Available online at www.sciencedirect.com
ScienceDirect
Cement and Concrete Research 38 (2008) 681 – 688
Cement and Concrete Research

The role of sulfide in the immobilization of Cr(VI) in fly ash geopolymers

Jianguo Zhang [a,b], John L. Provis [a,*], Dingwu Feng [a], Jannie S.J. van Deventer [a]

[a] *Department of Chemical and Biomolecular Engineering, The University of Melbourne, Victoria 3010, Australia*
[b] *Beijing Research Institute of Chemical Engineering and Metallurgy, Beijing 101149, China*

Received 18 September 2007; accepted 24 January 2008

Abstract

The use of fly ash-based geopolymer binders to immobilize chromium is investigated in detail, with particular regard to the role of the sulfide ion as a reductant for Cr(VI) treatment. In the absence of sulfide, Cr added as Cr(VI) is highly leachable. However, addition of a small quantity of Na_2S reduces the Cr to Cr(III), and enables leaching efficiencies in excess of 99.9% to be reached after 90 days' exposure to deionized water, Na_2CO_3 or $MgSO_4$ solutions. Leaching in H_2SO_4 is somewhat greater than this, due most probably to the oxidation of the Cr(III) present. Addition of the Cr(VI) as a highly soluble salt is preferable to its addition as a sparingly soluble salt, because a higher salt solubility means the Cr(VI) is more available for reduction prior to geopolymeric setting. The potential value of geopolymer technology as an immobilization process for problematic heavy metal waste streams is highlighted by these results, and the need for a full understanding of binder chemistry in any immobilization system outlined.

Keywords: Geopolymer; Waste management; Chromium; Fly ash; Immobilization

1. Introduction

Geopolymer technology [1] has for a number of years been proposed as an alternative to Portland-based cements for the immobilization of toxic heavy metal-containing wastes [2–4]. Recent work [5] has shown that Pb^{2+} and Cd^{2+} are very effectively immobilized by incorporation into fly ash-based geopolymers, however Cr^{6+} was observed to be problematic. Similar difficulties in the treatment of Cr^{6+} have also been observed by Palomo and Palacios [6]. In this study, the efficacy of addition of S^{2-} as a reducing agent during immobilization of Cr (VI) in geopolymers is investigated. It has previously been noted that reduction of Cr(VI) to Cr(III), either by addition of $FeSO_4$ or by the sulfide present in blast furnace slags, is beneficial for immobilization in Portland cement-based matrices [7,8].

Chromium is a widespread environmental pollutant, produced by industries including electroplating, production of pigments, stainless steels and other alloys, leather and textiles, as well as ore and petroleum refining [9]. Cr(VI) is particularly toxic, and is also relatively mobile in the environment. Immobilization of the waste streams from these and other industries is therefore of paramount importance. Cr(III) is both less toxic and less mobile, being relatively insoluble as $Cr(OH)_3$ and also as mixed hydroxide phases containing some Ca [10]. Some substitution into calcium (alumino)silicate hydrate (C–A–S–H) phases is also believed to be possible [8,10,11]. However, Cr(VI) addition tends to have deleterious effects on the strength development of Portland cement-based (OPC) systems [12]. Wang and Vipulanandan [12] studied Cr(VI) immobilization in OPC, and found that a maximum loading of 0.2% Cr as K_2CrO_4 was possible while complying with the requirements of the TCLP leach test. In OPC blends with higher Al content, CrO_4^{2-} substitution into the SO_4^{2-} sites of ettringite and hydrocalumite is also possible [13], although the solubilities of these phases are unsatisfactorily high in terms of their use in immobilization [14].

Alkali activation of slags has also been the subject of some attention with regards to chromium immobilization. Deja [15] studied the immobilization of Cr^{6+} in alkali-activated slag binders, and showed that not only is Cr^{6+} quite effectively immobilized in these systems, but that it also leads to an improvement in mechanical strength development in both carbonate- and silicate-activated systems. This work also indicated that reducing conditions in the hydrated slag pastes

---

* Corresponding author. Tel.: +61 3 8344 8755; fax: +61 3 8344 4153.
E-mail address: jprovis@unimelb.edu.au (J.L. Provis).

0008-8846/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.cemconres.2008.01.006

(i.e. available S^{2-} ions) play a positive role in the immobilization process by mechanisms such as partial reduction of Cr^{6+} to Cr^{3+}.

There is no report in the literature detailing the successful use of alkali activated fly ash (geopolymer) binders for immobilization of Cr(VI). Bankowski et al. [16] did report a very slight Cr leachability from a brown coal fly ash, which was reduced to undetectable levels by encapsulation of the ash in a metakaolin-based geopolymer. However, the concentrations involved are too low to be able to report successful immobilization. Palomo and Palacios [6] studied fly ash activated by 8 M NaOH, doped with 2.6% Cr(VI) as CrO_3. They found that the presence of this level of Cr(VI) significantly inhibited hardening during alkali activation, and the resulting product did not develop sufficient mechanical strength.

Previously [5], geopolymers were synthesized by activation of fly ash with sodium silicate solutions, and doped with 0.5% Cr(VI) as Na_2CrO_4 or 0.125% Cr(VI) as $PbCrO_4$. Addition of chromium in either of these forms actually gave an increased compressive strength when compared with uncontaminated mortar samples. However, long-term leaching tests in different media showed that in excess of 75% Cr extraction was observed from the Na_2CrO_4-containing samples in dilute H_2SO_4, in deionized water, in $MgSO_4$ and in Na_2CO_3 solution. Cr added as sparingly soluble $PbCrO_4$ was slightly less readily extracted, with between 50 and 75% extraction observed at 90 days. This is clearly not a satisfactory level of immobilization performance, which is attributed to the high mobility of Cr(VI) in aqueous systems.

In this paper, S^{2-} is added to fly ash geopolymer formulations to be used in the immobilization of Cr(VI), with the aim of reducing much of the Cr(VI) to Cr(III) and hence improving the observed immobilization performance. Sulfide is a significant component of blast furnace slag, another industrial waste material that is commonly used as a precursor in geopolymer synthesis [17,18]. The chemistry of slag is complex, and so sulfide is instead added in soluble salt form to enable clearer identification of the chemical processes taking place in chromium immobilization. Slag incorporation has previously been observed to have a significant effect on the permeability of geopolymer mortars [19], as well as playing a role in strength development and durability [20,21]. The use of a sulfide salt in preference to slag in this investigation will to some extent reduce such complications, and will enable isolation of the chemical factors influencing immobilization as opposed to the effects of microstructural details.

2. Experimental

2.1. Materials

Coal fly ash, Class F according to ASTM C618, was obtained from Gladstone Power Station, Queensland, Australia, through Queensland Cement Limited (QCL). The fly ash has a d_{50} of 8.47 μm, with 1% of particles over 110 μm. The oxide composition as determined by X-ray fluorescence (XRF) is shown in Table 1.

Analytical-grade reagents NaOH, Na_2CrO_4, $PbCrO_4$ and $Na_2S.9H_2O$ were obtained from Sigma Aldrich (Australia). Medium sand (600–1180 μm) was used in preparing mortar samples. Distilled/deionized water was used throughout. Sodium silicate activating solutions (1.5 SiO_2:Na_2O:11H_2O) were made by dissolving NaOH pellets and silica fume (Aerosil 200, Degussa) in distilled water, and were allowed to equilibrate for at least 24 h before the synthesis of geopolymers. This composition was chosen because it corresponds to the activating solution SiO_2/Na_2O ratio which gives the highest strength for geopolymers derived both from fly ash [22], and metakaolin [23,24].

2.2. Geopolymer synthesis

Fly ash, sand and heavy metal salts were dry mixed by rotating in a sealed container for 15 min. Sodium silicate solution, 1.5SiO_2:Na_2O:11H_2O, was used as the alkaline activator in all cases, and all samples were made as mortars. Where sulfide was added to mixes, 0.5% by total sample mass of S^{2-} was added in the form of $Na_2S.9H_2O$ into the activating solution before mixing with the solids. The liquid to solid mass ratio (L/S) was chosen to be as low as possible while obtaining a reasonable sample rheology. In 50% fly ash and 50% sand activated by 1.5SiO_2:Na_2O:11H_2O, L/S = 0.238 gave a workable sample. The mixed powders were combined with the solution and mixed for 30 min. Specimens were then cast in plastic molds and vibrated for 2 min to remove large air bubbles. All samples were cured at 40 °C with 100% humidity at an oven for 24 h. The samples were then demolded and sealed in plastic bags for curing at room temperature until the other tests were carried out at 7, 14 and 28 days.

2.3. Sample analysis

Compressive strength testing was performed as per Australian Standard AS1012.9, using three 50 mm cubes of each sample composition. All samples were tested at the age of 7, 14 and 28 days. An Amsler FM 2750 (Roell Amsler, Gottmodingen, Germany) compressive strength-testing apparatus was used. The standard deviation of each set of samples was approximately 10%.

X-ray diffractometry (XRD) was conducted using a Philips PW 1800 diffractometer with CuKα radiation generated at 30 mA and 40 kV. Specimens were step-scanned as random powder mounts from 5 to 55° 2θ at 0.02° 2θ steps and integrated at the rate of 1.0 s per step.

Microstructural images of the fractured and carbon-coated samples were obtained using a Philips XL30 LaB_6 Scanning

Table 1
Chemical composition of fly ash as oxides

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MnO	CaO	MgO	K_2O	Na_2O	P_2O_5	SO_3	LOI [a]
wt.%	46.4	28.3	11.7	1.4	0.2	5.1	1.4	0.6	0.3	0.9	0.3	3.3

[a] LOI: Loss on ignition at 1000 °C.

Table 2
Compositions and compressive strength development of geopolymer samples

ID	Heavy metals added	Sulfides added	Compressive strength (MPa)		
			7 days	14 days	28 days
FS0	–	–	41.9	62.2	60.6
FS1	–	0.5% as $Na_2S{\cdot}9H_2O$	45.9	60.0	60.4
FS2	0.5% Cr as Na_2CrO_4	–	38.4	50.4	67.4
FS3	0.5% Cr as Na_2CrO_4	0.5% as $Na_2S{\cdot}9H_2O$	47.7	56.4	79.1
FS4	0.5% Pb, 0.125% Cr as $PbCrO_4$	–	46.4	53.6	63.3
FS5	0.5% Pb, 0.125% Cr as $PbCrO_4$	0.5% as $Na_2S{\cdot}9H_2O$	51.8	63.8	75.7

Electron Microscope (SEM) coupled with an Oxford Instruments EDS (ISIS ATW Si Detector) at an accelerating voltage of 20 kV.

Infrared (FTIR) spectra were collected using a Varian FTS 7000 FTIR Spectrometer in absorbance mode using a Specac MKII Golden Gate single reflectance diamond ATR attachment with KRS-5 optics. All spectra were obtained with 64 scans per spectrum.

All XRD, SEM and FTIR measurements were carried out at a sample age of 14 days. Before XRD and FTIR analysis, sand particles were removed from the crushed samples using a 75 µm sieve.

2.4. Leaching experiments

Static leaching experiments were carried out on the alkali-activated fly ash matrices. 32 × 24 × 22 mm cuboid samples were prepared for leaching tests. The leaching medium volume in each case is 400 mL, and a different sample was used for every time point in each series to minimize compositional errors due to removal of solution for sampling. The total concentration of chromium in the leached solution was determined by use of an ICP Optical Emission Spectrometer (Varian 720-ES).

3. Results and discussion

3.1. Sample characterization

The compressive strengths of all samples tested are presented in Table 2. From these data, it can be seen that the best mechanical compressive strength is achieved by the geopolymer paste with fly ash activated by sodium silicate. It is seen that the addition of a small amount of sodium sulfide has a negligible effect on the strength development of an otherwise uncontaminated geopolymer mortar. As was observed previously [5], addition of Cr(VI) as either Na_2CrO_4 or $PbCrO_4$ has a slight positive effect on 28-day strength, which is in stark contrast to its highly detrimental effect on OPC strength development. However, the most notable aspect of the data presented in Table 2 is that the addition of sulfide to the Cr-containing matrices gives in both cases a clear increase in the final strength obtained.

The samples were also studied by X-ray diffractometry (XRD) and Fourier transform infrared (FTIR) spectroscopy. XRD (Fig. 1) showed that no new crystalline phases were observable in any of the contaminated samples; the only observable sharp peaks were those due to unreacted mullite, quartz and iron oxide phases from the fly ash, as well as some calcite as previously observed [5]. Calcite was detected in

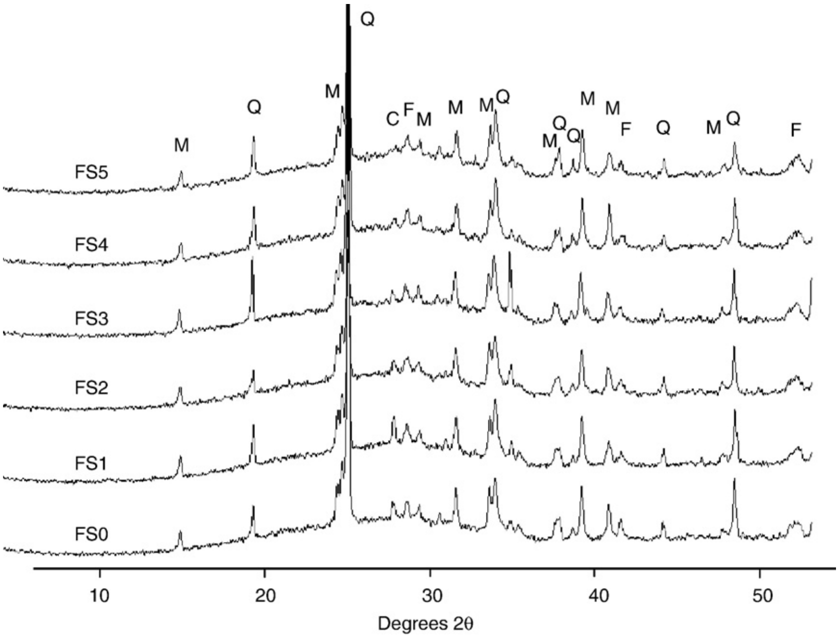

Fig. 1. X-ray diffractograms of all samples studied. Phases marked are quartz (Q), mullite (M), calcite (C), and iron oxides (magnetite, hematite and/or maghemite) (F). All crystalline phases observed are remnants of the crystalline phases in the original fly ash.

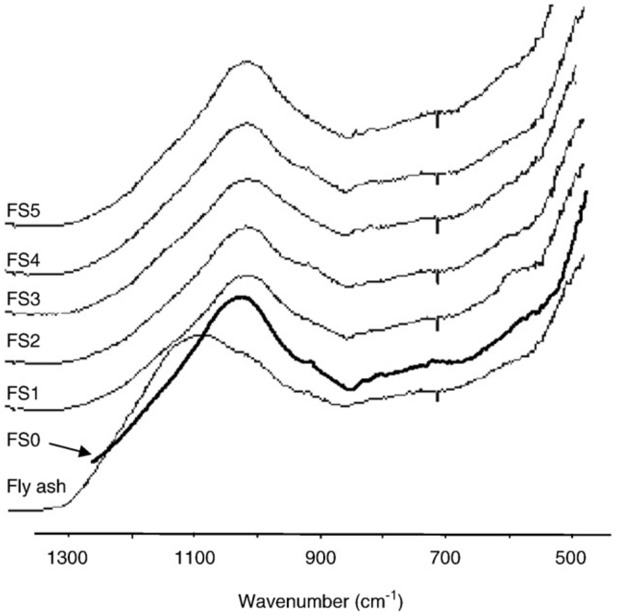

Fig. 2. FTIR spectra of the unreacted fly ash and the geopolymer samples, as detailed in Table 2. The dip at ~680 cm^{-1} in most spectra is due to an instrumental effect.

smaller quantities in sulfide-containing samples than in those without sulfide, in agreement with the FTIR spectra (Fig. 2) showing a peak at 873 cm^{-1} only in the absence of sulfide. It is not clear why S^{2-} should interfere with calcite formation, given that calcite and sulfide are in fact generated together in geological formations by reduction of calcium sulfate by carbonaceous matter [25]. No distinct sulfur-containing compounds or minerals are observed by XRD or FTIR, but this is not unexpected due to the low sulfur content of all samples studied. Comparing FS0 to FS1 shows that the addition of 0.5% S as Na_2S has reduced the wavenumber of the Si–O–(Si,Al) asymmetric stretching band from 975 to 969 cm^{-1}. This band is known to be particularly sensitive to the details of geopolymeric gel nanostructure [26,27]. With addition of 0.5% Cr as Na_2CrO_4 (FS2) it shows a 10 cm^{-1} shift, and with addition of 0.5% Cr as Na_2CrO_4 and 0.5% S as Na_2S, a shift of almost 15 cm^{-1} is observed. These are quite large shifts in peak position, indicating that the addition of the contaminant salts has had a notable effect on gel formation. However, the strength data in Table 2 show that these effects may by no means be considered deleterious.

Scanning electron microscopy (SEM) shows that few if any microstructural changes are induced by the addition of small amounts of $Na_2S{\cdot}9H_2O$ to fly ash-based geopolymers. SEM characterization of Cr-contaminated geopolymers has been published in detail recently [5]. Elemental mapping for Cr in samples with added Na_2CrO_4 shows that the contaminant element appears to be well dispersed, while $PbCrO_4$ does not give the same extent of dispersion due to its lower solubility. Addition of sodium sulfide to the Na_2CrO_4-containing samples appears to give a slightly lesser extent of dispersion than in the absence of a reductant, but no large regions of very high chromium enrichment are observable.

Sample FS5, with both Na_2S and $PbCrO_4$, does show a significant deviation from the behavior of the corresponding sulfide-free sample FS4. In particular, the correlation between the locations of Pb atoms and of Cr atoms is significantly weaker in FS5 than in FS4, showing that the reduction of Cr(VI) to Cr(III) has resulted in the breakdown of many of the initial $PbCrO_4$ particles. Regions that are enriched in one or the other of Pb and Cr – but not always in a ratio corresponding to the stoichiometry of $PbCrO_4$ – are observed. Fig. 3a shows one such region; the marked area appears to be the remnant of a $PbCrO_4$ particle, where the Cr has been

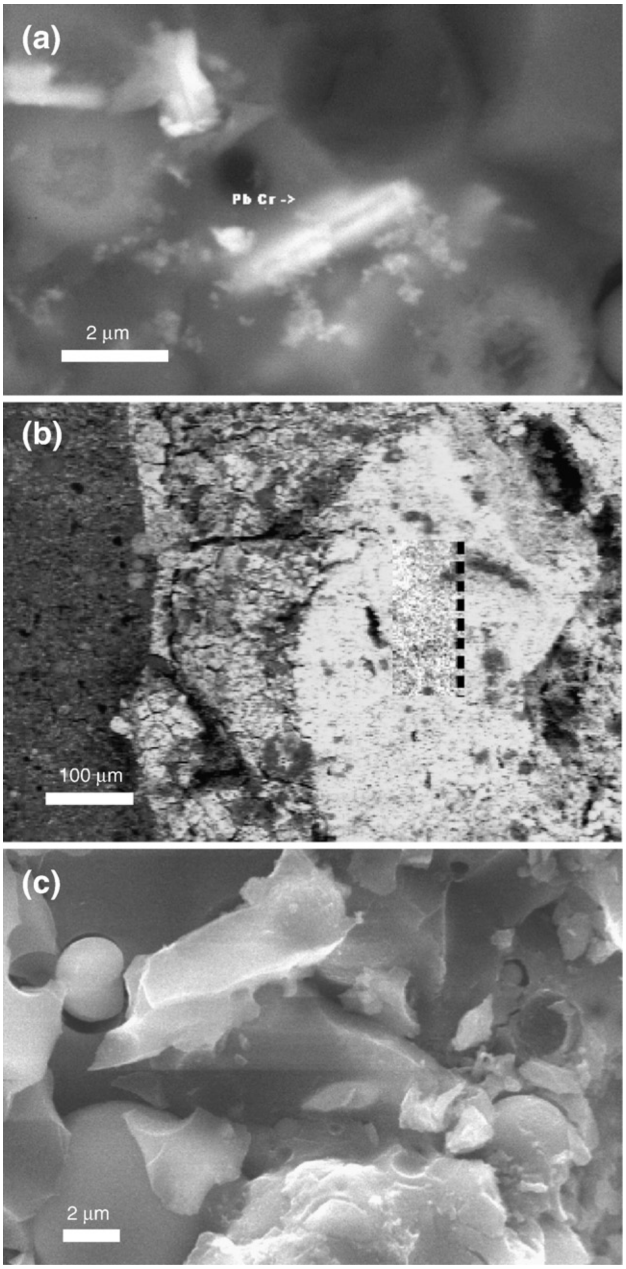

Fig. 3. SEM micrographs of fracture surface of geopolymer with 0.125% Cr as $PbCrO_4$ and 0.5% S as Na_2S (sample FS5). (a) Region shown is Pb-rich, ~1.4 at.% Cr and 3.0 at.% Pb by elemental analysis; (b) region marked with dashed line is slightly Cr-rich, ~12.4 at.% Cr and 11.3 at.% Pb; (c) typical fracture surface of bulk gel.

mobilized during geopolymerization and has left behind a Pb-enriched (Pb/Cr atom ratio ~ 2) region. Fig. 3b shows an example of a region displaying some degree of Cr enrichment; it is possible that such areas correspond with the formation of small $Cr(OH)_3$ particles where dissolved chromate has been reduced and precipitated in a specific region. The level of Pb in the region depicted in Fig. 3b is also high, meaning that the brightness in this backscattered electron image is much greater than in the other images. The fact that the number of highly Pb-enriched regions appears to be greater than the number of notably Cr-enriched regions suggests that the 'missing' Cr is relatively well dispersed throughout the geopolymer binder.

3.2. Leach testing

Although the alkali activated fly ash geopolymeric binder synthesized without sulfide showed very good mechanical strength development in the presence of Cr(VI), it showed little ability to resist attack by acid, mineral salts or even water. However, Fig. 4 clearly shows the improvement in immobilization performance that is achieved by the addition of 0.5% S^{2-} as $Na_2S{\cdot}9H_2O$, for geopolymers with 0.5% Cr added as Na_2CrO_4. In the case of leaching in deionized water and mineral salts, an improvement of better than three orders of magnitude is observed, with the immobilization efficiency in these cases increasing from less than 20% to more than 99.9%. This is shown in Fig. 4a, c and d, where in each case the two sets of data being compared cannot even be plotted on the same sets of axes.

However, Fig. 4b shows that the improvement in leaching performance in a sulfuric acid medium is nowhere near as great as is observed in any of the other cases. It is likely that the oxidizing effects of H_2SO_4 significantly counteracted the reducing action of the Na_2S in this system, reducing immobilization efficiency to around 80% — this is still much better than the 10% immobilization observed in H_2SO_4 without Na_2S, but is probably unsatisfactory for use in practice. This provides further evidence that the immobilized Cr in the sulfide-containing systems is in general reduced to Cr(III), and that this is the key mechanism underpinning the success of Cr immobilization. Fig. 4c shows that an apparent steady state is reached at around 20% Cr extraction, suggesting that this may be as much Cr(III) as could be readily oxidized to Cr(VI) by the available volume of H_2SO_4. It may also be that acid-base (rather than strictly redox) reactions between H_2SO_4 and $Cr(OH)_3$ are providing the dominant effect here, although the distinctions in mechanism are difficult to draw directly from leaching data. It may also be suggested that the higher extent of release into

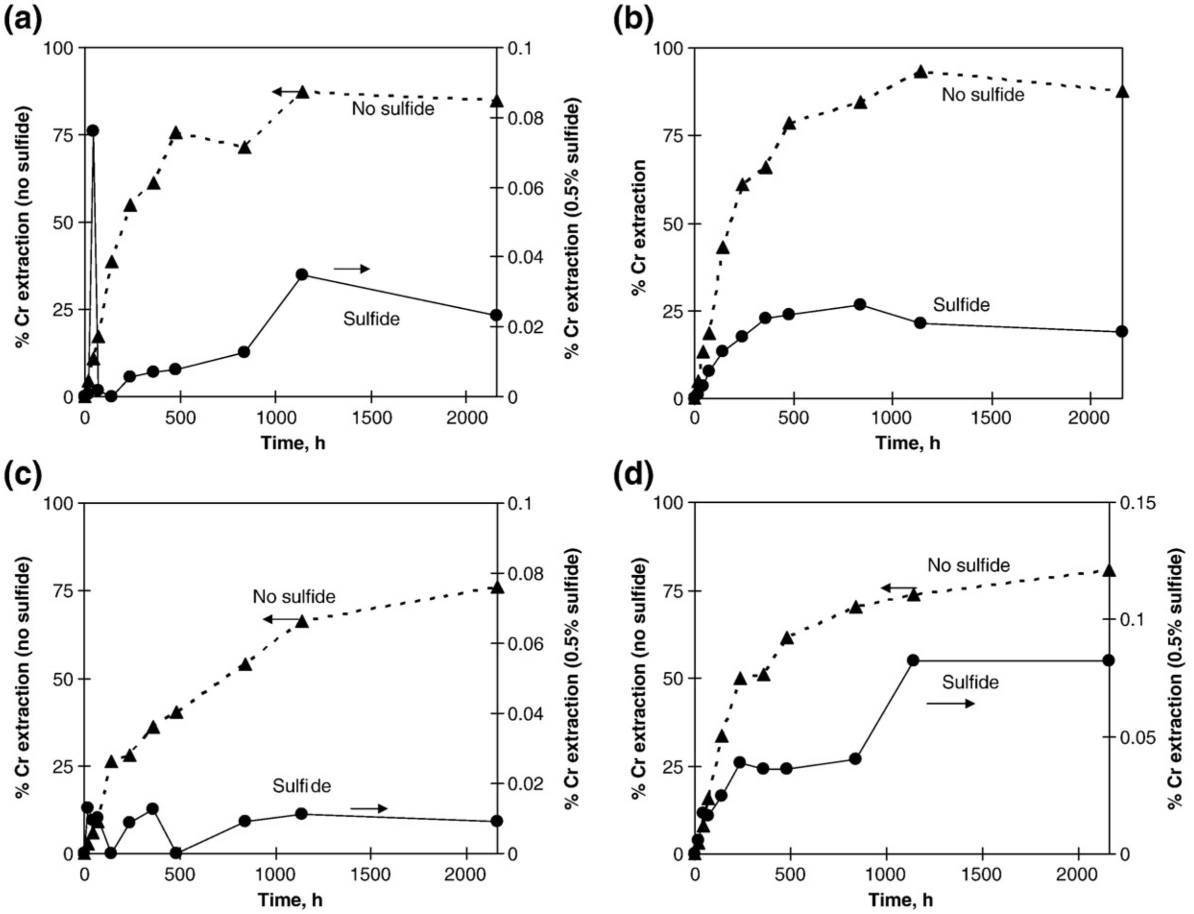

Fig. 4. Cr extraction into different leach solutions from geopolymers with 0.5% Cr added as Na_2CrO_4, in the presence and absence of sulfide. (a) Deionized water, (b) H_2SO_4 at an initial pH = 1.0, (c) 5.0% $MgSO_4$, and (d) 5.0% Na_2CO_3.

H_2SO_4 solution is related to the greater extent of matrix degradation in this system than in any of the other leach solutions studied, although both the apparent attainment of a steady state and the significant effect of sulfide tend to suggest that this effect is not dominant.

The first point in the 'sulfide' curve in Fig. 4a shows what appears to be a sharp initial spike in Cr concentration. It is not clear from the data whether this point is an outlier, or whether it represents a physical process taking place in the very early stages of the exposure of this sample to deionized water. It is well known that immersion of geopolymers in water results in a release of alkali and an increase in the pH of the water. It may therefore be that some small amount of Cr (~0.08% of the Cr present) was leached very early in this static test, (or was initially present on the sample surface) and then reprecipitated in the hydroxide form as the pH increased. Alternatively, this point may simply be an outlier, it is difficult to be certain at such small leaching extents.

It is also of note that the immobilization performance of the fly ash-based geopolymer for immobilization of Cr added as Na_2CrO_4 appears to be significantly better than the performance of comparable alkali-activated slag matrices [15]. It is proposed that this may be related to the higher Fe content of the ash used here compared to blast furnace slags; Fe is known to act as a catalyst for Cr reduction according to mechanisms outlined by Lan et al. [28].

Fig. 5 shows leaching results for the samples with Cr(VI) added as Pb_2CrO_4. The same trend is observed in Fig. 5 as was shown in Fig. 4 with regards to the nature of the leaching solution; water, Na_2CO_3 and $MgSO_4$ all show roughly similar extents of leaching, while H_2SO_4 again gives by far the highest extent of extraction. However, it is notable that the extent of Cr extraction observed in all the sulfide-containing samples in Fig. 5 is at least an order of magnitude higher than in Fig. 4, meaning that addition of 75% less Cr, and in a less soluble form, has decreased the immobilization efficiency markedly. This is also in contrast to the performance of the two sets of sulfide-free samples, in which the samples containing $PbCrO_4$ show significantly better immobilization than those with Na_2CrO_4.

The reasons for these differences in immobilization efficiency may be explained by reference to the binder chemistry. When a soluble salt such as Na_2CrO_4 is added and in the absence of a reductant, the Cr is readily available and leaches rapidly, so addition as sparingly soluble $PbCrO_4$ is preferable where no sulfide is used. Where Na_2S is added, the situation is reversed: the availability of Cr from the soluble salt means that it is more readily reduced by the S^{2-} and microencapsulated throughout the binder phase, possibly as insoluble $Cr(OH)_3$. However, if the Cr is added in sparingly soluble form, this process will not be completed prior to geopolymeric setting, and some remnant $PbCrO_4$ will then be available for leaching. This

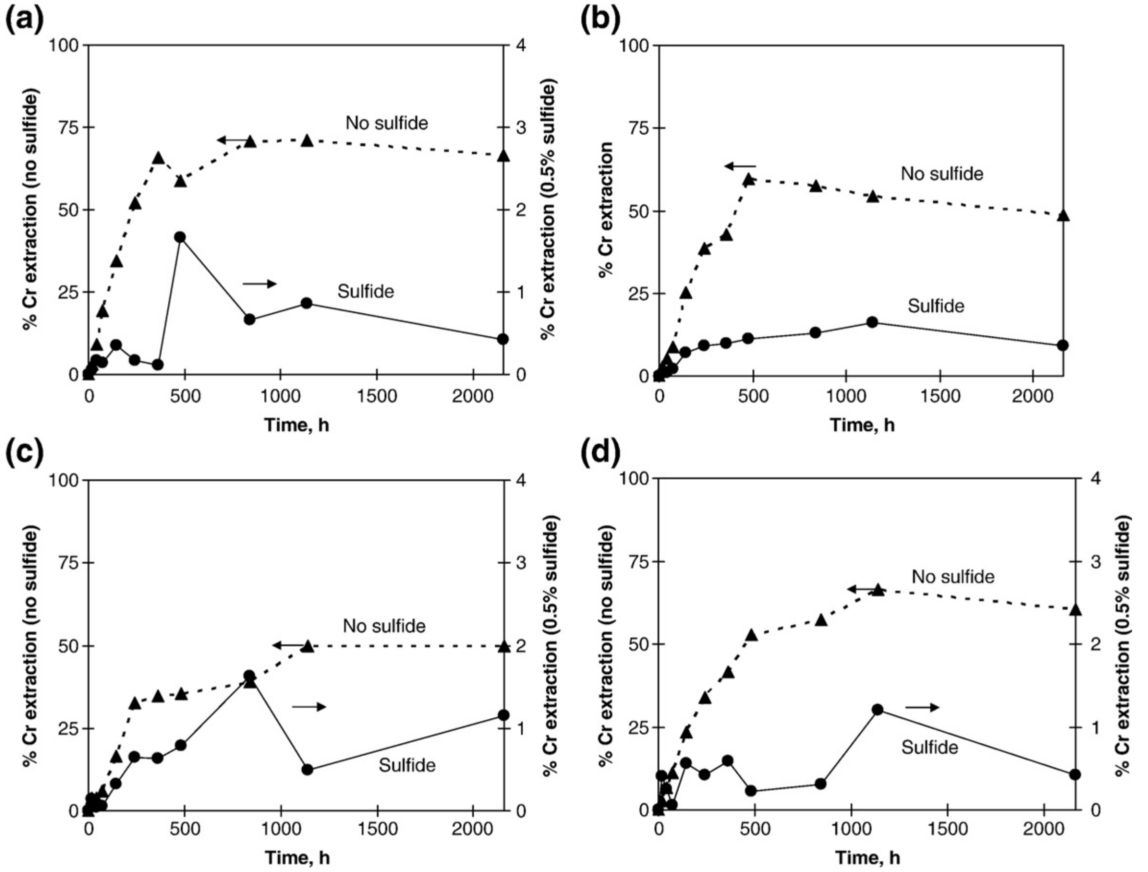

Fig. 5. Cr extraction into different leach solutions from geopolymers with 0.125% Cr added as $PbCrO_4$, in the presence and absence of sulfide. (a) Deionized water, (b) H_2SO_4 at an initial pH = 1.0, (c) 5.0% $MgSO_4$, and (d) 5.0% Na_2CO_3.

then explains the lower leach rate for the sulfide-free systems, but much higher leach rate for sulfide-containing systems, where Cr is added as $PbCrO_4$ compared to addition as Na_2CrO_4. This has some interesting implications for waste conditioning prior to immobilization in geopolymeric binders; it may be that some of the steps that are commonly taken to reduce the solubility of Cr in salt form before mixing with the immobilization matrix are in fact undesirable when the Cr is to be bound in a sulfide-containing geopolymer.

This work then has importance in terms of the use of geopolymers in 'real-world' immobilization applications. In an industrial context, it is much more likely that sulfide will be added to a geopolymeric matrix in the form of slag than as reagent-grade $Na_2S{\cdot}9H_2O$. Given that the conversion of slag to binder material within a geopolymeric matrix is likely to take place over a relatively extended time period, this ongoing S^{2-} release may assist in maintaining the Cr as Cr(III), even in oxidizing surroundings. However, further work is required to analyze the exact effects and mechanisms involved in this process, which necessitates a much fuller understanding of slag-geopolymer interactions and Cr redox chemistry in the geopolymer context than is currently available. It may also be that the addition of slag would enable the binding of remnant Cr (VI) as $CaCrO_4$ or within ettringite-type phases as discussed in Section 2 of this paper.

4. Conclusions

S^{2-} ions play a critical role in the immobilization of Cr(VI) in alkali-activated fly ash (geopolymer) matrices, by reducing Cr (VI) to Cr(III) and enabling precipitation in highly insoluble forms. Whereas chromium in sulfide-free geopolymers is highly mobile and very readily leached, addition of as little as 0.5% S^{2-} as $Na_2S{\cdot}9H_2O$ has been shown here to be highly effective in immobilizing Cr against attack by deionized water or mineral salt solutions for at least 90 days. Leaching efficiencies in excess of 99.9% are obtained when the Cr is initially added to the binder as Na_2CrO_4. Leaching in H_2SO_4 remains more problematic, most likely due to the re-oxidation of the Cr to highly mobile Cr (VI) species, but the addition of sulfide still provides a major increase in leaching resistance compared to a simple geopolymer binder. Addition of the Cr as a sparingly soluble salt actually provides less effective immobilization than does addition as a highly soluble salt in the presence of sulfide. This further demonstrates the importance of understanding binder chemistry and binder-contaminant interactions in the selection of the most appropriate immobilization process for a given waste stream, and highlights the value of geopolymer technology as one component of a suite of available heavy metal immobilization technologies.

Acknowledgements

The authors thank the Particulate Processing Centre (a Special Research Centre of the Australian Research Council), and The China Scholarship Council, for financial support of this research.

References

[1] P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. van Deventer, Geopolymer technology: the current state of the art, J. Mater. Sci. 42 (9) (2007) 2917–2933.

[2] J. Davidovits, D.C. Comrie, Long term durability of hazardous toxic and nuclear waste disposals, in: J. Davidovits, J. Orlinski (Eds.), Proceedings of Geopolymer '88 – First European Conference on Soft Mineralurgy, Universite de Technologie de Compeigne, Compeigne, France, 1988, pp. 125–134.

[3] J.G.S. van Jaarsveld, J.S.J. van Deventer, L. Lorenzen, The potential use of geopolymeric materials to immobilise toxic metals. 1. Theory and applications, Miner. Eng. 10 (7) (1997) 659–669.

[4] J.G.S. van Jaarsveld, J.S.J. van Deventer, A. Schwartzman, The potential use of geopolymeric materials to immobilise toxic metals: part II. Material and leaching characteristics, Miner. Eng. 12 (1) (1999) 75–91.

[5] J. Zhang, J.L. Provis, D. Feng, J.S.J. van Deventer, Geopolymers for immobilization of Cr^{6+}, Cd^{2+}, and Pb^{2+}, J Hazard Mater in press, DOI 10.1016/j.jhazmat.2008.01.053 (2008).

[6] A. Palomo, M. Palacios, Alkali-activated cementitious materials: alternative matrices for the immobilisation of hazardous wastes – Part II. Stabilisation of chromium and lead, Cem. Concr. Res. 33 (2) (2003) 289–295.

[7] M.L. Allan, L.E. Kukacka, Blast furnace slag-modified grouts for in situ stabilization of chromium-contaminated soil, Waste Manag. 15 (3) (1995) 193–202.

[8] F.P. Glasser, Fundamental aspects of cement solidification and stabilisation, J. Hazard. Mater. 52 (2–3) (1997) 151–170.

[9] G. Laforest, J. Duchesne, Immobilization of chromium (VI) evaluated by binding isotherms for ground granulated blast furnace slag and ordinary Portland cement, Cem. Concr. Res. 35 (12) (2005) 2322–2332.

[10] O.E. Omotoso, D.G. Ivey, R. Mikula, Quantitative X-ray diffraction analysis of chromium(III) doped tricalcium silicate pastes, Cem. Concr. Res. 26 (9) (1996) 1369–1379.

[11] A. Kindness, A. Macias, F.P. Glasser, Immobilization of chromium in cement matrices, Waste Manag. 14 (1) (1994) 3–11.

[12] S. Wang, C. Vipulanandan, Solidification/stabilization of Cr(VI) with cement. Leachability and XRD analyses, Cem. Concr. Res. 30 (2000) 385–389.

[13] C.D. Palmer, Precipitates in a Cr(VI)-contaminated concrete, Environ. Sci. Technol. 34 (19) (2000) 4185–4192.

[14] R.B. Perkins, C.D. Palmer, Solubility of chromate hydrocalumite ($3CaO{\cdot}Al_2O_3{\cdot}CaCrO_4{\cdot}nH_2O$) 5–75 °C, Cem. Concr. Res. 31 (7) (2001) 983–992.

[15] J. Deja, Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-activated slag binders, Cem. Concr. Res. 32 (12) (2002) 1971–1979.

[16] P. Bankowski, L. Zou, R. Hodges, Reduction of metal leaching in brown coal fly ash using geopolymers, J. Hazard. Mater. B114 (1–3) (2004) 59–67.

[17] C.K. Yip, J.S.J. van Deventer, Microanalysis of calcium silicate hydrate gel formed within a geopolymeric binder, J. Mater. Sci. 38 (18) (2003) 3851–3860.

[18] A. Buchwald, H. Hilbig, C. Kaps, Alkali-activated metakaolin-slag blends – performance and structure in dependence on their composition, J. Mater. Sci. 42 (9) (2007) 3024–3032.

[19] Y. Muntingh, M.Sc. Thesis, University of Stellenbosch, South Africa, 2006.

[20] F. Puertas, A. Fernández-Jiménez, Mineralogical and microstructural characterisation of alkali-activated fly ash/slag pastes, Cem. Concr. Compos. 25 (3) (2003) 287–292.

[21] C.K. Yip, G.C. Lukey, J.S.J. van Deventer, Effect of blast furnace slag addition on microstructure and properties of metakaolinite geopolymeric materials, Ceram. Trans. 153 (2003) 187–209.

[22] J.S.J. van Deventer, J.L. Provis, C.A. Rees, C.Z. Yong, P. Duxson, G.C. Lukey, Progress on research and commercialisation of geopolymers, in: Z. Ertl (Ed.), Alkali Activated Materials – Research, Production and Utilization, Agentura Action, Prague, Czech Republic, 2007, pp. 725–734.

[23] P. Duxson, J.L. Provis, G.C. Lukey, S.W. Mallicoat, W.M. Kriven, J.S.J. van Deventer, Understanding the relationship between geopolymer

composition, microstructure and mechanical properties, Colloids Surf., A 269 (1–3) (2005) 47–58.

[24] P. Duxson, S.W. Mallicoat, G.C. Lukey, W.M. Kriven, J.S.J. van Deventer, The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin-based geopolymers, Colloids Surf., A 292 (1) (2007) 8–20.

[25] H.R. Krouse, C.A. Viau, L.S. Eliuk, A. Ueda, S. Halas, Chemical and isotopic evidence of thermochemical sulphate reduction by light hydrocarbon gases in deep carbonate reservoirs, Nature 333 (6172) (1988) 415–419.

[26] C.A. Rees, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, ATR-FTIR analysis of fly ash geopolymer gel ageing, Langmuir 23 (15) (2007) 8170–8179.

[27] C.A. Rees, J.L. Provis, G.C. Lukey, J.S.J. van Deventer, In situ ATR-FTIR study of the early stages of fly ash geopolymer gel formation, Langmuir 23 (17) (2007) 9076–9082.

[28] Y. Lan, B. Deng, C. Kim, E.C. Thornton, Influence of soil minerals on chromium(VI) reduction by sulfide under anoxic conditions, Geochem. Trans. 8 (4) (2007), doi:10.1186/1467-4866-1188-1184.