

Modelling of the glass phase in fly ashes using network connectivity theory[†]

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Abstract: The amorphous phase of fly ash dominates degradation behaviour because glass has a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass make the bond breakage easier. It would be advantageous to predict the presence and subsequent degradability of glass on the basis of the solid-state chemistry of the fly ash. To this end, and inorganic polymer model was applied to a selection of European fly ashes to determine the value known as cross-link density (CLD). A cross-link density value of less than two implies that the material is amorphous in nature and the lower the CLD below two, the greater the reactivity and solubility of the glass. Applying this model may facilitate the selection of the most suitable fly ash for a particular recycling application where glass reactivity or dissolution rates are important. To check the applicability of the model to the glass phase of fly ashes, CLD calculations have been performed by removing the contribution to the ash composition from the known crystal phases. The model would be then expected to give a maximum CLD value of two for all the materials. While this approach has been applied successfully to synthetic glasses and glass-ceramics in the past, only very limited applicability has been found with fly ashes. This is believed to be due to the inherent heterogeneity of the glass phase in fly ash.

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INTRODUCTION

Large volumes of fly ashes are produced by coal-burning power plants worldwide and it is becoming increasingly important to find ways of utilising this waste material. Currently, only a small percentage of fly ash is recycled, mainly by the cement industry, and the remainder ends up in large ponds or landfill sites.¹ Fly ashes are highly complex multiphase materials containing various amorphous and crystalline phases. Due to the highly heterogeneous nature of the coal used, as well as variations in the combustion process, the physical and chemical properties of the ashes vary on a plant by plant basis.

Fly ash mainly consists of the inorganic content of coal left behind after the combustion process. The crystalline phases are widely regarded as forming by direct solid state reaction from the mineral phases present in the coal.² Table 1 summarises the principal phases found in various coals and the phases formed after combustion.

The types of crystal phase, the amount present and their distribution therefore directly reflect the content

and distribution of mineral phases in the original coal as well as the combustion technology used. This is the accepted view.² An alternative view is that the crystalline phases present in fly ashes may form, not directly by solid state reaction, but upon crystallisation by cooling of a largely amorphous glass melt. In this case, equilibrium phase diagrams could be employed to make predictions as to what crystalline phases should form on cooling. The principal crystalline phases present in fly ash formed by the combustion of bituminous coals are mullite, quartz, magnetite/haematite and lime in minor amounts, whilst the crystalline phases in high-calcium lignite-based coals are quartz, lime, anorthite, mullite and anhydrite. These phases are the ones predicted from the CaO–SiO₂–Al₂O₃ and Fe₂O₃–SiO₂–Al₂O₃ phase diagrams, and thus are expected to be present upon cooling the ash from the molten state. However, the ternary phase diagrams are based on heterogeneous dissolution of elements in the fly ash and this does not occur in practice. Furthermore, the ternary phase diagram is only pertinent under equilibrium conditions and even

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Table 1. The principal phases found in coals and the phases formed after combustion

Common coal minerals	Chemical formula	Phases formed after combustion	Chemical formula
Quartz	SiO ₂	Quartz	SiO ₂
Kaolinite	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	Mullite	Al ₆ Si ₂ O ₁₃
Illites	K ₂ O·3Al ₂ O ₃ ·6SiO ₂ ·2H ₂ O	Mullite	Al ₆ Si ₂ O ₁₃
Pyrite	FeS ₂	Haematite, magnetite, iron sulfide	Fe ₂ O ₃ , FeO, FeS
Calcite	CaCO ₃	Lime, anhydrite	CaO, CaSO ₄
Siderite	FeCO ₃	Haematite, magnetite	Fe ₂ O ₃ , FeO

then will only approximate crudely to the multi-component fly ash compositions. Therefore, detailed analysis on the basis of the phase diagram is not possible.

Evidence for the view that crystalline phases form by crystallisation of an amorphous melt is supported by the spherical shape of many fly ash particles,³ which suggests that the particles have gone through a viscous fluid state. This latter view emphasises the glassy amorphous nature of fly ashes. It is the amorphous phase in a fly ash that will dominate the pozzolanic behaviour as well as degradation under both alkaline and acid conditions. Glasses have a higher potential energy than the equivalent crystal structure and the variation of bond angles and distances in a glass facilitate bond breakage. It is the degradation behaviour of fly ashes under alkaline conditions that is important in the use of fly ash as an additive in Portland cement and also for the potential synthesis of zeolites. It should be borne in mind, however, that it is very difficult to determine any kind of absolute understanding of the glass in a given fly ash because of the complex inter- and intra-particle heterogeneity of these materials.⁴

It would be desirable to predict the formation of certain phases such as mullite (Al₆Si₂O₁₃) because of its industrial applications as, for example, a refractory ceramic. It would therefore be useful if one could develop a way of evaluating the likelihood of mullite formation in a fly ash on the basis of the solid-state chemistry of the glass phase.

An approach to predicting the presence of mullite in fly ashes is to use Lowenstein's structural criteria for aluminosilicates.⁵ Lowenstein defined important restrictions on the amount of aluminium that may be present in either crystalline or amorphous aluminosilicates and Lowenstein's criteria are based on an interpretation of Pauling's Electrostatic Valence rule.⁶ He has stated that whenever two tetrahedra are linked by a single bridging oxygen then the centre of only one of them may be occupied by an aluminium atom and the other centre must be occupied by silicon or another small ion with an electrovalence of four or more, such as phosphorus. Also, whenever two aluminium ions are linked by a bridging oxygen anion, then at least one of them must be in a five or six co-ordinate state towards oxygen. These criteria impose a limit of 50% for aluminium substitution in silicate minerals (ie the

Si:Al ratio must be greater than or equal to one) and, indeed, this limit is observed in nature; for example in anorthite, Ca(Al₂Si₂O₈). Where this limit is realised, silicate and aluminate tetrahedra must occur in strict alternation in the network to avoid electrostatic instability. Therefore, Lowenstein's criteria have important implications for the crystallisation of aluminosilicate glasses in that exceeding the 50% substitution limit (by having an Si:Al ratio <1) in the glass will result in electrostatic instability and lead to the crystallisation of aluminium-containing crystalline phases such as mullite in which aluminium is in higher co-ordination states than four.

For aluminium to take up a four co-ordinate state in an aluminosilicate network two rules must be obeyed:

- (1) A charge balancing cation must be present to compensate for the 3⁺ charge of aluminium when surrounded by four oxygens.
- (2) The Si:Al ratio must be greater than one in order to avoid aluminium atoms being in adjacent tetrahedral sites.

Co-ordination states greater than four are unfavourable for glass formation and generally result in aluminium crystallising out of the glass in the form of phases where the aluminium atoms are in a higher coordination state. The composition of the glass phase/s present in fly ashes will influence the degradation behaviour. Two factors are likely to dominate the degradation behaviour:

- (1) The silicon to aluminium ratio of the glass. A high Si:Al ratio will favour alkaline hydrolysis, whilst a low Si:Al ratio will favour acid hydrolysis.⁷
- (2) The extent of network disruption and the number of non-bridging oxygens present will influence degradation. High network modifier contents in the fly ash such as K, Na, Mg and Ca⁸ will result in formation of non-bridging oxygens once all the aluminium atoms have been charged balanced. The greater the degree of disruption of the glass network, the greater the susceptibility of the glass to degradation.

Ray⁹ regarded inorganic glasses as network polymers and used two terms, network connectivity and cross-link density (CLD), to characterise glass structure. Ray⁹ used the CLD parameter to predict the properties of glasses and in particular the glass transition

Power station	Power (MW)	Power company	Location
Teruel	1050	ENDESA	North-east Spain
Escucha	160	FECSA	North-east Spain
Robla	625	Unión FENOSA	Northern Spain
Compos	1312	ENDESA	Northern Spain
Meirama	550	Unión FENOSA	Northern Spain
Narcea	569	Unión FENOSA	Northern Spain
Pontes	1400	ENDESA	North-west Spain
Puerto	220	ENECO	Central Spain
Espiel	938	ENECO	Southern Spain
Barrios	550	SE	Southern Spain
Sribera	672	IBERDROLA/E Bierzo	Northern Spain
Alkaline	450	EP2	The Netherlands
Nijmegen	600	Centrale Gelderland	The Netherlands
Neutral	600	EPZ	The Netherlands
CCB	600	Centrale Borssele	The Netherlands
Acid	600	EPZ	The Netherlands
Amer-8	600	Amer Centrale	The Netherlands
Amer-9	600	Amer Centrale	The Netherlands
Hemweg8	600	Centrale Amsterdam	The Netherlands
Lignite	Unknown	AMYNTAION and LKPA	Northern Greece
Fusina	980	ENEL SpA	Italy
Monfalcone	336	ENEL SpA	Italy
Sardegna	Unknown	ENEL SpA	Italy

Table 2. Fly ashes selected and sampled in this study

temperature (T_g) and degradability as a function of composition.

MATERIALS AND METHODS

Fly ashes from 23 European pulverised coal combustion power plants were selected for this study (Table 2), which represented a very broad range of chemical and mineralogical compositions. The fly ashes were sampled at the electrostatic precipitators, with the exception of 'As Pontes', which is made up of a mixture of fly ash and molten slag. The samples were supplied by various Spanish power generation facilities and Contento Trade (Udine, Italy).

Major element concentrations were determined in the fly ash samples (by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES)) using a special two-step digestion method devised for the analysis of major and trace elements in coal and combustion wastes. Silica contents were determined directly by X-ray fluorescence (XRF). The mineral compositions of the fly ashes were determined by X-ray diffraction (XRD) using a powder diffractometer with CuK_α radiation. Quantitative XRD analysis was performed using the reference intensity method (RIM). CaF_2 was employed as the internal standard.

Once the chemical and mineralogical compositions were obtained, the glass composition was determined by subtraction of the proportion of the oxides present in the crystalline phases. CLD values for the glass component were obtained with these data for each fly ash.⁹

The formulae for cross-link density and connectivity

are given as follows:

$$\text{Network connectivity} = \frac{2 + \text{total no bridging oxygens} - \text{no broken by modifying ions}}{\text{total no of possible bridges}}$$

$$\text{Cross-link density} = \frac{\text{total no bridging oxygens} - \text{no broken by modifying ions}}{\text{total no of possible bridges}}$$

This approach has been used previously to successfully predict the degradability of bio-active glasses¹⁰ and gasifier slag glasses.¹¹

In calculating the cross-link density of a glass, various structural assumptions must be made:

- Silicon exists in a four coordinate tetrahedral state surrounded by four oxygens.
- Aluminium is charge balanced first by any phosphate present (see Fig 1) then by any network-modifying atoms present (Na, K, Mg and Ca). In fly ashes, phosphate content is generally very low so we must assume that network modifiers take up the charge-balancing role.

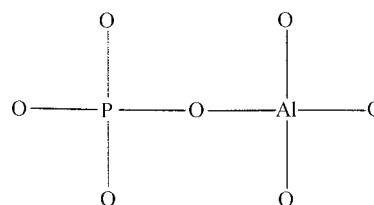


Figure 1. Charge compensation by phosphorus: Al^{3+} is short of one unit of positive charge to take up a four coordinate role in the glass network. Al^{3+} can be charge compensated by an adjacent P^{5+} . AlPO_4^- is structurally similar to Si_2O_7 in an aluminosilicate glass network.

Fly ash	Weight percent							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Teruel	48.3	23.9	16.0	5.4	1.0	0.2	1.4	0.20
Escucha	49.5	26.7	12.3	2.3	0.9	0.3	1.9	0.20
Robla	44.1	23.2	14.3	8.9	1.8	0.3	2.6	0.80
Compos	51.2	25.5	7.5	2.8	2.0	0.8	3.9	0.40
Meirama	49.2	17.6	10.4	11.8	2.0	0.4	0.4	0.20
Narcea	55.2	23.3	6.9	4.0	2.5	0.7	3.8	0.30
Pontes	41.5	30.1	12.6	5.6	1.6	0.6	1.9	0.20
Puerto	58.6	27.4	7.3	0.8	1.0	0.3	2.4	0.10
Espiel	52.3	28.5	5.9	2.0	1.5	0.5	4.0	0.40
Barrios	42.6	35.6	2.6	8.4	2.1	0.3	0.6	1.70
Sribera	48.9	30.6	7.2	3.0	1.6	0.6	3.9	0.10
Alkaline	46.8	24.8	9.0	6.8	3.7	1.2	2.0	0.7
Nijmegen	45.3	25.0	8.8	6.4	1.4	0.8	1.1	1.0
Neutral	53.3	26.1	7.4	3.1	0.6	0.1	0.6	1.5
CCB	59.6	27.0	3.3	0.5	0.9	0.3	2.9	0.1
Acid	51.3	28.9	8.4	1.8	1.0	0.5	2.5	0.2
Amer-8	45.2	26.5	7.1	6.1	1.6	0.8	1.2	1.1
Amer-9	52.4	25.8	7.0	5.6	1.6	0.7	1.4	0.9
Hemweg8	53.2	26.0	4.9	7.1	1.6	0.5	0.8	1.0
Lignite	28.5	17.9	8.4	27.3	3.8	0.2	1.0	0.3
Fusina	48.2	25.9	8.8	2.3	1.5	0.5	2.6	0.3
Monfalcone	50.8	33.4	6.4	2.4	0.8	0.4	0.7	0.3
Sardegna	41.7	29.0	3.8	10.0	2.4	0.5	0.8	1.5

Table 3. Fly ash compositions in wt%

- Any surplus network-modifying cations form non-bridging oxygens and serve to disrupt the glass network.
- Iron is present as an Fe³⁺ cation and behaves like Al³⁺, ie as an intermediate cation.

RESULTS AND DISCUSSION

The fly ash compositions in wt% have been determined and are given in Table 3. The compositions of the fly ashes were recalculated in mole fractions. The results are given in Table 4.

Fly ash	Mole fractions							
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	P ₂ O ₅
Teruel	0.63	0.18	0.08	0.08	0.02	0.00	0.01	0.00
Escucha	0.66	0.21	0.06	0.03	0.02	0.00	0.02	0.00
Robla	0.57	0.18	0.07	0.12	0.03	0.00	0.02	0.00
Compos	0.64	0.20	0.04	0.04	0.04	0.01	0.03	0.00
Meirama	0.62	0.13	0.05	0.16	0.04	0.00	0.00	0.00
Narcea	0.67	0.17	0.03	0.05	0.05	0.01	0.03	0.00
Pontes	0.56	0.24	0.06	0.08	0.03	0.01	0.02	0.00
Puerto	0.72	0.20	0.03	0.01	0.02	0.00	0.02	0.00
Espiel	0.66	0.21	0.03	0.03	0.03	0.01	0.03	0.00
Barrios	0.55	0.27	0.01	0.12	0.04	0.00	0.00	0.01
Sribera	0.62	0.23	0.03	0.04	0.03	0.01	0.03	0.00
Alkaline	0.58	0.18	0.04	0.09	0.07	0.01	0.02	0.00
Nijmegen	0.61	0.20	0.04	0.09	0.03	0.01	0.01	0.01
Neutral	0.69	0.20	0.04	0.04	0.01	0.00	0.00	0.01
CCB	0.84	0.12	0.01	0.00	0.01	0.00	0.01	0.00
Acid	0.67	0.22	0.04	0.03	0.02	0.01	0.02	0.00
Amer-8	0.61	0.21	0.04	0.09	0.03	0.01	0.01	0.01
Amer-9	0.65	0.19	0.03	0.07	0.03	0.01	0.01	0.00
Hemweg8	0.65	0.19	0.02	0.09	0.03	0.01	0.01	0.01
Lignite	0.36	0.13	0.04	0.37	0.07	0.00	0.01	0.00
Fusina	0.65	0.21	0.04	0.03	0.03	0.01	0.02	0.00
Monfalcone	0.65	0.25	0.03	0.03	0.02	0.00	0.01	0.00
Sardegna	0.55	0.22	0.02	0.14	0.05	0.01	0.01	0.01

Table 4. Composition of all fly ashes calculated in mole fractions

Table 5. Mineralogical composition of fly ash samples (% wt as deduced from XRD analysis)

Fly ash	Mullite	Quartz	Cristobalite	Anhydrite	Calcite	Lime	Haematite	Magnetite	Feldspar	Ettringite	Glass
Teruel	19.4	8.6	<0.3	1.5	<0.3	<1.0	5.9	1.3	<1.0	<1.0	62.7
Escucha	24.4	9.6	<0.3	0.9	<0.3	<1.0	<0.3	5.0	<1.0	<1.0	55.5
Robla	4.2	1.7	<0.3	1.5	<0.3	1.9	<0.3	3.8	0.9	<1.0	84.9
Compost	3.2	3.1	<0.3	0.3	<0.3	<1.0	<0.3	1.4	<1.0	<1.0	88.8
Meirama	19.6	6.9	4.5	2.6	<0.3	<1.0	2.5	<0.3	0.7	<1.0	62.5
Narcea	3.8	6.6	<0.3	0.2	<0.3	0.7	<0.3	1.5	0.2	<1.0	85.6
Pontes	29.4	6.2	<0.3	1.0	<0.3	<1.0	5.5	<0.3	3.1	1.6	51.8
Puerto	20.7	10.4	<0.3	<0.3	<0.3	<1.0	<0.3	3.5	<1.0	<1.0	64.7
Espiel	7.4	2.7	<0.3	<0.3	<0.3	<1.0	<0.3	1.8	<1.0	<1.0	85.7
Barrios	40.4	3.4	<0.3	1.3	<0.3	1.1	<0.3	0.5	1.5	<1.0	48.4
Sribera	18.4	5.0	<0.3	<0.3	<0.3	<1.0	<0.3	1.0	<1.0	<1.0	74.4
Alkaline	20.1	11.2	<0.3	1.4	<0.3	1.1	<0.3	1.2	<1.0	<1.0	63.1
Nijmegen	4.9	6.1	<0.3	<0.3	<0.3	1.0	<0.3	1.0	<0.3	<1.0	82.2
Neutral	10.9	7.1	<0.3	<0.3	<0.3	<0.3	<0.3	0.9	0.2	<1.0	80.1
CCB	9.8	9.4	<0.3	<0.3	<0.3	<0.3	<0.3	<0.3	0.1	<1.0	80.1
Acid	9.1	6.0	<0.3	<0.3	<0.3	<0.3	<0.3	0.8	0.6	<1.0	83.1
Amer-8	8.2	6.9	<0.3	<0.3	0.6	1.0	<0.3	0.8	<0.3	<1.0	77.8
Amer-9	9.1	12.5	<0.3	<0.3	<0.3	0.6	<0.3	0.5	0.2	<1.0	77.4
Hemweg8	6.6	7.8	<0.3	<0.3	<0.3	0.5	<0.3	0.9	<0.3	<1.0	83.9
Lignite	<0.3	9.2	<0.3	15.0	0.6	5.8	3.5	<0.3	<0.3	<1.0	61.5
Fusina	17.4	6.4	<0.3	<0.3	<0.3	1.1	<0.3	0.1	<0.3	<1.0	71.6
Monfalcone	25.9	3.2	0.5	<0.3	<0.3	<0.3	<0.3	0.5	<0.3	<1.0	73.1
Sardegna	14.5	4.0	<0.3	0.2	<0.3	2.5	<0.3	0.3	0.8	<1.0	74.0

To determine residual glass content of each of the fly ashes, materials that are bound up in the crystalline phases were subtracted from the overall chemical composition of the fly ash. This is only undertaken when the crystalline phases are present in quantities greater than 1 wt%. The mineral composition of the fly ashes as deduced from XRD analysis is reported in Table 5. Calculations of the CLD and Si:Al ratio, with

respect to the mineralogical quantities, are given in Table 6.

Following Lowenstein's criteria, for glass to form in the first instance, the Si:Al ratio must be greater than one and the CLD must be less than two. The fly ash with the highest Si:Al and lowest CLD would be predicted to be the most degradable under conditions of basic hydrolysis. This implies that the maximum

Table 6. Cross-link density values for all fly ashes with corrections for mineral content (wt%)

Fly ash	Mullite	Quartz	Cristobalite	Anhydrite	Lime	Haematite	Magnetite	Feldspar	Ettringite	Si:Al	CLD
Teruel	19.4	8.6		1.5		5.9	1.3			3.49	2.09
Escucha	24.4	9.6					5			3.58	2.21
Robia	4.2	1.7		1.5	1.9		3.8			2.09	2.13
Compos	3.2	3.1					1.4			1.78	2.20
Meirama	19.6	6.9	4.5	2.6		2.5				9.25	1.59
Narcea	3.8	6.6					1.5			2.14	2.12
Pontes	29.4	6.2		1		5.5		3.1	1.6	3.07	1.99
Puerto	20.7	10.4					3.5			3.07	2.20
Espiel	7.4	2.7					1.8			1.87	2.22
Barrios	40.4	3.4		1.3	1.1			1.5		4.01	1.65
Sribera	18.4	5					1			2.12	2.26
Alkaline	20.1	11.2		1.4	1.1		1.2			2.84	1.89
Nijmegen	4.9	6.1								1.74	2.19
Neutral	10.9	7.1								2.26	2.25
CCB	9.8	9.4								3.81	2.17
Acid	9.1	6								1.83	2.30
Amer-8	8.2	6.9								1.68	2.17
Amer-9	9.1	12.5								1.85	2.02
Hemweg8	6.6	7.8								1.89	2.12
Lignite		9.2		15	5.8	3.5				1.10	1.63
Fusina	17.4	6.4			1.1					3.23	2.31
Monfalcone	25.9	3.2								3.38	2.38
Sardegna	14.5	4			2.5					2.33	2.19

CLD value in the glass phase of a fly ash is two because all materials that have a value higher than this will undergo crystallisation, leaving an amorphous phase with a CLD of around two. The experimental results, however, do not bear this out. As expected, with all the fly ashes, the glass phase was found to have an Si:Al ratio of greater than one. However, in most cases CLD values were greater than two even when the contribution from the crystalline phases has been discounted. This analysis assumes the glasses to be homogeneous in each sample. However, considerable heterogeneity may exist and fly ash particles may be present that consist of glass phases far removed from the average composition.

CONCLUSIONS

A cross-link density value of less than two implies that the material is amorphous in nature and the lower the CLD below two, the greater the reactivity and solubility of the glass. It would be expected that all the fly ashes would have a CLD of less than two, when corrections have been made for contributions from the mineral phases, and the ashes could then be ranked in order of ease of degradability. However, whilst the model is known to work with synthetic glasses, only limited applicability has been found with fly ashes.

In many of the fly ash glasses, CLD values are greater than two and yet the material is amorphous. CLD values much greater than two in a glass are highly unlikely. It is possible that a small amount of aluminium may be held in a 5/6 co-ordination state by rapid quenching which would prevent mullite crystallisation, but the amount present is likely to be very small. An average value of greater than 2.0 suggests that some of the assumptions being made, which are known to hold for homogeneous materials, do not apply for heterogeneous materials like fly ashes.

The fact that these materials are heterogeneous is clearly important, considering the sensitivity of reactions within the $\text{SiO}_2\text{-Al}_2\text{O}_3$ phase system to the exact composition of the material in question.¹² For

example, the possibility of amorphous phase separation has not been addressed in the present work.

It is also possible that very small crystals of mullite or quartz exist in the glassy phase but are too small to be determined by X-ray diffraction and are thus considered as contributing to the amorphous phase rather than the mineral phase.

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REFERENCES

- 1 Jablonski GL and Tyron SS, Overview of coal combustion by-product utilisation, in *Proceedings of the 5th International Pittsburgh Coal Conference*, Pittsburgh, PA, University of Pittsburgh, 15 (1988).
- 2 Raask E, *Mineral Impurities in Coal Combustion: Behaviour, Problems and Remedial Measures*, Hemisphere Publishing Corp, Springer-Verlag (1985).
- 3 Georgakopoulos A, Filippidis A and Kassoli-Fournaraki A, Morphology and trace element contents of the fly ash from Main and Northern Lignite fields, Ptolemais, Greece. *Fuel* 73(11):1802–1804 (1994).
- 4 Hemmings RT and Berry EE, On the glass in coal fly ashes: recent advances. *Mat Res Soc Symp Proc* 113:3–38 (1988).
- 5 Lowenstein W, The distribution of aluminium in the tetrahedra of silicates and aluminates. *Am Mineral* 39:92–96 (1954).
- 6 Pauling LC, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals; An Introduction to Modern Crystal Chemistry*, Cornell University Press (1960).
- 7 Hill RG and Wilson AD, Some structural aspects of glasses used in ionomer cements. *Glass Technology* 29:150–158 (1988).
- 8 Vogel W, *Chemistry of Glass*, The American Ceramic Society, Inc, Columbus, Ohio, USA (1985).
- 9 Ray NH, Inorganic oxide glasses as inorganic polymers. *Br Polym J* 7(5):307–317 (1975).
- 10 Hill RG, An alternative view of the degradation of bioglass. *J Mat Sci Lett* 15(13):1122–1125 (1996).
- 11 Sullivan A, Hill RG and Waters K, A preliminary investigation of glass polyalkenoate cements based on waste gasifier slags. *J Mat Sci Lett* 19:323–325 (2000).
- 12 Pask JA, Importance of starting materials on reactions and phase equilibria in the $\text{Al}_2\text{O}_3\text{-SiO}_2$ system. *J Eur Ceram Soc* 16:101–108 (1996).