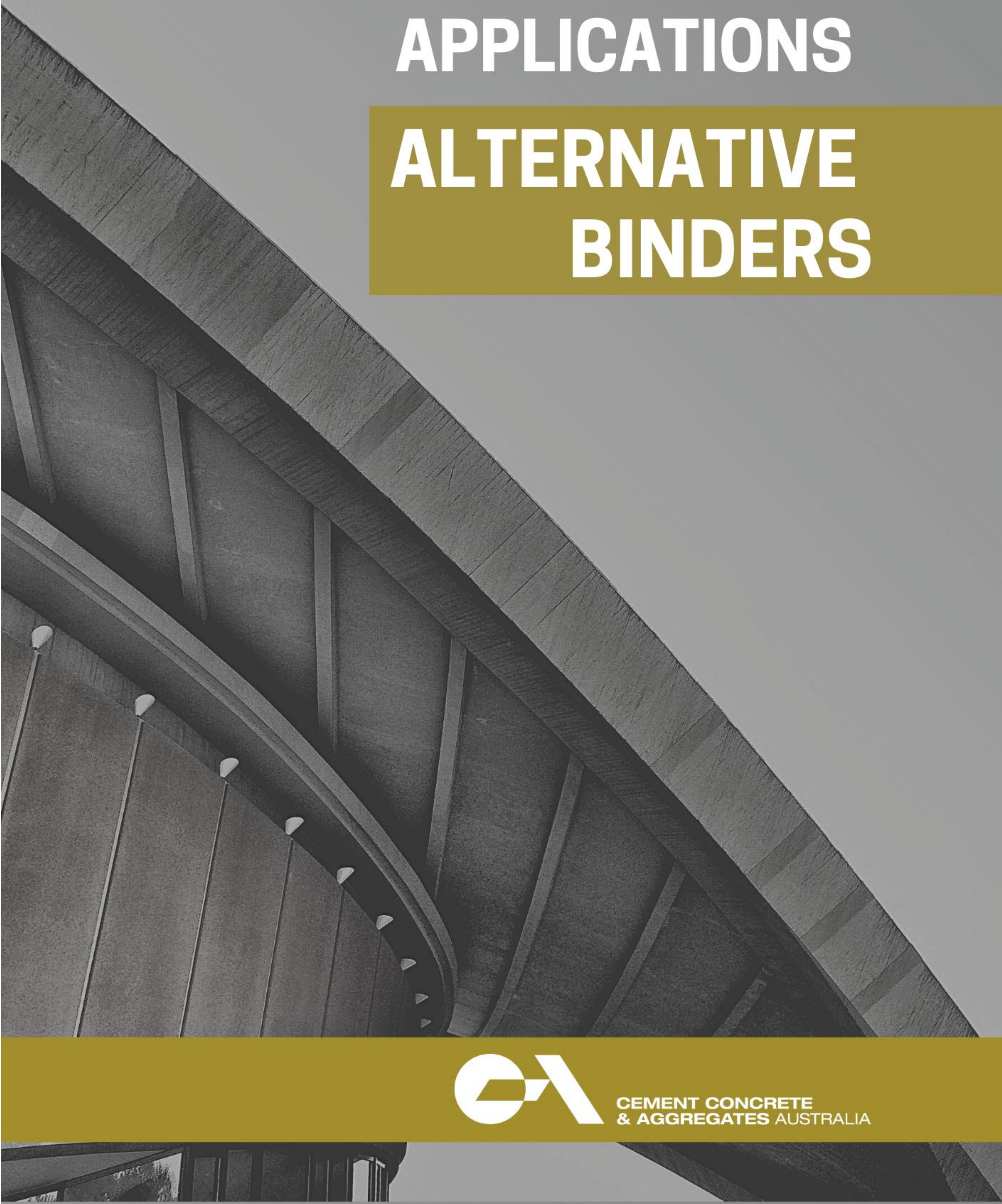
PART VII. DEVELOPMENTAL APPLICATIONS

ALTERNATIVE BINDERS



CEMENT CONCRETE
& AGGREGATES AUSTRALIA

This Section examines the need for alternative binder materials and provides information on the nature and use of some of the common alternative binders under investigation. While this type of work is being carried out extensively at universities, only a small amount of commercial activity is currently underway to use the new and/or novel binder materials being developed to (potentially) replace conventional 'Portland' cement.

CONTENTS

1. INTRODUCTION

In Part X of this Guide, environmental concerns related to the use of conventional cement and concrete are discussed. Concrete is used in huge quantities worldwide – an estimated 33 billion tonnes per annum – and any product used in that quantity is likely to create environmental concerns through the sheer volume of material alone. For concrete, its volume is not the only concern. Cement production accounts for about 7-8% of the anthropogenic CO_2 produced in the world, and as other industries 'de-carbonise', this proportion is likely to rise. It is this specific issue that has led to the interest in developing cements and binder materials that may be an effective replacement for conventional 'Portland' cement.

2. ALTERNATIVE BINDERS IN PERSPECTIVE

From a purely technical perspective, the task of developing and proving an alternative binder (or group of binders) to replace 'Portland' cement does not seem too daunting – that is, until the scale of the challenge is realised. Currently, in excess of four billion tonnes of 'Portland' cement is being produced annually throughout the world – with more than half of that being produced in China alone. From a raw materials perspective, the manufacture of 'Portland' cement is not seriously constrained as the fundamental raw materials – limestone and clay – are abundant materials. Once cement clinker has been made in the high temperature, high emissions kiln process, subsequent issues like the handling and processing of the large volumes of clinker and cement are quite simple manufacturing processes. For 'Portland' cement manufacture, the main complexity arises in the clinker manufacturing stage.

For any alternative binder system or systems, one of the primary considerations has to be raw materials availability. As will be shown later in this Section, the raw materials which are being used in the most popular alternative binders are 'wastes' – namely fly ash and blast furnace slag. When the availability of these materials is examined, it is found that there is <1 billion tonnes of these materials combined being produced annually on a worldwide basis. So, even if these materials are fully utilised in manufacturing alternative binders there is still a very significant shortfall in terms of overall 'concrete binder' requirements for any replacement material or group of materials that might take the place of 'Portland' cement.

A variety of approaches to the development of potential alternatives to 'Portland' cement have been taken over many decades. The main approaches taken to date are described in the following discussions.

3. ALKALI ACTIVATED BINDERS (INCLUDING 'GEOPOLYMERS')

By far the largest body of work in attempts to develop alternative binders has been focussed on a suite of alkali-activated materials. While the fundamentals of alkali-activation have been known since the early 1900's, it was the work of V.D. Glukhovsky in the 1950's and that of J. Davidovits in the 1970's that more clearly defined these materials and created the path for their utilisation. As will be described below, this topic is not without its uncertainties and recriminations, but unquestionably the alkali-activated materials have created the greatest research interest, and to the relatively minor extent that it has occurred, the most significant commercial application of alternative binders.

'Portland' cement is comprised of a purposefully created set of anhydrous, synthetic minerals. When water is added to these minerals they hydrate – that is, they combine with the water to form hydrated reaction products which form as porous gels and which are very efficient at binding aggregate materials together to form mortar or concrete. The water is an integral component of these hydrate gels, and they cannot exist without it.

In contrast to purposefully made cement, alkali activated binders use as their main volumetric component, one or more vitreous (glassy) amorphous materials – some of which are natural materials and some of which are nominally 'waste' materials (e.g. fly ash and granulated blast furnace slag). These materials can be <u>activated</u> by a range of alkaline compounds – usually strong alkalis (e.g. sodium or potassium hydroxide, sodium or potassium carbonate, sodium silicate). The nature of the reaction products from this activation (a) depend on the chemistry of both the base material(s) and the activator(s), and (b) are the source of some contention when it comes to naming these binder types.

The wide variety of potential reactants (base materials and activators) means that a wide range of reaction products can be obtained with the alkali activated binder systems.
*(**NOTE**: This stands in contrast with 'Portland' cement which contains a common set of minerals (albeit often in different proportions) and a comparatively similar set of reaction products in terms of chemical composition and performance.)*

The range of base materials used is quite wide and can include both low-calcium and high-calcium fly ashes; granulated blast furnace slags; metakaolin; zeolites; 'red mud' (from aluminium processing); activated clays; recycled glass and many others.

In terms of reaction chemistry, these base materials can be separated most simply into 'high calcium' and 'low calcium' groups. This basic parameter is a significant determinant of (a) the rate of activation reaction; (b) the type of reaction product; (c) the strength and durability performance of concrete; and (d) proper nomenclature.

'High calcium' materials (e.g. granulated blast furnace slag) are readily activated to form calcium silicate hydrate type reaction products and produce concrete that (a) sets at ambient temperatures and (b) produces good (early and later age) strengths and low permeability concrete.

'Low calcium' materials (e.g. low-calcium fly ash and metakaolin) are readily activated by strong alkalis to form polymeric reaction products and produce concrete that is more likely to (a) require heating to obtain adequate early-age strengths and (b) ultimately produce good concrete strengths, and (c) while this concrete tends to have higher permeability, it also tends to have excellent resistance to sulfate attack.

This latter type of alkali activated binder using primarily Class 'F' fly ash is the type patented in the 1970's by J. Davidovits. He used the name 'Geopolymer' for this product and he insists that it is a separate material from conventional alkali activated materials or AAM's as they are now known. He uses, as the differentiator, the 'fact' that his 'Geopolymers' are polymeric materials containing cross-linked chains of Si, Al, O and other atoms and that it is this structure that gives 'Geopolymers' their performance characteristics. He contrasts this structure with the gel-type structure of the calcium silicate hydrate products found in, for example, 'Portland' cement and (activated) slag hydration products. The contrasting processes are described in **Figure 23.1** below.

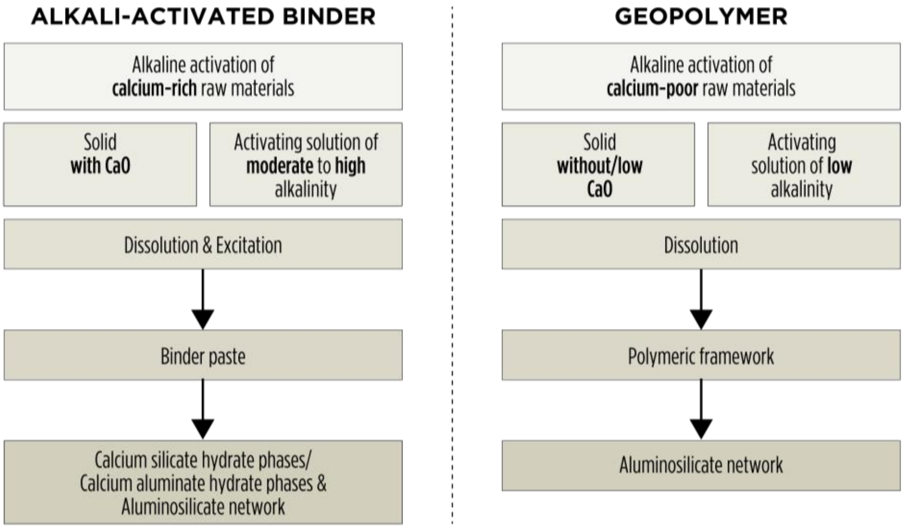


Figure 23.1 – Contrasting Reaction Processed for AAM's and Geopolymers (after Vishojit Bahadur Thapa and Daniele Waldmann, 'A short review on alkali activated binders and geopolymer binders')

Unquestionably, the term 'Geopolymer' has become the most commonly used term for the whole suite of AAM's – particularly in Australia which presently leads the world in AAM research and application.

Much of the Australian work uses a combination of granulated blast furnace slag and (Class 'F') fly ash as the base materials for AAM/'Geopolymer' products, with activation typically by a combination of sodium hydroxide and sodium silicate. In the conventional sense, a separate 'binder' is not added to the concrete mix. The base and activator materials comprising the binder, along with the aggregates and water, are charged into the concrete mixer and the materials are mixed together for an appropriate time. As with conventional concrete, the mixes are tested for slump and compressive strength and any other property of interest – generally using the same test methods as for conventional concrete.

While not being hugely different in appearance to 'Portland' cement concrete, there are generally some defining characteristics of AAM/'Geopolymer' concrete including:

- The 'paste' is of lower viscosity and the mix can appear to be quite 'bony';
- Typically, the water:binder ratio will be lower (about or below 0.3);
- The mix will respond very well to vibration when compacting;
- A final finish will be more difficult to achieve (due to lower 'paste' viscosity);
- The slump will be more sensitive to water addition;
- The concrete will respond very well to heat in terms of the rate of strength development.

While the AAM/'Geopolymer' concrete has some differences to conventional concrete, none of these are insurmountable as demonstrated by the demanding commercial uses to date.

3.1 COMMERCIAL USES OF GEOPOLYMERS

A number of companies in Australia have initiated the commercial use of concrete products using alternative binders and that they have invariably called (and patented as) 'Geopolymer' concrete.

Rocla and Zeobond were two of the initial pioneers of commercial 'geopolymer' concrete in Australia. More recently, the Wagner Group in Queensland have used their 'Geopolymer' product [known commercially as *Earth Friendly Concrete (EFC)*] in two significant projects (as well as other less well-known applications).

EFC was used for the construction of precast floor panels that were used in the construction of the Global Change Institute building at the University of Queensland. These panels (**Figure 23.2**) were found, after testing, to meet the performance requirements of AS 3600 and were thus able to be used in this structure.

Figure 23.2 – 'Geopolymer' Precast Floor Panels used in Global Change Institute, University of QLD

EFC was also used in over 40,000 m^3 of concrete in the construction of the Wellcamp (Brisbane West) Airport near Toowoomba in Queensland. This concrete was not used for runways but was used for other aircraft taxi-way pavement and more generally for tilt panels, culverts and kerbs (**Figure 23.3**).

4 SULFATE ACTIVATED BINDERS

In the previous section, alkali activation of granulated blast furnace slag (slag) was discussed. Slag is a versatile material and it has been well understood for decades that it can also be very successfully activated using sulfates (e.g. gypsum, sodium or potassium sulfate). Binders that employ this activation are sometimes known as 'super-sulfated cements'.

Figure 23.3 – 'Geopolymer' Concrete Use – Aircraft Pavement and General Building – Wellcamp Airport

With these cements, the sulfate ion initiates the hydration of slag leading to the formation of calcium silicate hydrate and ettringite. Generally, a small proportion of 'Portland' cement is also added to the binder to provide improved early-age strength.

As no calcination or kiln firing is required, super-sulfated cements have low embodied CO_2 levels and low embodied energy and are much more environment-friendly than 'Portland' cement. The hydration reaction gives low levels of exothermic reaction and heat production, so these cements are considered to be low-heat types. The resultant concrete results in good strength performance and good durability performance, particularly in terms of resistance to attack by sulfate ions. Excellent drying shrinkage performance is also claimed with this concrete.

One unusual area where sulfate activation of slag is seen is in producing mine backfill in metalliferous mines where sulfur-containing ores are mined. When slag is used as a cementitious material to produce the low-strength backfill, some quite exceptional strengths (early and later-age) are obtained with low binder contents due to activation of the slag by the high levels of sulfate in the mine wastes used in the manufacture of the backfill.

4.1 COMMERCIAL USES OF *ENVISIA*™

In the commercial world, the use of super-sulfate cements in Australia has been limited until recently. Boral has produced a concrete product known as *Envisia*™ which uses sulfate-activated slag as the main part of the binder material. *Envisia*™ concrete has been used on major projects in both Sydney and Melbourne, including the Barangaroo complex and Punchbowl Mosque in Sydney and the Stokehouse in Melbourne (**Figure 23.4**). The benefits claimed from using *Envisia*™ include all of those described above, but most particularly its low CO_2 and embodied energy, its durability performance and its low shrinkage characteristic.

Figure 23.4 – The Stokehouse (Melbourne) was constructed using Envisia™ Concrete

5 OTHER NOVEL PROCESSES

The above binder types and processes are modified versions of the existing processes used to make conventional 'Portland' cement concrete. There is research being undertaken that uses significantly different processes to produce structural products. Several are discussed below.

5.1 '*CARBICRETE*'

Carbicrete is a process developed in Canada in which concrete is produced using 'wastes and CO_2'. The process uses ground granulated slag to replace 'Portland' cement and then injects CO_2 to 'cure' the concrete. In this process, it is claimed that CO_2 production is avoided through using no cement, and that CO_2 can be taken from other sources for use as a curing agent, thus doubling up on its overall CO_2 reduction potential. The process is said to involve the injection of CO_2 into a concrete mix containing ground slag – where the CO_2 and calcium silicate in the slag react to form calcium carbonate which is the binding material. When used in block-making, it is claimed that, as well as being a nett consumer of CO_2, the blocks have strengths about 50% higher than conventional blocks.

To date, there has been no commercial production of blocks using this technology. The owners of the technology are intending to build a demonstration plant and then try to sell the technology to others.

5.2 '*SOLIDIA*'

This technology is another CO_2-cured concrete system (as is another similar process called *CarbonCure*) that also includes the use of a modified cement type that creates lower levels of CO_2 emissions up-front. The claim is that overall, about a 70% reduction in CO_2 emissions relative to conventional 'Portland' cement use is possible with this technology, as well as reduced water use in concrete making. Like most of the CO_2 cured processes, they are able to be applied readily to the production of concrete products (e.g. bricks and blocks) but to date have limited application in premixed concrete. This company is working with a major concrete producer to remedy this weakness and has claimed some success. The further complication in moving from bricks/blocks to premixed concrete is the need to be able to meet well-established requirements in Standards and specifications. This is a challenge for all new technologies (see sub-section 6 below).

5.3 MAGNESIUM OXYCHLORIDE CEMENT

Magnesium oxychloride cement (MOC) is produced from magnesium mining wastes which include magnesium oxide and magnesium chloride components which may also be obtained from seawater. MOC has demonstrated good compressive strength performance but suffers from a number of performance weaknesses that have limited its use. These weaknesses include (a) relatively poor resistance to water ingress and (b) issues related to corrosion resistance of embedded steel which may be a consequence of the presence of high levels of chloride ion.

5.4 ACTIVATION OF MINERAL-BASED MATERIALS

Given the constraints on fly ash and slag availability as noted in sub-section 2, more substantial sources of the base materials have been considered. One of these materials is meta-kaolin, an anhydrous, calcined form of the clay material kaolinite. If kaolinite is heated in a kiln at about 600-800°C, it becomes a highly pozzolanic and reactive material. It has been used as a pozzolan in conventional concrete and has also been used as a base material in AAM's.

While much of the work on meta-kaolin to date has been done with quite pure clay, test work has also shown that quite impure clay materials containing kaolin, once activated, can still be quite efficient pozzolans and base materials for AAM's.

It is obvious that the availability of clay materials world-wide is much greater than that of fly ash and slag which suggests these mineral materials may provide more viable base materials for the production of alternative binders.

6. ISSUES WHEN ADOPTING ALTERNATIVE BINDER TECHNOLOGIES

Given the relatively long history of use of 'Portland' cement based concrete and its universal adoption, it is probably no surprise that any new cement or concrete technology will need to prove that it reliably produces products with effectively equivalent performance to the conventional materials and also at competitive cost. These two issues are the primary 'hurdles' that need to be overcome for any alternative binder technologies. In addition, protocols need to be established to calculate the embodied CO_2 levels in these materials in a standardised way so that proper comparisons between different alternative binder types and with 'Portland' cement can be made.

Standards – Given the amount of research being carried out internationally on alkali activated material (AAM) binders, it is not surprising that this group of materials has come to the attention of those seeking to standardise the composition and/or testing requirements for both the binders and the resultant concrete. In Europe, RILEM committees have been established to (a) develop performance-based specifications and make recommendations for the development of Standards, and (b) make recommendations regarding appropriate test methodologies and protocols for the analysis of the durability of AAM binders and mortars and concretes made with the AAM binders.

*(**NOTE**: RILEM is the International Union of Laboratories and Experts in Construction Materials, Systems and Structures.)*

In Australia, there is no Australian Standard applicable to AAM binders or concrete, however Standards Australia are currently developing a Handbook to cover AAM's and Geopolymers. In addition, some State Government bodies (e.g. VicRoads and QTMR in Victoria and Queensland respectively) have published specifications for 'Geopolymer' concretes. These are not for use for structural purposes, but rather for footpaths, noise barriers, Jersey barriers etc.

The current lack of accepted Standards means that there is reluctance by specifiers, designers and builders to use the new materials in structures with high risk profiles (e.g. high-rise buildings, bridges etc.)

Cost – Despite the use of (nominal) 'wastes' as part of the formulation in most of the alternative materials, their cost is still often higher than the conventional concrete alternative. The activator materials are expensive, and at present relatively low volumes of alternative products are being manufactured. Without incentives or a tax system that penalises CO_2 emissions, cost will be an ongoing prohibitive factor limiting their adoption.

Embodied CO_2 Calculations – The primary reason for investigating or using alternative binder materials is their lower embodied CO_2 levels. Currently, researchers and producers involved with alternative binders are able to make claims about levels of CO_2 reduction relative to 'Portland' cement without reference to a standardised method. As these claims will have both technical and commercial implications, an accepted, common calculation methodology will be required.

7. SUMMARY

The primary reason that alternative binders that might replace 'Portland' cement are being sought is to try to reduce the levels of embodied energy and embodied CO_2 in concrete. A huge amount of research in this area has been underway for at least a decade and while there have been some commercial applications of, for example, concrete using AAM and super-sulfated binders, it has been minimal. Most of these technologies involve alkali activation of fly ash and slag and it has been shown that even if all of the available fly ash and slag being produced in the world was used for binder production, it would not go close to being a practical option for complete 'Portland' cement replacement.

While many of the newer binder technologies being trialled still rely on fly ash and slag, it has been shown that some mineral materials can be activated at quite low temperatures and be used in both conventional and alternative binder scenarios.

With any new technology comes the need to integrate it into common use, and where the incumbent technology is well established, this can be problematic. For alternative binders, the main issues are (a) lack of standardisation, (b) cost and (c) the lack of a yardstick by which to measure embodied CO_2 levels. Considerable work is being done internationally on standardisation of specifications and test methods for alternative binder materials and concrete and this should assist in reducing one of the major acceptance hurdles for these products.

8. RELEVANT AUSTRALIAN STANDARDS AND SPECIFICATIONS

1) AS 3600 – *Concrete structures*
2) QTMR Specification MRTS270 – *Precast Geopolymer Concrete Elements* (November 2018)
3) VicRoads Section 703 – *Geopolymer Concrete – General Concrete Paving*

9. REFERENCES

1) Concrete Institute of Australia Recommended Practice Z16, *'Geopolymer Concrete'*
2) RILEM TC224-AAM State-of-the-Art Report, *'Alkali Activated Materials'*
3) Bligh, R. and Glasby T. (2013), *'Development of geopolymer precast floor panels for the Global Change Institute at University of Queensland'*, Proceedings Concrete Institute of Australia Biennial Conference, Concrete 2013 – Understanding Concrete, Gold Coast, Australia
4) Glasby, T. et al (2015), *'EFC geopolymer concrete aircraft pavements at Brisbane West Wellcamp Airport'*, Proceedings Concrete Institute of Australia Biennial Conference, Concrete 2015, Melbourne, Australia
5) Chandler, J. et al, (2013) *'Development and commercialisation of low carbon, low shrinkage, highly durable Envisia® concrete'*, Proceedings Concrete Institute of Australia Biennial Conference, Concrete 2013 – Understanding Concrete, Gold Coast, Australia

CCAA OFFICES

NATIONAL OFFICE (NSW)
Level 10
163 -175 O'Riordan Street
Mascot NSW 2020

POSTAL ADDRESS
PO Box 124
Mascot NSW 1460
Telephone: (02) 9667 8300

QUEENSLAND
Level 14, 300 Ann Street,
Brisbane QLD 4000
Telephone: (07) 3227 5200

VICTORIA
Suite 910/1 Queens Road
Melbourne VIC 3004
Telephone: (03) 9825 0200

WESTERN AUSTRALIA
45 Ventnor Avenue
West Perth WA 6005
Telephone: (08) 9389 4452

SOUTH AUSTRALIA
Level 30, Westpac House
91 King William Street
Adelaide SA 5000
Telephone: (02) 9667 8300

TASMANIA
PO Box 1441
Lindisfarne TAS 7015
Telephone: (03) 6491 2529

ONLINE DETAILS
www.ccaa.com.au
Email: info@ccaa.com.au