA and 60 wt% PFA samples. Regardless of whether the matrix contained enough liquid to dissolve the fly ash, MgO was unreacted.

4.3. *Leaching data*

Trace metals were given priority in terms of stabilisation, due to their toxicity, and emphasis was placed on reducing their leach rates. In Tables 3 and 4, trace metal analysis from PFA– and LFA–geopolymer matrices are given. Metals that showed a decrease in leaching were arsenic, barium, selenium and strontium. When the leach rates are compared to the rates of untreated fly ash the results are encouraging. The maximum reduction obtained for arsenic was 98% at percentages as high as 70 wt% LFA. The reduction was consistent throughout the leaching data for both types of fly ash. The maximum reduction for barium was 80% at 10 wt% LFA addition. Selenium and strontium showed good results with reductions as high as 96% for strontium at a PFA addition of 10 wt% and 92% for selenium at a PFA loading of 10 wt%. The leach rates of arsenic, barium, selenium and strontium were reduced below the leach rates expected if dilution was

Table 3
Trace metal analysis from PFA–geopolymer material (μg/L)

PFA (%)	As	Ba	Cr	Cu	Mn	Mo	Ni	Se	Sr	V	Zn
100	12	270	4	18	10	11	26	740	31200	n.d.	38
60	2	120	n.d.	n.d.	n.d.	14	n.d.	110	11500	10	n.d.
50	n.d.	110	n.d.	n.d.	2	13	n.d.	100	9900	7	40
40	2	70	n.d.	n.d.	n.d.	17	n.d.	130	5500	50	n.d.
30	2	80	n.d.	n.d.	260	13	160	110	4500	40	30
20	1	80	n.d.	n.d.	140	12	90	60	2400	40	30
10	1	70	n.d.	4	280	14	100	60	1100	130	70

n.d.: Not detected.

Table 4
Trace metal analysis from LFA–geopolymer material (μg/L)

LFA (%)	As	Ba	Cr	Cu	Mn	Mo	Ni	Se	Sr	V	Zn
100	75	150	n.d.	10	510	18	14	140	11300	1	4
70	1	140	n.d.	n.d.	10	12	n.d.	100	11200	10	8
60	3	240	n.d.	10	310	18	15	90	9600	20	70
50	1	290	n.d.	4	540	14	30	90	6900	23	40
40	2	290	n.d.	n.d.	580	10	35	80	5200	40	340
30	n.d.	130	n.d.	2	820	6	69	60	2600	32	140
20	2	70	n.d.	n.d.	420	7	45	40	1400	70	30
10	3	30	n.d.	1	240	7	40	10	500	155	61

n.d.: Not detected.

simply occurring and there was no interaction between the fly ash and the geopolymer. As the percentage of fly ash was increased the incremental increase in leach rates became smaller for these trace metals. Others such as chromium, copper and molybdenum did not respond to stabilisation by the geopolymer and manganese, nickel, vanadium and zinc increased in leaching. Trace elements such as chromium, copper and molybdenum, although showed constant leach rates, actually increased in leaching since as the percentage of fly ash was reduced, the leach rates remained constant.

Overall these trace metal concentrations are low making it is difficult to firmly establish whether the geopolymer has played a role in stabilisation of the trace elements. Other factors such as formation of precipitates and complex silicates could be responsible for lower leaching rates.

The leach rates of three major elements were also chosen to understand the system as a whole, even though calcium, magnesium and potassium are not considered as hazardous, they do contribute largely to the composition of this fly ash. The leaching results in Figs. 5 and 6 on a geopolymer basis, show a general trend that a geopolymer structure has the ability to reduce the leaching rate of calcium and potassium, particularly at low percentages of fly ash. Leaching results for both types of untreated fly ashes are also shown allowing the stabilised material to be compared with unstabilised material. PFA–geopolymer shows an increase in leaching of magnesium compared to untreated PFA. This implies that some reactions are preferred over those of geopolymerisation. A comparison of PFA and LFA in Figs. 5 and 6 shows that LFA samples generally have lower leach rates than PFA. Samples containing more than 40 wt% fly ash, although prepared, were not plotted on Figs. 5 and 6, since a clear trend after this percentage was not observed for the major elements.

4.4. SEM results

Pure geopolymer SEM images show undissolved clay particles, which are typical of geopolymers. Surrounding the clay particles is the gel phase formed from dissolved silica and alumina species (Fig. 7a).

Addition of 20 wt% fly ash results in the dissolution of fly ash particles and the distribution of fly ash constituents throughout the geopolymer network (Fig. 7b). Back scatter electron (BSE) imaging better demonstrates the distribution by showing elements with greater atomic mass as lighter regions on the image.

Increasing the percentage of fly ash to 40 wt% alters the appearance of the BSE image (Fig. 7c). Here, the geopolymer phase is less dominant and the fly ash particles appear to be undissolved. At this percentage, there is insufficient geopoly-

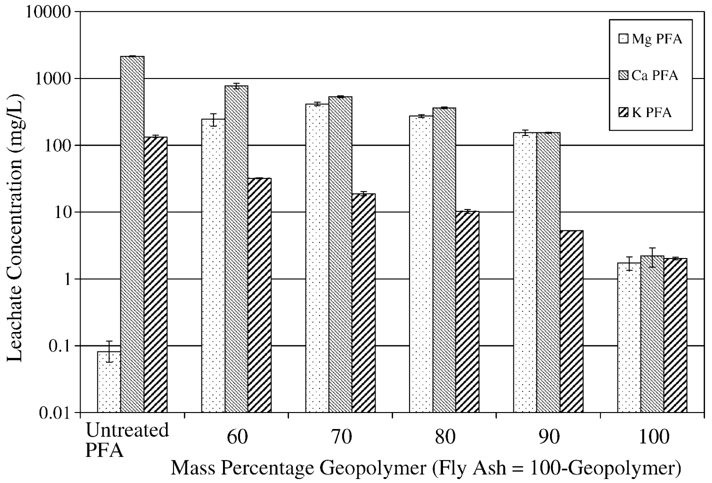


Fig. 5. Major element leachate analysis from PFA–geopolymer material with varying amounts of fly ash.

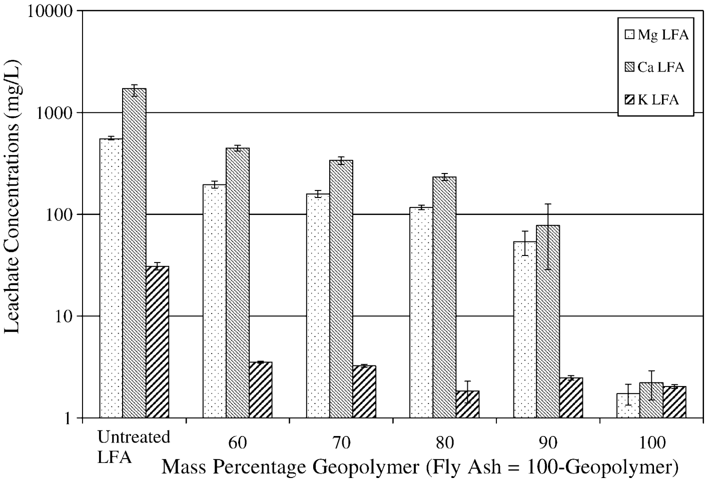


Fig. 6. Major element leachate analysis from LFA–geopolymer material with varying amounts of fly ash.

mer to encapsulate the fly ash particles and binding into a consolidated mass occurs on a surface reaction basis. Therefore, matrices containing 40 wt% PFA and LFA exhibited an increase in leaching, which can be related to the observations in the SEM images.

At 60 wt% fly ash, the BSE image shows the geopolymer phase as small dark regions distributed throughout the lighter fly ash phase (Fig. 7d). A difference in structure between the fly ash and geopolymer can be seen when comparing the dark regions on the BSE image with the SE image. Similar geopolymeric features have also been observed in other samples.

5. Discussion

The fly ash–geopolymer system is a mass of competing reactions between fly ash and geopolymer reactants, being metakaolin, sodium silicate, sodium hydroxide and water. An increased degree of side reactions results in a reduced amount of geopolymer formation. The amount of possible geopolymer phase formed is limited, as when the percentage of fly ash is increased, the reactants that are critical to geopolymer formation are diluted and further consumed by side reactions with the fly ash. The maximum addition of fly ash to the geopolymer was 60 wt% for PFA and 70 wt% for

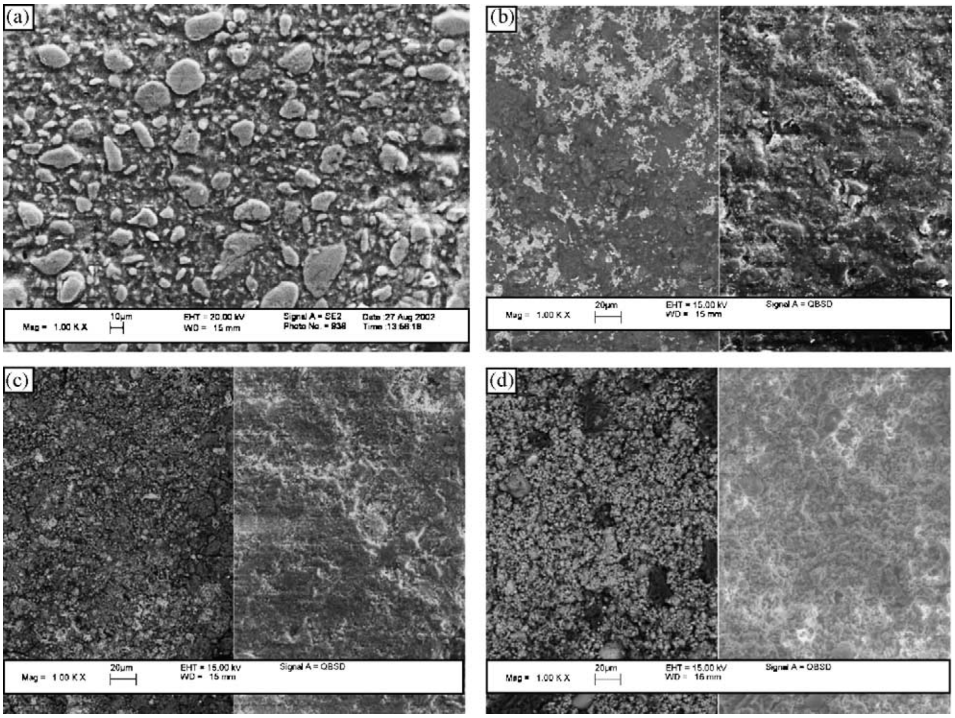


Fig. 7. BSE (left) and SE (right) images in (b) to (d) of (a) geopolymer, (b) 20 wt% PFA, (c) 40 wt% PFA, (d) 60 wt% PFA.

LFA. The criteria for maximum addition were based on the material remaining after the leaching test. The geopolymer phase is not soluble and stabilised fly ash–geopolymer still remains after the leaching test. Addition of PFA at 60 wt% and LFA at 70 wt% produced a minimal amount of material after the leaching test. Increasing the PFA and LFA content in the geopolymer by another 10 wt% did not produce any remaining geopolymer after leaching. The structural integrity of these samples was reduced such that they dissolved during the leaching test, indicating that no geopolymer formation had originally taken place and solidification was not achieved. In fact, the reduction in structural integrity was observed at 50 wt% PFA and LFA, when the water content was reduced below 32.2 wt%. This would account for the poor stabilisation observed in the leaching data, which lead to the omission of data points for samples containing 50 wt% or more fly ash from Figs. 5 and 6. This same observation was not noticed for trace metals, which showed clearer trends regardless of the water content.

Close observation shows that some leachate concentrations increase and reach a maximum at certain percentages of fly ash addition. This observation might be the result of ineffective stabilisation caused by fly ash constituents reacting with geopolymer reactants to form compounds that are more soluble than the original compounds. For example, the solubility of $Mg(OH)_2$ is 0.009 g/L which is more than 0.006 g/L of MgO [18]. $Mg(OH)_2$ could be formed from the reaction of MgO present in fly ash with NaOH used in geopolymerisation. Manganese, vanadium and nickel also showed an increase in leaching, particularly at lower percentages of fly ash addition, reinforcing that as the percentage of geopolymer increases the reactions with geopolymer reactants also increase. The leaching rates of calcium and potassium are reduced for PFA and LFA. This is expected, since it is well known that both these elements can participate in geopolymer networks in charge balancing roles [9,19].

In 20 wt% PFA BSE image (Fig. 7), it can be seen that geopolymer appears as the darker phase and the fly ash as the lighter distributed regions. At this percentage, the fly ash is completely encapsulated by the geopolymer. If an undissolved particle were present, then leaching would be occurring through a physical barrier, placing emphasis on synthesising geopolymers with low porosity. Since a majority of the fly ash is dissolved it is reasonable to assume that metals are trapped in the geopolymer network. Whether this is physical or chemical is still unclear.

The ability of the geopolymer to bind the fly ash reaches a maximum at 40 wt% fly ash where surface reactions are responsible for consolidation. At 60 wt% fly ash, the geopolymer is not responsible for the binding of the fly ash, meaning another mechanism must be responsible, hence poorer stabilisation and no observed trends in leaching data. Table 1 indicates that the fly ash has high concentration of calcium and XRD spectrums have indicated that calcium is present as calcium oxide and calcium sulphate. Upon hydration calcium oxide forms $Ca(OH)_2$ and calcium sulphate forms $CaSO_4{\cdot}1/2H_2O$ and $CaSO_4{\cdot}2H_2O$. All three compounds might be responsible for the consolidation of the fly ash. Calcium hydroxide can initiate cementitious type reactions producing calcium silica hydrates or bind with already dissolved geopolymeric precursors to produce calcium silicates or calcium aluminosilicates. Similarly, when calcium sulphate is hydrated the result is gypsum or a hemihydrate (plaster of Paris) that is able to bind the material together. The leach rates are dependent on the increase in fly ash addition and the reactions of fly ash with geopolymeric precursors. Therefore, reactions that lead to the formation of precipitates are an important characteristic of this system at high percentage of fly ash.

There are several major differences between PFA and LFA. LFA was collected from ash disposal ponds and has been in contact with water. The decrease in percentages of calcium, magnesium, sulphur and sodium compounds observed in XRF analysis of PFA and LFA (Table 1) indicates that these ions are present as easily soluble compounds. There was also an increase in the silica and alumina percentages. Therefore, when LFA is added to geopolymers it results in a greater capacity of addition. Conversely, the washing operation also concentrates heavy metals as indicated by the increase in loss on ignition for LFA compared to PFA shown in Table 1, thus making stabilisation of trace elements more difficult in LFA–geopolymers.

Some successful stabilisation of brown coal fly ash by geopolymerisation is achieved. It establishes the possibility of using geopolymers as stabilisation materials to further reduce the leaching of metals from the fly ash in the landfill. Strontium and barium, two elements present in fly ash that can still pose an environmental threat, demonstrated a very effective reduction in leaching after stabilisation by the geopolymer. Stabilisation of other elements on the Victorian EPA guidelines (Table 5) was also achieved to further reduce leach rates.

Table 5
Comparison of stabilisation to Victorian EPA guidelines

Contaminate (mg/L)	Permissible elutriable fraction	Maximum leachate concentration from PFA–geopolymer	Leachate concentration from unstabilised PFA
Arsenic	5.0	0.002	0.012
Cadmium	0.5	n.d	n.d
Chromium	5.0	n.d	0.004
Copper	10	0.004	0.018
Cobalt	–	n.d	n.d
Lead	5.0	n.d	n.d
Mercury	0.1	n.d	n.d
Molybdenum	–	0.017	0.011
Nickel	–	0.16	0.026
Tin	–	n.d	n.d
Selenium	1	0.130	0.740
Zinc	50	0.070	0.038

–: No set guidelines, n.d.: not detected.

6. Conclusions

Geopolymers can be used to encapsulate wastes such as heavy metals and mine tailings. In this study, a geopolymer material was utilised to encapsulate brown coal fly ash. The geopolymer was blended with the fly ash to determine its capacity and effectiveness to stabilise the fly ash against leaching. The formation of geopolymer is reduced as the percentage of fly ash added is increased as shown by XRD analysis. In matrices containing 60 wt% PFA, there is insufficient geopolymer to provide adequate stabilisation. XRD spectrum of this matrix is similar to that of unstabilised PFA suggesting that little chemical change has occurred during geopolymerisation. The addition of PFA over 60 wt% and LFA over 70 wt% failed to produce matrices that cured into geopolymeric materials, placing the maximum loading at these values.

Scanning electron microscopy images related each image to a specific point on the leaching curve. It was possible to determine the mechanism of particle encapsulation based on the interaction between fly ash and the geopolymer. Low percentage fly ash (20 wt%) images show that fly ash is completely dissolved and encapsulated by the geopolymer. At 40 wt% fly ash, the geopolymer is diluted by the fly ash and it appears that surface reactions bind the waste particles together. When the fly ash percentage was increased to 60 wt%, the geopolymer was unable to stabilise the waste due to dilution by the fly ash.

Other mechanisms were responsible for the binding of the fly ash–geopolymer matrix once percentages had increased over 40 wt% fly ash. The formation of gypsum and calcium sulphate hydrates, in perhaps cement type or plaster type reactions, led to the consolidation of the waste but not stabilisation.

Leaching of calcium and potassium has been reduced by the geopolymer. Leached fly ash, which has been in contact with water prior to stabilisation, showed lower leaching rates than precipitator fly ash. Heavy metal stabilisation was better in precipitator fly ash than leached fly ash for the same reason. Significant reductions in leaching were found for calcium, arsenic, strontium, selenium and barium. A comparison of the stabilised fly ash was made against Victorian EPA guidelines and it was found that most listed elements were below the maximum allowable elutriable fraction in unstabilised fly ash. The geopolymer helped to further reduce the leach rates of some of the elements on the list, as well as other elements not listed, but also of concerns.

The geopolymer was effective at stabilising low percentages of fly ash, but less effective as the percentage of fly ash increases. There appears to be potential in using this method of stabilisation, however, research still needs to be conducted into optimising a geopolymer formulation for this unique fly ash.

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