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MILESTONES IN THE ANALYSIS OF ALKALI-ACTIVATED BINDERS

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ABSTRACT

The use of alkali activation to achieve environmental savings in the production of construction materials is currently an extremely active area of research and development. There is now a diverse range of chemistries and applications that have been developed within the broader theme of ‘alkali-activated materials’, including the subclass of lower-calcium binders which are also known as ‘geopolymers’. Academic research and commercial development have combined to bring these materials to a level of technological maturity where larger-scale deployment is now taking place. This paper reviews some of the key aspects of alkali-activation technology which have brought the field to this point, with a particular view towards re-assessing key points and comments which have been raised in several historical reviews and discussions of this class of materials. Conclusions are therefore drawn regarding which among these key questions have been answered, and which remain outstanding in an engineering or scientific sense.

Keywords: Fly ash, alkali-activation, slag, concrete

1 INTRODUCTION

Detailed reviews of the chemical, engineering or durability properties of alkali-activated materials have been presented in a number of recent publications including [1-5]. In this paper a combination of historical and forward-looking perspectives is used to provide insight into how these materials have been developed, analysed and used during the past decades, and how this information can be used to support and enhance future developments in the area.

The first publication related to alkali-activated binders is a 1908 patent by the German chemist Kühl [6], who described a process whereby a basic blast furnace slag can be interground with lime and sodium sulfate or carbonate, and then mixed with water to produce a useful binder from slags which would otherwise hydrate only very slowly. However, this type of material was only really brought into practical application decades later, when Purdon published a detailed study of the interaction of slags with different activators in 1940 [7], and later took these materials into commercial production under the name ‘Purdocement’ (or ‘Le Purdociment’ in French). Several structures produced using Purdocement in the 1950s are still in existence, and have been surveyed in a recent publication by Buchwald et al. [8]. However, the production of Purdocement never reached full economic viability, and the company was liquidated in 1957 [8]. For the next several decades, the main developments in this area were centred in Kiev, as the group initially led by Glukhovsky [9], and later by Krivenko [10], developed and produced alkali-activated mixes based on a very diverse range of precursor and activator chemistries, including both low-calcium and high-calcium binder systems. These materials were deployed in a wide range of applications [11], and have provided very good performance in service over a period of several decades [12]. In the 1970s, Davidovits developed a series of binders derived from the interaction between metakaolin and alkaline solutions, which in 1979 he named ‘geopolymers’ [13]. This name has since been applied much more widely to various alkali-aluminosilicate binder systems, and is now widely recognised as a more or less generic term for alkali-activated binder systems. Research and development activities in the field of alkali activation began to expand during the 1980s and 1990s, and it is now a highly active area including efforts in scientific investigation, commercial deployment, and national and international standardisation [5].

From this basis, and more than 100 years after the initial developments in the area, it seems timely to reassess some of the strengths and weaknesses of alkali activation technology which have been identified in key publications during the past decades, and to provide commentary regarding which areas are still in need of further attention to support deployment of these materials in the widest possible range of applications.

2 DISCUSSION – FOUR MILESTONE PAPERS REVISITED

2.1 The work of Purdon revisited

The first detailed scientific publication in the field of alkali-activation is a paper published by Purdon in 1940 [7], who commented that the incorporation of sodium hydroxide into a slag-based cement increases both initial and final strength compared to the use of lime, anhydrite or Portland cement clinker, which at the time were all used to convert slags to binders. He also noted that the addition of the NaOH at the time of concrete mixing, rather than intergrinding of a solid activator, offered advantages in reducing problems due to the hygroscopic nature of the solid alkaline compounds, and their tendency to carbonate; this was seen as being particularly beneficial for precasting operations. He identified the low water permeability, moderate shrinkage and low heat of hydration of alkali-activated slag as particularly appealing technical qualities. A wide-ranging series of experiments on alternative and mixed activators gave results for compressive and tensile strength which are summarised in Figure 1, and led to the recommendation that the generation of NaOH in-situ through the reaction of $Ca(OH)_2$ with Na_2CO_3 or Na_2SO_4 was in general the most effective among the various binary activator combinations tested. The addition of $Na_2S_2O_3$ was seen to enhance the strengths of many mixes, but for reasons which may be related to the cost of this compound, there seems to have been very little work on the use of this compound since the work of Purdon. He also found that the strength development was similar whether the two activator compounds were pre-mixed, with or without removal of $CaCO_3$ precipitates, or mixed directly in concrete formulation [7], which was taken as evidence that the formation of NaOH was the key mechanism by which the combined activator solutions were acting. It should be noted that this work did not consider the possibility of alkali silicate activators; this concept was introduced and developed later by Glukhovsky [9], but has proven to be the basis of much of the subsequent research in alkali-activation due to the faster strength development achieved in these systems. Some later authors have actually considered $Ca(OH)_2$ as a retarder in silicate-activated slag binders when added directly into the activating solution [14], but this is more likely to be because it introduces a reduction in the effectiveness of the activator through precipitation of silicate gel in colloidal particles [15] rather than a true retardation effect in the binder.

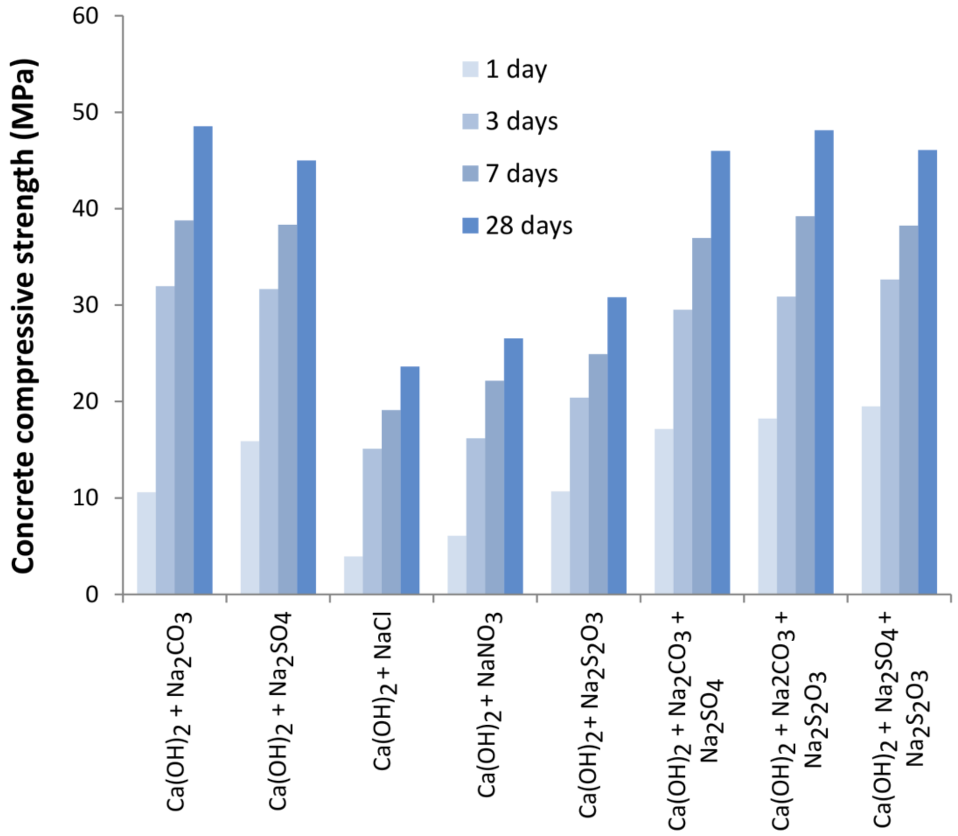

Figure 1. Compressive strengths of alkali-activated slag concretes produced using various combinations of activator compounds, dosed to give the equivalent of 6% NaOH in the mix water assuming that all Na added is converted to NaOH. Data from [7].

Figure 2 shows an additional data set from the work of Purdon [7], which relates 1-day alkali-activated slag concrete strengths to the doses of Na_2CO_3 and $Ca(OH)_2$ added as activators. There is a clear optimum in activator dose, beyond which the strength decreases. Based on developments since that time in alkali-activation chemistry, and calcium (alumino)silicate hydrate chemistry in general, it has become evident that the combination of changes in phase stability and binder micro/nanostructure which take place at very high activator doses lead to the presence of this optimum. The fact that this optimum is distinct and sharp, meaning that the performance of the material is quite sensitive to the formulation conditions, led to a suggestion that these materials are probably less suitable for 'small undertakings in which the proportioning of the concrete is often done in a haphazard fashion', but that the materials would be ideally suited to precasting [7]. This conclusion has been reached by a number of independent investigators in the subsequent decades, particularly with regard to the sensitivity of the materials to curing conditions [16-18] in addition to variability in formulations and in precursor chemistry [19, 20].

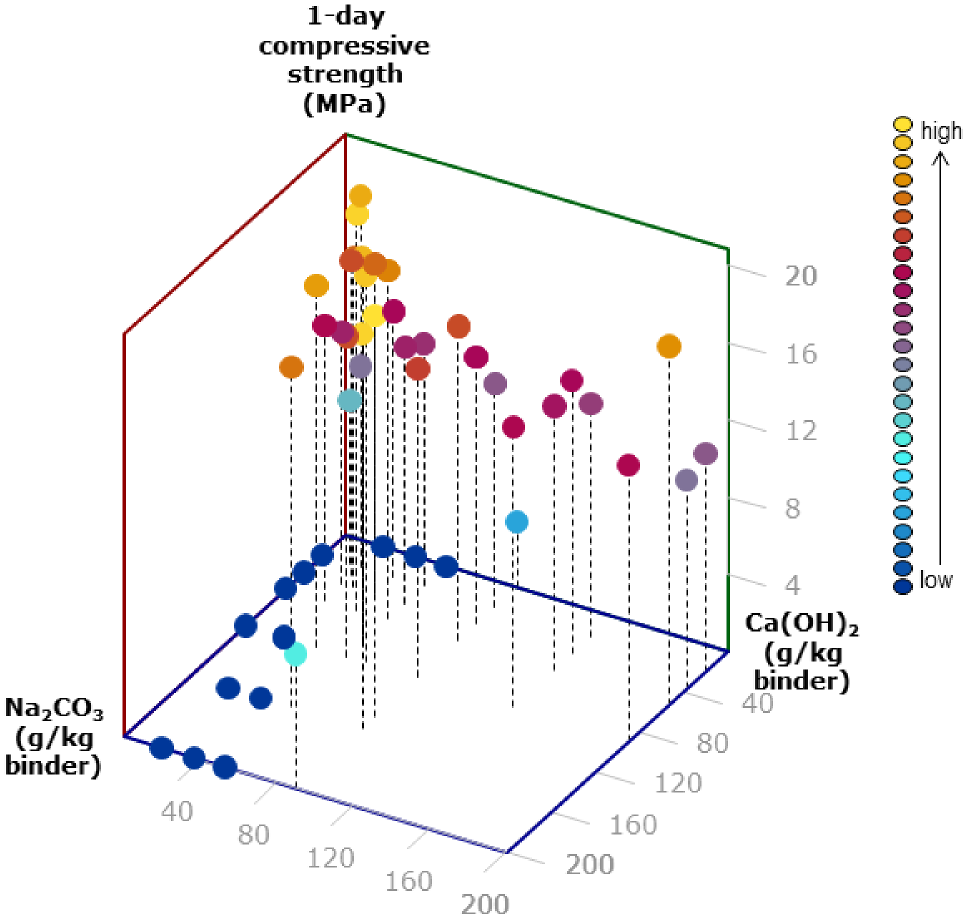

Figure 2. Compressive strengths of concretes based on blast furnace slag with different contents of Na_2CO_3 and $Ca(OH)_2$ as activators, at 400 kg/m^3 binder content. Legend shows the colour-coding of strength data, which are taken from [7].

2.2 Issues highlighted by Talling & Brandstetr [21] in 1989

Talling and Brandstetr published a review covering predominantly eastern European work in alkali-activation of slags, in an American Concrete Institute conference in Trondheim in 1989 [21], with an extensive list of bibliographical references up to that date. Although it is not specifically a milestone paper in terms of presentation of technical results, it is notable for presenting a lot of information in the English language for the first time, and also for providing some forward-looking commentary, which is the reason for its inclusion in this review. Their discussion highlighted various strengths and advantages of alkali-activation technology, and concluded by raising a list of outstanding technical issues requiring further attention. These are reproduced below in italics, followed in each instance by comments regarding how the state of the art has advanced in the 25 years since the publication of that paper.

The possibility of altering the composition and properties of the slags

This possibility has not been followed through in much detail, although alkali-activated products based on synthetic slags are now commercially deployed in western Europe [22].

The characteristics of different kinds of slags

The majority of work in the academic literature to date has been based around blast furnace slag systems, but the influence of blast furnace slag chemistry on the properties of alkali-activated binders is now much better understood [23-25]. Work on non-blast furnace slags is beginning to spread beyond the large volume of work which was historically published in the Russian language, but the diversity and low production volumes of such slags appear to be restricting efforts in this area.

Newly formed hydration compounds and their quantification

This was also described by Wang et al. [14] in 1995 as subject to 'considerable confusion', but is probably the area in which the most progress has been made during the past 25 years; the current state of knowledge is summarised in [4], including descriptions of both primary and secondary binder phases which form in alkali-activated binders of high and low calcium content. However, there is certainly still further work needed related to the roles of alkalis and aluminium in calcium silicate hydrate type gels, and also the factors controlling gel coexistence in binders which contain both calcium aluminosilicate hydrate (C-A-S-H) and sodium aluminosilicate hydrate (N-A-S-H) products.

Identification of minor components in the raw material which may have a deleterious effect

Work in this area has mainly focused on potentially hazardous elements contained in fly ashes, for example [26, 27], while minor components which may influence strength development or concrete durability (e.g. Zn, Cl) have received somewhat less attention. Blast furnace slags appear to be low in potentially deleterious species, although the influence of precursor chemistry on issues such as corrosion of embedded steel remains to be considered in detail.

Simple and effective testing procedures; Standardisation and codes of practice

These points have been covered in some detail through the work of RILEM TC 224-AAM [5], which surveyed the standards environment related to alkali-activated materials, and RILEM TC 247-DTA (http://www.rilem.org/gene/main.php?base=8750&gp_id=290), which is now assessing the questions around the application of standardised durability testing methods to alkali-activated materials.

2.3 Points raised by Davidovits (1991) [28]

In a seminal paper which has now attracted more than 500 citations, Davidovits [28] described many aspects of the chemistry and technology of geopolymers (defined specifically in that work as low-calcium aluminosilicate binders). This paper highlighted the now-almost-abandoned 'poly-sialate' nomenclature for the chemical units present in geopolymers. The inability of this naming scheme to describe non-integer Si/Al ratios, and the inappropriateness of describing the three-dimensional structure of the alkali aluminosilicate gel according to this essentially chain-like terminology, mean that it is no longer used in a scientific context as the understanding of geopolymer materials has further advanced. However, the connections between zeolite chemistry and geopolymer gel structure which were proposed in this paper have since been advanced and now form the backbone of the modern chemical description of alkali aluminosilicate binder gels [29, 30]. The mechanism of reaction was proposed to take place via 'still hypothetical monomers, the orthosialate ions' [28]; these ions have since been identified specifically as part of the array of small silicate and aluminosilicate species which are present in concentrated aqueous alkaline solutions [31, 32], Figure 3. The two species depicted in this image are by no means the only aluminosilicate oligomers which form in aqueous solution, but they are both the simplest, and the most predominant under the conditions prevailing during most geopolymer synthesis processes.

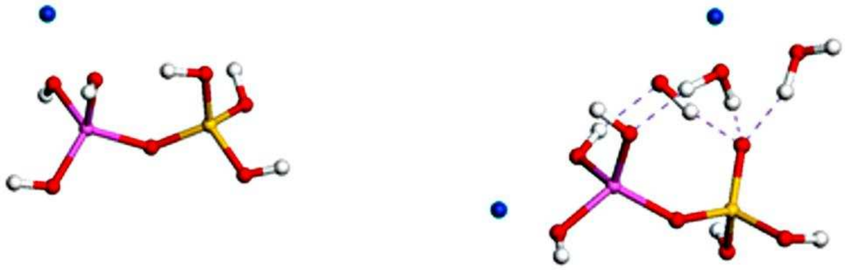

Figure 3. Structures of aluminosilicate oligomers which represent the 'hypothetical monomers' discussed by Davidovits [28]. Structures were calculated by density functional theory calculations [33]; blue is Na, yellow is Si, purple is Al, red is O, and white is H. The species on the left carries a single negative charge which is balanced by Na^+, the species on the right carries two negative charges, balanced by two Na^+ cations, one of which is relatively strongly hydrated. Dashed lines show intermolecular and intramolecular hydrogen bonds.

The 1991 paper of Davidovits [28] also introduced the use of solid-state NMR to the analysis of geopolymers, and showed that the Al in the aluminosilicate gel is present in tetrahedral coordination. There have since been numerous papers which have applied this technique to various alkali-activated systems, and the results are in general in good agreement with the data presented in that initial work.

The work of Davidovits was primarily focused on the production of low-cost, thermally stable materials as castable refractories, and also in waste immobilisation applications. Since that time, commercialisation in the area of alkali-activation has tended to focus more on higher-volume applications in concrete production, driven by carbon dioxide emissions savings (which was foreshadowed in this Davidovits paper [28], long before sustainability issues became a central and mainstream focus in the cement and concrete industry), although there has continued to be a great deal of academic interest in these materials for both refractory and immobilisation applications.

2.4 Revisiting the 2007 'State of the Art' [34]

In 2007, as part of a Special Issue of Journal of Materials Science dedicated to geopolymer technology, a collaboration between leading research teams in Australia and Spain led to the publication of a high-profile ‘state of the art’ review paper on low-calcium alkali-activated (geopolymer) materials [34]. This paper has since accrued more than 450 citations in Scopus (more than 600 in Google Scholar), and as such is the second-most cited paper in this research field behind the 1991 paper of Davidovits [28]. As a review of the state of the art at the time, it represents an important landmark, and also raised some issues which are worthy of discussion in a retrospective sense:

Reaction path modelling

The Duxson et al. review paper [34] presented an often-reproduced schematic illustration of the process of geopolymer reaction, formation and hardening, based on an evolution of the basic concepts originally proposed by Glukhovsky [9]. This diagram has since been re-used in many publications by various authors, discussing a wide range of alkali-activated binder systems, while it was originally sketched specifically for the case of a calcium-free binder in [34]. It does not describe the formation of secondary products which are essential to the binder chemistry of Ca-rich alkali-activated systems, and specifically illustrates zeolite-like molecular structures which are not the main binder phase in alkali-activated slag binders and other similar high-calcium systems [35]. It is therefore recommended that future authors describing such systems should instead base their analysis on the more detailed conceptual diagram presented in [4], as this is relevant to both high- and low-calcium materials. The schematic diagram in [34] is undoubtedly still relevant to low-calcium systems, but its use beyond this scope is not accurate or representative of what is known about the chemistry of alkali-activated materials.

The discussion around this diagram also comments that ‘the actual process of particle-to-gel conversion has never been confirmed in the highly alkaline and poorly solvated conditions prevailing during geopolymer synthesis’ [34]. This was the case in 2007, but in the intervening period, advances in experimental and simulation methodologies have provided direct confirmation of this conversion process [36-39], which is now well established in the scientific literature.

Solid state magic angle spinning nuclear magnetic resonance (MAS NMR) spectroscopy

Much of the analysis presented in [34] is based around the interpretation and analysis of ^{29}Si MAS NMR spectra of metakaolin-based and fly ash-based binders. It is noted in [34] that it is essential to separate the contributions of reaction products and residual raw materials whenever conducting quantitative analysis of such spectra. This comment has been reinforced a number of times in the literature since that time, and the application of this technique to ever more complex systems (in particular blended binders containing both fly ash and a secondary source of either calcium or aluminium [40-42]) has proven successful and powerful. Nonetheless, there are still numerous publications released each year in which the contributions of unreacted precursors are not taken into consideration, but the comment remains that this should be considered an essential starting point for any spectral deconvolution procedure.

Structural ordering in low-calcium geopolymers

It is also noted in [34] that ‘the assertion that geopolymeric materials... are indeed totally amorphous appears to be bolder than prudence would commend... new techniques and *methods*... will be developed.’ This has in fact been the case, both with respect to the much more widespread use of MAS NMR as an analytical probe of short-range ordering in these materials, and also with the rapid rise of the pair distribution function (PDF) analysis technique as a key structural probe of alkali-activated binder systems. Pair distribution function analysis is based on the use of high-resolution, high-energy X-ray or high-momentum transfer neutron scattering data to directly define and determine interatomic correlation distances [43], and therefore has obvious relevance to the study of construction materials based on calcium silicate or alkali aluminosilicate gels which are ordered only on a very short length scale [44, 45]. This technique has been applied with significant success to the analysis of geopolymer materials [30, 39, 44-47], and has in fact demonstrated that the fundamental binder phase is quite ordered on a length scale of up to approximately 8-10 Å, with the exact radius on which correlations are observed varying as a function of the binder chemistry (alkali cation and Si/Al ratio).

Engineering properties and applications

The key conclusion of [34] was that geopolymer concretes based on fly ash appeared to be offering high potential for commercial deployment, but that further work was needed in validating the chemical properties of the binder in the long term, and that the compatibility between calcium-rich and alkali-aluminosilicate gels seemed to offer the key to the future of these materials. Since that time, there have been a number of studies of the engineering properties of concrete specimens (reinforced or unreinforced) based on solely fly ash-derived binders, including [48-53]. However, studies of durability-related properties such as [54, 55] have highlighted the likely importance of inclusion of a calcium source in the mix designs as a way to control porosity and pore structure, and these more calcium-rich mixes currently appear to be the more likely way forward for applications in reinforced concretes [1].

2.5 Next steps and the way forward

Recent review papers [2-4] and the RILEM State of the Art Report [5] have highlighted key steps which need to be addressed for the future development of alkali-activated materials, some of which are summarised as follows:

- Availability of admixtures to control properties in the fresh state
- Quality control and supply of precursors in sufficient quantities for full-scale concrete production. Supply volume is likely to become problematic for blast furnace slag, which is almost fully utilised in most parts of the world, but less so for fly ash (which is still largely considered a waste material), or for metakaolin which can be produced inexpensively from abundant natural resources. Quality control is much more of an issue for fly ashes than for the other materials considered, particularly with regard to unburnt carbon content.
- Durability testing (method development and validation), particularly with regard to the initiation, propagation and effects of steel corrosion
- Long-term engineering properties such as creep and shrinkage
- Nanoscale materials characterisation in heterogeneous binder systems, and gel stability relationships
- Life-cycle inventory data and case studies
- Standardisation

This is not a complete listing of the open questions in this area, and it is certain that some of these issues will turn out, in the coming years, to be more critical than others. None of these is in itself a reason why alkali-activated binders should not be deployed in service – in fact, commercial development and deployment of these materials is now proceeding rapidly, in many countries, while many of these questions remain to some extent open. Nonetheless, these are all areas in which further scientific developments will be able to influence and enhance commercialisation efforts, and aid in bringing alkali-activated materials into mainstream utilisation.

3 CONCLUDING REMARKS

This paper has provided a brief look back at some of the important papers which have been published through the history of alkali-activation technology, with a view towards assessing some of the technical points raised in those papers, and reassessing the progress that has been made in specific areas of this field of technology in recent years. It is evident that some areas of the technology of alkali-activation have developed greatly, while others have been less emphasised than was anticipated in past studies. In terms of the scientific and engineering development of these materials, one aspect which was not considered in detail in historical studies is the issue of organic admixtures; this is an aspect of Portland cement concrete technology which has advanced enormously in the past two decades, and is currently a critical topic for the deployment of alkali-activated materials. Most of the historical research in alkali-activation also comments on very low shrinkage, and high impermeability, in these materials. These claims have since been validated for laboratory specimens, and for materials cured under controlled conditions. However, the performance in these areas of alkali-activated materials cured under uncontrolled or inappropriate conditions still requires attention and optimisation. Issues such as quality control of waste-derived raw materials, and analysis of durability performance (particularly related to protection of embedded steel), certainly offer scope for future research investigation, and the potential for further value-added developments in alkali-activation technology.

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REFERENCES

[1] van Deventer, J.S.J., Provis, J.L. and Duxson, P.: 'Technical and commercial progress in the adoption of geopolymer cement', Miner. Eng. **29** (2012) 89-104.
[2] Provis, J.L.: 'Geopolymers and other alkali activated materials - Why, how, and what?', Mater. Struct. **47** (1) (2014) 11-25.
[3] Bernal, S.A. and Provis, J.L.: 'Durability of alkali-activated materials: progress and perspectives', J. Am. Ceram. Soc. **97** (4) (2014) 997-1008.

[4] Provis, J.L. and Bernal, S.A.: 'Geopolymers and related alkali-activated materials', Annu. Rev. Mater. Res. **44** (1) (2014) 299-327.

[5] Provis, J.L. and van Deventer, J.S.J., (eds.): Alkali-Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM. (Springer/RILEM, Dordrecht, 2014)

[6] Kühl, H.: Slag cement and process of making the same. U.S. Patent 900,939 (1908).

[7] Purdon, A.O.: 'The action of alkalis on blast-furnace slag', J. Soc. Chem. Ind.- Trans. Commun. **59** (1940) 191-202.

[8] Buchwald, A., Vanooteghem, M., Gruyaert, E., Hilbig, H. and Belie, N.: 'Purdocement: application of alkali-activated slag cement in Belgium in the 1950s', Mater. Struct. (2014) in press, DOI 10.1617/s11527-013-0200-8.

[9] Glukhovsky, V.D.: Gruntosilikaty (Soil Silicates). (Gosstroyizdat, Kiev, 1959)

[10] Krivenko, P.V.: 'Alkaline cements'. In: Krivenko, P.V., (ed.) Proceedings of the First International Conference on Alkaline Cements and Concretes, (Kiev, Ukraine, VIPOL Stock Company, 1994), 11-129.

[11] Shi, C., Krivenko, P.V. and Roy, D.M.: Alkali-Activated Cements and Concretes. (Taylor & Francis, Abingdon, UK, 2006)

[12] Xu, H., Provis, J.L., van Deventer, J.S.J. and Krivenko, P.V.: 'Characterization of aged slag concretes', ACI Mater. J. **105** (2) (2008) 131-139.

[13] Davidovits, J.: Geopolymer Chemistry and Applications. (Institut Géopolymère, Saint-Quentin, France, 2008)

[14] Wang, S.-D., Pu, X.-C., Scrivener, K.L. and Pratt, P.L.: 'Alkali-activated slag cement and concrete: a review of properties and problems', Adv. Cem. Res. **7** (27) (1995) 93-102.

[15] Gaboriaud, F., Nonat, A., Chaumont, D. and Craievich, A.: 'Structural model of gelation processes of a sodium silicate sol destabilized by calcium ions: combination of SAXS and rheological measurements', J. Non-Cryst. Solids **351** (4) (2005) 351-354.

[16] Cwirzen, A., Engblom, R., Punkki, J. and Habermehl-Cwirzen, K.: 'Effects of curing: comparison of optimised alkali-activated PC-FA-BFS and PC concretes', Mag. Concr. Res. **66** (6) (2014) 315-323.

[17] Kovalchuk, G., Fernández-Jiménez, A. and Palomo, A.: 'Alkali-activated fly ash: Effect of thermal curing conditions on mechanical and microstructural development – Part II', Fuel **86** (3) (2007) 315-322.

[18] Małolepszy, J. and Deja, J.: 'The influence of curing conditions on the mechanical properties of alkali-activated slag binders', Silic. Industr. **53** (11-12) (1988) 179-186.

[19] Hewlett, P.C.: Lea's Chemistry of Cement and Concrete, 4th Ed. (Elsevier, Oxford, UK, 1998)

[20] Wang, S.D., Scrivener, K.L. and Pratt, P.L.: 'Factors affecting the strength of alkali-activated slag', Cem. Concr. Res. **24** (6) (1994) 1033-1043.

[21] Talling, B. and Brandstetr, J.: 'Present state and future of alkali-activated slag concretes'. In: Malhotra, V.M., (ed.) 3rd International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, ACI SP114, (Trondheim, Norway, American Concrete Institute, 1989), 1519-1546.

[22] Buchwald, A. and Wierckx, J.: 'ASCEM cement technology - Alkali-activated cement based on synthetic slag made from fly ash'. In: Shi, C. and Shen, X., (eds.) First International Conference on Advances in Chemically-Activated Materials, (Jinan, China, RILEM, 2010), 15-21.

[23] Ben Haha, M., Lothenbach, B., Le Saout, G. and Winnefeld, F.: 'Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag -- Part I: Effect of MgO', Cem. Concr. Res. **41** (9) (2011) 955-963.

[24] Ben Haha, M., Lothenbach, B., Le Saout, G. and Winnefeld, F.: 'Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag -- Part II: Effect of Al_2O_3', Cem. Concr. Res. **42** (1) (2012) 74-83.

[25] Bernal, S.A., San Nicolas, R., Myers, R.J., Mejía de Gutiérrez, R., Puertas, F., van Deventer, J.S.J. and Provis, J.L.: 'MgO content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders', Cem. Concr. Res. **57** (2014) 33-43.

[26] Izquierdo, M., Querol, X., Davidovits, J., Antenucci, D., Nugteren, H. and Fernández-Pereira, C.: 'Coal fly ash-slag-based geopolymers: Microstructure and metal leaching', J. Hazard. Mater. **166** (1) (2009) 561-566.

[27] Provis, J.L., Rose, V., Bernal, S.A. and van Deventer, J.S.J.: 'High resolution nanoprobe X-ray fluorescence characterization of heterogeneous calcium and heavy metal distributions in alkali activated fly ash', Langmuir **25** (19) (2009) 11897-11904.

[28] Davidovits, J.: 'Geopolymers - Inorganic polymeric new materials', J. Therm. Anal. **37** (8) (1991) 1633-1656.

[29] Provis, J.L., Lukey, G.C. and van Deventer, J.S.J.: 'Do geopolymers actually contain nanocrystalline zeolites? - A reexamination of existing results', Chem. Mater. **17** (12) (2005) 3075-3085.

[30] Bell, J.L., Sarin, P., Provis, J.L., Haggerty, R.P., Driemeyer, P.E., Chupas, P.J., van Deventer, J.S.J. and Kriven, W.M.: 'Atomic structure of a cesium aluminosilicate geopolymer: A pair distribution function study', Chem. Mater. **20** (14) (2008) 4768-4776.

[31] Kinrade, S.D. and Swaddle, T.W.: 'Direct detection of aluminosilicate species in aqueous solution by silicon-29 and aluminum-27 NMR spectroscopy', Inorg. Chem. **28** (10) (1989) 1952-1954.

[32] Swaddle, T.W., Salerno, J. and Tregloan, P.A.: 'Aqueous aluminates, silicates, and aluminosilicates', Chem. Soc. Rev. **23** (5) (1994) 319-325.

[33] White, C.E., Provis, J.L., Kearley, G.J., Riley, D.P. and van Deventer, J.S.J.: 'Density functional modelling of silicate and aluminosilicate dimerisation solution chemistry', Dalton Trans. **40** (6) (2011) 1348-1355.

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

[35] Bernal, S.A., Provis, J.L., Fernández-Jiménez, A., Krivenko, P.V., Kavalerova, E., Palacios, M. and Shi, C.: 'Binder chemistry – High-calcium alkali-activated materials'. In: Provis, J.L. and van Deventer, J.S.J. (eds.) 'Alkali-Activated Materials: State-of-the-Art Report, RILEM TC 224-AAM', Springer/RILEM, Dordrecht (2014), 59-91.

[36] Hajimohammadi, A., Provis, J.L. and van Deventer, J.S.J.: 'The effect of alumina release rate on the mechanism of geopolymer gel formation', Chem. Mater. **22** (18) (2010) 5199-5208.

[37] Hajimohammadi, A., Provis, J.L. and van Deventer, J.S.J.: 'The effect of silica availability on the mechanism of geopolymerisation', Cem. Concr. Res. **41** (3) (2011) 210-216.

[38] White, C.E., Provis, J.L., Proffen, T. and van Deventer, J.S.J.: 'Molecular mechanisms responsible for the structural changes occurring during geopolymerization: Multiscale simulation', AIChE J. **58** (7) (2012) 2241-2253.

[39] White, C.E., Provis, J.L., Bloomer, B., Henson, N.J. and Page, K.: 'In situ X-ray pair distribution function analysis of geopolymer gel nanostructure formation kinetics', Phys. Chem. Chem. Phys. **15** (22) (2013) 8573-8582.

[40] Bernal, S.A., Provis, J.L., Walkley, B., San Nicolas, R., Gehman, J.D., Brice, D.G., Kilcullen, A., Duxson, P. and van Deventer, J.S.J.: 'Gel nanostructure in alkali-activated binders based on slag and fly ash, and effects of accelerated carbonation', Cem. Concr. Res. **53** (2013) 127-144.

[41] Dombrowski, K., Buchwald, A. and Weil, M.: 'The influence of calcium content on the structure and thermal performance of fly ash based geopolymers', J. Mater. Sci. **42** (9) (2007) 3033-3043.

[42] Ruiz-Santaquiteria, C., Skibsted, J., Fernández-Jiménez, A. and Palomo, A.: 'Alkaline solution/binder ratio as a determining factor in the alkaline activation of aluminosilicates', Cem. Concr. Res. **42** (9) (2012) 1242-1251.

[43] Egami, T. and Billinge, S.J.L.: Underneath the Bragg Peaks: Structural Analysis of Complex Materials. (Plenum, Oxford, 2003)

[44] Meral, C., Benmore, C.J. and Monteiro, P.J.M.: 'The study of disorder and nanocrystallinity in C-S-H, supplementary cementitious materials and geopolymers using pair distribution function analysis', Cem. Concr. Res. **41** (7) (2011) 696-710.

[45] White, C.E.: 'Pair distribution function analysis of amorphous geopolymer precursors and binders: The importance of complementary molecular simulation', Z. Kristallogr. **227** (2012) 304-312.

[46] White, C.E., Provis, J.L., Proffen, T. and van Deventer, J.S.J.: 'The effects of temperature on the local structure of metakaolin-based geopolymer binder: A neutron pair distribution function investigation', J. Am. Ceram. Soc. **93** (10) (2010) 3486-3492.

[47] White, C.E., Page, K., Henson, N.J. and Provis, J.L.: 'In situ synchrotron X-ray pair distribution function analysis of the early stages of gel formation in metakaolin-based geopolymers', Appl. Clay. Sci. **73** (2013) 17-25.

[48] Yost, J.R., Radlińska, A., Ernst, S., Salera, M. and Martignetti, N.J.: 'Structural behavior of alkali activated fly ash concrete. Part 2: structural testing and experimental findings', Mater. Struct. **46** (3) (2013) 449-462.

[49] Diaz-Loya, E.I., Allouche, E.N. and Vaidya, S.: 'Mechanical properties of fly-ash-based geopolymer concrete', ACI Mater. J. **108** (3) (2011) 300-306.

[50] Badar, M.S., Kupwade-Patil, K., Bernal, S.A., Provis, J.L. and Allouche, E.N.: 'Corrosion of steel bars induced by accelerated carbonation in low and high calcium fly ash geopolymer concretes', Constr. Build. Mater. **61** (2014) 79-89.

[51] Sagoe-Crentsil, K., Brown, T. and Taylor, A.: 'Drying shrinkage and creep performance of geopolymer concrete', J. Sust. Cem.-Based Mater. **2** (1) (2013) 35-42.

[52] Wallah, S.E.: 'Drying shrinkage of heat-cured fly ash-based geopolymer concrete', Mod. Appl. Sci. **3** (12) (2009) 14-21.

[53] Wallah, S.E.: 'Creep behaviour of fly ash-based geopolymer concrete', Civil Eng. Dimension **12** (2) (2010) 73-78.

[54] Provis, J.L., Myers, R.J., White, C.E., Rose, V. and van Deventer, J.S.J.: 'X-ray microtomography shows pore structure and tortuosity in alkali-activated binders', Cem. Concr. Res. **42** (6) (2012) 855-864.

[55] Ismail, I., Bernal, S.A., Provis, J.L., San Nicolas, R., Brice, D.G., Kilcullen, A.R., Hamdan, S. and van Deventer, J.S.J.: 'Influence of fly ash on the water and chloride permeability of alkali-activated slag mortars and concretes', Constr. Build. Mater. **48** (2013) 1187-1201.