Cement & Concrete Composites 41 (2013) 29–33

Contents lists available at SciVerse ScienceDirect

Cement & Concrete Composites

journal homepage: www.elsevier.com/locate/cemconcomp

Bayer-geopolymers: An exploration of synergy between the alumina and geopolymer industries

Arie van Riessen [a,*], Evan Jamieson [b], Catherine S. Kealley [a], Robert D. Hart [a], Ross P. Williams [a]

[a] Centre for Materials Research, Curtin University, GPO Box U1987, Perth, WA 6845, Australia
[b] Technology Delivery Group, Alcoa of Australia, PO Box 161, Kwinana, WA 6966, Australia

ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form 15 April 2013
Accepted 24 April 2013
Available online 3 May 2013

Keywords:
Geopolymer
Bayer liquor
Alumina
Fly ash
Sodium aluminate

ABSTRACT

Previously, caustic residues such as red mud and sodium oxalate have been used to provide filler and as a supplementary source of alkali for geopolymers. However, rather than incorporation of dilute alkali residues within geopolymer precursors, a significant counter-intuitive approach is to synthesise geopolymers using Bayer process liquors as a primary source of caustic sodium aluminate and to add locally available fly ash as a source of reactive silica and additional alumina.

In addition to the potential for using significant quantities of industrial residues to manufacture geopolymers, these relatively new cements have the ability to bind a range of contaminants. As the Bayer process could achieve significant process impurity removal by utilisation of plant liquor, synergy between the alumina and geopolymer industries could be achieved.

Geopolymers with a Si/Al ratio of 2.3 and a Na/Al ratio of 0.8 were targeted. With only synthetic plant liquor as the alkali activator, geopolymers with a mean compressive strength of 33 MPa were synthesised, while use of processed plant liquor resulted in compressive strengths of 43 MPa.

1. Introduction

1.1. Geopolymer industry

Aluminosilicate inorganic polymers or geopolymers are amorphous materials that have the potential to replace Ordinary Portland Cement (OPC) as cementitious binders. Advantages geopolymers have over OPC include; their high compressive and flexural strength, high temperature resistance, and impressive acid resistance [1–3]. Another potential benefit from the replacement of OPC by geopolymer cements is the reduction in CO_2 emissions. One tonne of OPC releases approximately 0.95 tonnes of CO_2 while geopolymer production creates only between 0.2 and 0.5 tonnes of CO_2 per tonne of product, depending on inclusion of lifecycle and transport factors [4–6]. Geopolymers also have the potential to incorporate cations, anions and organic species within their 3-dimensional structure [7,8]. Geopolymers have been considered as a replacement for OPC in applications such as cement pathways, pavers, mine backfill, railway sleepers, sewerage pipes and earth retaining walls [9–12].

Geoploymers have been formed from a range of aluminate and silicate materials including metakaolin, fly ash, blast furnace slags and mineral processing wastes [13]. Knowledge of the chemistry of the reactive feedstock components may be used to design geopolymer materials with predicted end properties thus avoiding a process of trial and error [9,13–17]. The critical feed stocks for a geopolymer include; (i) caustic soda, (ii) soluble silica, and (iii) soluble alumina. All three feed stocks must be available in large quantities and at a cost appropriate for commercial applications.

The standard preparation of geopolymers usually requires a solution containing a high concentration of caustic soda with dissolved silica (or sodium silicate) being added to a soluble source of silica and alumina (usually fly ash, metakaolin or blast furnace slag) [18]. This is the usual method of making geopolymer binders with Si/Al of around 2. Brew and MacKenzie [18] and Phair and van Deventer [19] demonstrated that geopolymers may also be made from caustic sodium aluminate starting solutions which are added to sources of soluble silica.

Geopolymers are commonly cured at slightly elevated temperatures (~70–90 °C); addition of calcium-containing compounds such a lime or blast furnace slags can promote ambient temperature setting [20].

1.2. Alumina industry

In the Bayer process for the production of alumina from bauxitic ores, gibbsite and/or boehmite rich materials are digested in highly caustic solutions at elevated temperatures. The remaining solids, usually iron oxides, quartz and other resistant minerals, are sepa-

---

* Corresponding author. Tel.: +61 8 9266 7090; fax: +61 8 9266 2377.
E-mail address: a.vanriessen@curtin.edu.au (A. van Riessen).

0958-9465/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.cemconcomp.2013.04.010

rated from the sodium aluminate slurry in a sand trap and thickener. The solids (red mud and red sand) are counter current washed to recover the caustic solutions and then pumped to drying beds. The mud and sand may be treated and stored separately and have been recovered for reuse [21–23]. A number of papers have described use of the mud as a source of aluminosilicate for manufacture of geopolymer or simply as a filler in geopolymer [24]. It should be noted that a detailed review of Bayer residue is outside the scope of this paper and readers are directed to Klauber et al. [25] for further information. The remaining valuable caustic liquor is recovered via an underdrain system and returned to the Bayer process circuit. The thickener overflow solution concentrated in aluminate is cooled then aluminium hydroxide (hydrate seed) is added to induce further precipitation. The precipitated aluminium hydroxide product is then separated from the spent caustic aluminate liquor which is returned to the process circuit. During the constant recirculation of caustic liquor, organic and inorganic impurities can build up within the circuit and suppress alumina yield. Some impurities such as sulphate can be removed through the "Desilication" process in which reactive silica is added to the process and then reacts with caustic and alumina to form an alumino-silicate 'desilication product' predominantly either sodalite or cancrinite [26]. In some refineries, a significant amount of organic material is also dissolved in the aluminate solution reducing productivity in many different ways. In addition the organics are oxidised to oxalate which may precipitate with hydrated alumina thus causing quality issues. There are many impurities for which there are no commercial removal processes.

1.3. The synergy

Economic evaluations of geopolymer production recognise that the supply of caustic is the most significant cost factor. The economic benefit of utilising concentrated sodium aluminate from the Bayer process varies between locations and would be considered commercially confidential, but has resulted in a patent application [27]. The economics of the Bayer process are contingent upon the capture and return of soda for further processing; thus is often called the Bayer cycle. The concept that Bayer process liquor could become a geopolymer feedstock is thus counter intuitive.

Processing the Bayer liquor so that it is a suitable feedstock for the geopolymer industry, transforms the export of that liquor and its replacement with fresh sodium hydroxide into an impurity removal process [27]. The use of process Bayer liquor for geopolymer manufacture will provide a mechanism for removing soluble impurities (organic and inorganic) from the alkaline process circuit. This aspect of Bayer geopolymer will not be addressed in this paper. The potential synergy between the alumina and geopolymer industries is significant; the Bayer process achieves substantial impurity removal and the geopolymer industry gains a potentially economic source of caustic.

Further advantages are that the alumina industry is well established with significant infrastructure such as road, rail and port hubs and it has teams of skilled scientists, engineers and operators that are trained in working with caustic aluminate solutions. The industry has traditionally been a major consumer of caustic and has significant quantities of "low value" steam (i.e. saturated temperature <100 °C). Finally the development of other secondary commodity products from the alumina industry is potentially synergistic with geopolymer production (for example, process sand, and calcium carbonate).

Table 1
Composition of Bayer liquors used to synthesis geopolymers.

	Al_2O_3 (wt.%)	Na_2O (wt.%)	H_2O (wt.%)
Synthetic sodium aluminate liquor	15	21	64
Processed plant liquor	15	24	61

Table 2
Bulk composition (XRF) of fly ash obtained from the Collie Power Station.

Oxide	wt.%
SiO_2	49.9(2)
Al_2O_3	24.8(2)
Fe_2O_3	16.60(4)
CaO	1.79(10)
K_2O	0.61(8)
TiO_2	1.36(2)
MgO	1.31(6)
Na_2O	0.4(1)
P_2O_5	1.52(4)
SrO	0.33(1)
BaO	0.45(1)
Other (includes LOI)	0.7(1)
Si/Al (molar ratio)	1.71(1)

Values in parentheses in this and all further tables correspond to the least significant figure in the estimated standard deviation to the left.

Table 3
The phase composition of Collie fly ash as determined by Rietveld quantitative analysis.

Mineral/Phase	wt.%
Primary quartz	13(1)
Secondary quartz	11.0(2)
Hematite	2.42(8)
Magnetite	2.0(1)
Mullite	14(1)
Maghemite C	6.6(3)
Amorphous	51(1)

Table 4
Composition of amorphous component of Collie fly ash.

Oxide	Amorphous (wt.%)
SiO_2	21(2)
Al_2O_3	15(1)
Sum of aluminosilicates	36 (3)
Si/Al (molar ratio)	1.2(1)

2. Experimental

2.1. Characterisation

The composition of the reactive component of the fly ash was determined using the method of Williams and van Riessen [14]; the composition of the reactive amorphous component is determined by subtracting the crystalline composition of the fly ash as determined by quantitative XRD phase analysis from the bulk chemical composition total analysis as determined by XRF. The XRF analysis was carried out by Ultratrace, a commercial Western Australian analytical laboratory. The sample preparation included grinding to a particle size of less than 75 μm and fusion in a lithium borate (Norrish 12:22) flux. The uncertainties quoted are based on the variation in the determination of standards with known compositions.

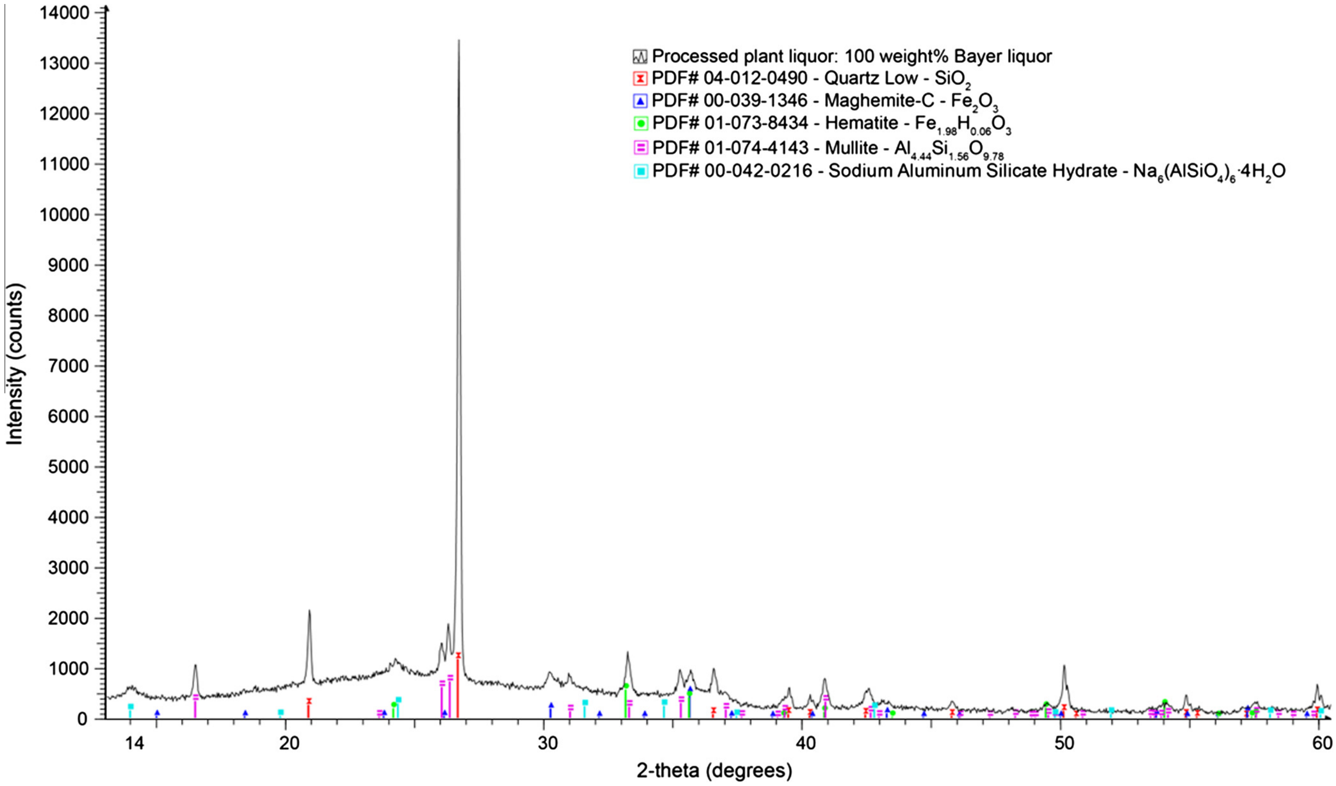

Fig. 1. XRD pattern of geopolymer made with 100 wt.% plant Bayer liquor.

The crystalline composition of the precursor fly ash and the geopolymers were obtained on an absolute scale using Rietveld refinement with XRD data. The samples were prepared by milling to ~5 µm particle size using a McCrone mill with calcium fluorite (Mesh −325, 99.5+%, Sigma Aldrich) as an internal standard. XRD patterns were obtained using Cu Kα radiation with a Bruker D8 Advance diffractometer equipped with a LynxEye detector (Bruker-AXS, Karlsruhe, Germany). The patterns were collected from 10° to 100° 2θ, with a nominal step size of 0.01°2θ and a collection time of 0.8 s per step, using a 0.3° divergence slit and 2.5° secondary Soller slit. A knife edge collimator and tight detector discriminator settings were applied to reduce air scatter and iron fluorescence signals.

Crystalline phases were identified by using the Search/Match algorithm, EVA 15.0 (Bruker-AXS, Germany) to search the Powder Diffraction File (PDF4 + 2009 edition). Relevant crystal structures used to carry out the Rietveld quantitative phase analysis using TOPAS 4.2 (Bruker-AXS, Germany) were obtained from the Inorganic Crystal Structure Database (ICSD 2009/2). Four replicates of each sample were micronized, measured and modelled independently to obtain an estimate of the uncertainty in the quantification. The quality of the fit of the refined structure models to the data was determined by visual inspection of the difference plot and also statistically by figures of merit and the estimated standard deviation of individual parameters. The figures of merit used were the weighted profile factor (R_{wp}) and the goodness of fit.

Compressive strength tests were carried using ASTM C39 for concrete specimens. For small specimens (25 mm diameter) the method was approximated; cylindrical specimens with a 2:1 height to diameter ratio were used and the strength tests were conducted on a Lloyds Instruments 6000R compressive/tensile strength machine fitted with a 50 kN load cell. Six samples from each formulation were tested and the mean and standard deviations reported.

Scanning electron microscopy (SEM) was conducted to determine the extent of reaction of the alkali activators with the aluminosilicates and the homogeneity of the microstructure. Gold coated fracture surfaces were viewed with a Zeiss Neon 40EsB.

2.2. Materials

Synthetic Bayer liquor, i.e. a clean sodium aluminate solution, and processed plant liquor were tested. The synthetic liquor corresponds to typical process plant concentrations without the associated impurities. The plant liquor provided by Alcoa of Australia Limited was processed to provide an activated feedstock. Table 1 shows the analyses of the two liquors used in this project.

Class F fly ash, used as a source of reactive silica and additional alumina, was obtained from the Collie Power Station, Western Australia. The elemental composition (XRF) in the oxide form is given in Table 2. Quantitative phase abundance as determined by Rietveld refinement with XRD data is provided in Table 3. By subtracting the crystalline phases from the bulk XRF results the composition of the amorphous component can be determined. It should be noted that crystalline phases below the detection limit of XRD analysis are included in the amorphous component. As these minor phases (including amorphous iron oxides) are not believed to play a role in the geopolymerisation process they have been excluded from the amorphous composition, thus reducing the amorphous component from 51 wt.% (Table 3) to 36 wt.% (Table 4). A detailed analysis of the fly ash has been provided previously [16,17].

To achieve specific Si/Al ratios, silica fume (Doral Fused Materials Ltd., 94% purity) was also included in the formulation.

2.3. Synthesis

On the basis of previous research with Collie fly ash, a geopolymer composition with a Si/Al = 2.3, Na/Al = 0.8 and H/

Table 5
Compressive strength results for the fly ash based geopolymer with increasing amounts of Bayer Liquor substitution. Target Si/Al = 2.3 and Na/Al = 0.8.

Liquor	%wt. Bayer liquor (replacing NaOH)	Compressive Strength (MPa)
NaOH	0	45(5)
Synthetic sodium aluminate liquor	60	28(3)
	80	30(3)
	100	33(6)
Processed plant liquor	60	41(6)
	80	43(5)
	100	43(4)

Si = 5.5 was targeted [1,14,16,17]. Reactive component calculations were used instead of direct measurement of the matrix composition [15]. To determine the effectiveness of the Bayer liquor as a source of alkali and alumina, a series of geopolymer mixes were made with varying ratios of caustic in the form of sodium silicate solution and as sodium aluminate liquor (Bayer liquor). For pastes made with 0%, 60% or 80% (wt.%) replacement of sodium hydroxide by Bayer liquor, sodium silicate solutions were prepared by dissolving silica fume (Doral Fused Materials Ltd.) in sodium hydroxide solution (AR Grade, Sigma–Aldrich, St. Louis, MO) at 70 °C.

For 100% replacement of sodium hydroxide by synthetic or plant Bayer liquor, fly ash was mixed with silica fume as dry powders, followed by the addition of Bayer liquor. These were mixed for a period of 10 min and placed into 25 mm diameter vials and sealed. The samples were cured at 70 °C for 24 h, then left at room temperature for a period of 28 days prior to compressive strength testing.

3. Results

The crystalline phases in the fly ash were identified by search/match of the PDF4 + database and found to be quartz (PDF 01-086-1560), hematite (PDF 01-089-0599), magnetite (PDF 01-079-0416), maghemite C (PDF 01-076-4113) and mullite. Mullite is a solid solution (with eta-alumina and sillimanite as end members); the best mullite structure to use was chosen on the basis of accurate determination of the lattice parameter by a Pauli refinement which is described in Williams and van Riessen [14].

Table 4 shows that 36 wt.% of the fly ash is amorphous aluminosilicate. It is important to note that the total (bulk) Si/Al ratio of 1.71 is quite different to the Si/Al ratio in the amorphous (considered to be the reactive component [14]) component of the fly ash which is 1.18. The crystalline components determined by Rietveld quantitative phase analysis (RQPA) are shown in Table 3. The crystalline structures for the phases quantified by RQPA in the fly ash samples were fluorite (the internal standard CaF_2 ICSD#60559), quartz (SiO_2 ICSD#100341), mullite ($Al_{3.9}Si_{1.6}O_{9.8}$ ICSD#89721), hematite (Fe_2O_3 ICSD#82137), magnetite (Fe_3O_4 ICSD#822370) and maghemite C ($Fe_{2.1}O_{2.7}$ ICSD#87119). There were two populations of quartz present; primary quartz with a large crystallite size and secondary quartz with very small crystallite size.

XRD patterns of the plant liquor geopolymers showed the expected phases quartz, mullite, maghemite and hematite from the fly ash plus a new minor phase, sodium aluminium silicate hydrate (PDF# 00-042-0216). The amorphous geopolymer was recognisable from the broad hump in the pattern centred at ~26°2θ (Fig. 1).

The compressive strengths of the synthetic and plant Bayer liquor geopolymers are shown in Table 5. The compressive strength

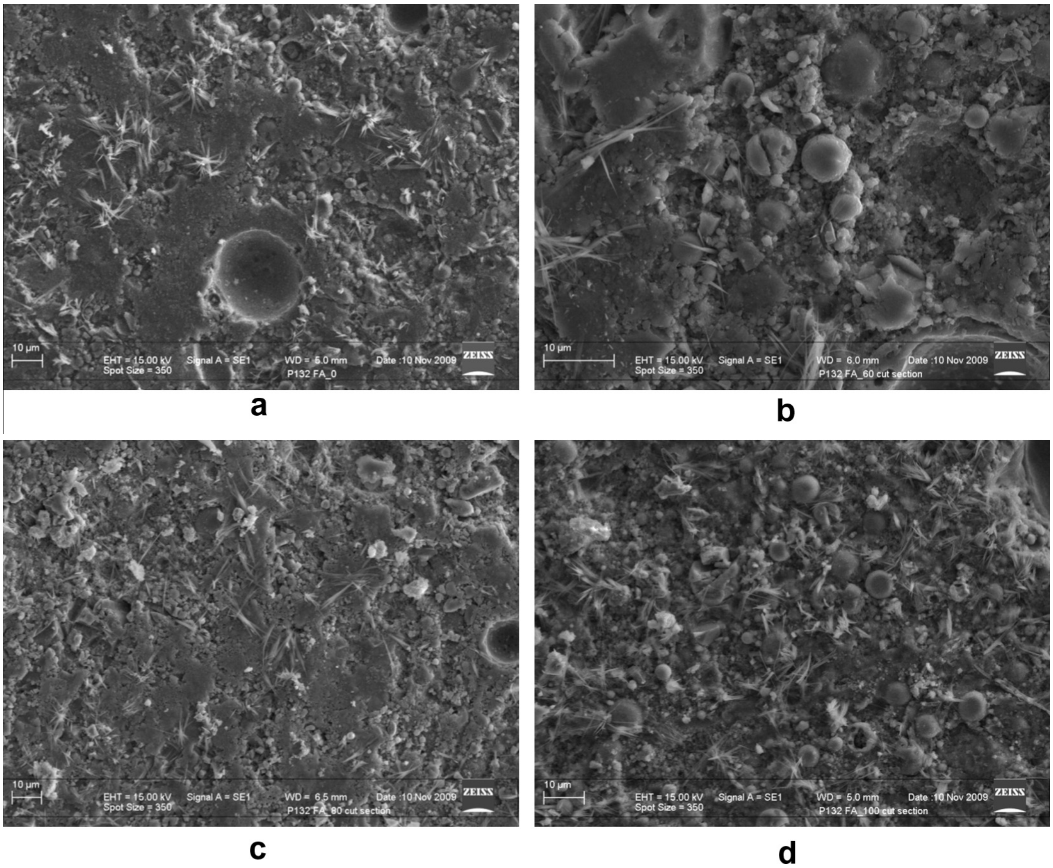

Fig. 2. SEM images showing typical microstructure of each of the samples, with a) 0%, b) 60%, c) 80% and d) 100% synthetic sodium aluminate Bayer liquor substitution.

of the reference geopolymer, produced without Bayer liquor, was 45 MPa. The addition of synthetic Bayer liquor produced geopolymers of slightly lower compressive strengths but consistent with samples from 60% to 100% synthetic Bayer replacement. For the 60–100% substituted processed Bayer plant liquor geopolymers, the compressive strength was again consistent. In fact the strength values were the same as for the 0% Bayer liquor sample within experimental uncertainties.

SEM images of fracture surfaces show a homogeneous microstructure for all samples. There were no obvious differences between samples made with different levels of Bayer. Fig. 2 show typical microstructures.

4. Conclusions

The reference geopolymer produced without Bayer liquor had a compressive strength of 45 MPa. Remarkably, the compressive strengths of the plant Bayer liquor samples were higher than the samples made with synthetic liquor. In addition, the amount of Bayer liquor used to replace NaOH did not have any impact on the compressive strength. This outcome clearly indicates that the contaminants in the plant liquor have no detrimental impact on geopolymerisation or strength development.

The research project has demonstrated that Bayer liquor can be utilised for the production of geopolymer products. The use of plant Bayer liquor as feed stock for the formation of geopolymer, acts as an impurity removal process for the Bayer process. This can partially offset the cost disadvantages associated with replacing the caustic liquor and suggests that the synergy between the alumina and geopolymer industries could be significant, even industry changing.

The combination of fly ash and plant Bayer liquor is a synergistic combination of two industrial by-products. The potential for extending this synergy further is significant and could lead to a new industry with attractive economic and environmental credentials.

Acknowledgement

Emily Xie is thanked for her efforts in sample preparation and data collection.

References

[1] Rangan BV. Studies on fly ash-based geopolymer concrete. Malays Constr Res J 2008;3:1–20.

[2] Rickard WDA, van Riessen A, Walls P. Thermal character of geopolymers synthesized from Class F fly ash containing high concentrations of iron and α-quartz. Int J Appl Ceram Technol 2010;7:81–8.

[3] Temuujin J, Minjigmaa A, Lee M, Chen-Tan N, van Riessen A. Characterisation of Class F fly ash geopolymer pastes immersed in acid and alkaline solutions. Cem Concr Compos 2011;33:1086–91.

[4] McLellan BC, Williams RP, Lay J, van Riessen A, Corder GD. Costs and carbon emissions for geopolymer pastes in comparison to ordinary Portland cement. J Clean Prod 2011;19:1080–90.

[5] Davidovits J. Geopolymer cements to minimise carbon dioxide greenhouse warming. Ceram Trans 1993;37:165–82.

[6] Davidovits J. Environmentally driven geopolymer cement applications. In: Williams JR, editor. Geopolymer 2002 third international conference: turning potential into profit, Geopolymer Institute, Melbourne.

[7] Tavor D, Wolfson A, Shamaev A, Shvarzman A. Recycling of industrial waste water by its immobilization in geopolymer cement. Ind Eng Chem Res 2007;46:6801–5.

[8] van Deventer JSJ, Provis JL, Duxson P, Lukey GC. Reaction mechanisms in the geopolymeric conversion of inorganic waste to useful products. J Hazard Mater 2007;A139:506–13.

[9] Avraamides J, van Riessen A, Jamieson E. Transforming mining residues into viable by-products. Energy Generation 2010:1–3.

[10] Gourley JT. Geopolymers; opportunities for environmentally friendly construction materials. Materials 2003 Conference: Adaptive Materials for a Modern Society, Sydney.

[11] Gourley JT, Johnson GB. Developments in geopolymer precast concrete. In: International workshop on geopolymers and geopolymer concrete, Perth, Australia; 2005.

[12] Southam DC, Brent GF, Felipe F, Carr C, Hart RD, Wright K. Towards more sustainable mine fills — Replacement of ordinary Portland cement with geopolymer cements. In: World gold conference Cairns, QLD; 2007:22–24.

[13] Hart RD, Lowe JL, Southam DC, Perera DS, Walls P, Vance ER, et al. Aluminosilicate inorganic polymers from waste materials. In: Proceedings, green processing, third international conference on sustainable processing of minerals and metals, Newcastle, Australia; 2006.

[14] Williams RP, van Riessen A. Determination of the reactive component of fly ashes for geopolymer production using XRF and XRD. Fuel 2010;89:3683–92.

[15] Williams RP, Hart RD, van Riessen A. Quantification of the extent of reaction of metakaolin-based geopolymers. J Am Ceram Soc 2011;94:2663–70.

[16] Chen-Tan NW, van Riessen A, Ly CV, Southam DC. Determining the reactivity of a fly ash for production of geopolymer. J Am Ceram Soc 2009;92(4):881–7.

[17] Rickard WDA, Williams RP, Temuujin J, van Riessen A. Assessing the suitability of three Australian fly ashes as an aluminosilicate source for geopolymers in high temperature applications. Mater Sci Eng A 2011;528:3390–7.

[18] Brew DRM, MacKenzie KJD. Geopolymer synthesis using silica fume and sodium aluminate. J Mater Sci 2007;42:3990–3.

[19] Phair J, van Deventer JSJ. Characterization of fly ash based geopolymeric binders activated with sodium aluminate. American Chemical Society [Web published 07/17/2002].

[20] Xu H, van Deventer JSJ. Geopolymerisation of multiple minerals. Miner Eng 2002;15:1131–9.

[21] Sriwahyuni A, Nikraz H, Jamieson E, Cooling D. Sustainable use of bauxite residue sand (red sand) in concrete. In: Proceedings, green processing, third international conference on sustainable processing of minerals and metals. Newcastle, Australia; 2006.

[22] Jitsangiam P, Nikraz H, Jamieson E. Sustainable use of a bauxite residue (red sand) in terms of roadway materials. In: second international conference on sustainable engineering and science. Auckland, New Zealand; February 2007.

[23] Jitsangiam P, Nikraz H, Jamieson E, Kitanovich R, Siripun K. Sustainable use of a bauxite residue (red sand) as highway embankment materials. In: third international conference on sustainability engineering and science. Auckland, New Zealand; 2008.

[24] He J, Jie Y, Zhang J, Yu Y, Zhang G. Synthesis and characterisation of red mud and rice husk ash-based geopolymer composites. Cem Concr Compos 2013;37:108–18.

[25] Klauber C, Gräfe M, Power G. Bauxite residue issues: II. Options for residue utilization. Hydrometallurgy 2011;108:11–32.

[26] Smith PG, Xu BG, Wingate CJ. Transformation of sodalite to cancrinite under high temperature Bayer digestion conditions. Light Metals. San Francisco, CA, USA: TMS; 2009. p. 51–6.

[27] Jamieson EJ. Method for management of contaminants in alkaline process liquors. International patent WO 2008/017109 A1, 14th February 2008.