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The role of chemical research in the commercial adoption of alkali activated concrete

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Abstract

Alkali-activated or geopolymer binders and concretes made predominantly from metallurgical slags and/or coal fly ash offer the opportunity for highly significant carbon dioxide savings in the construction materials industry when compared to the use of traditional Portland cement-based materials. As the third largest industrial emitter of carbon dioxide, contributing 5-8% of global carbon emissions, the Portland cement industry offers much potential for emission reduction, provided that there is confidence in the geopolymer concrete as a long-term durable material. Here, the role of chemical research in underpinning the adoption of geopolymers is explored, particularly in terms of understanding durability and changing standards.

Introduction

The development of construction materials (particularly concretes) based on alkali activation of aluminosilicates – termed alkali-activated materials, or AAM's, and including the class of materials often termed 'geopolymers' or 'inorganic polymer cements' – has been a fundamentally two-pronged process, which has involved decades of detailed chemical research at a fundamental level, combined with full-scale industrial application for verification purposes. The introduction of a new type of binder as an alternative to Portland cement in large-scale concrete production has required a long process of working to convince a notoriously conservative industry that alkali-activated materials are capable of performance equal to or better than that of Portland cement.

The uptake of alkali activation as a means of concrete production is currently being driven primarily by sustainability arguments, particularly to do with the reduction of the carbon footprint of the world's construction industry. This issue is covered extensively elsewhere,[1] and so will only be discussed briefly here. To summarise a series of extremely complex problems into a very brief statement: cement production contributes approximately 5-8 percent of the world's total anthropogenic CO_2 emissions,[2] and the technological options whereby this footprint may be reduced while retaining the existing and commonly used chemistry of Portland cement are becoming increasingly limited.[3-5] It has therefore become apparent that there is the need for a 'toolkit' of alternative cement types, which will enable the specific performance and durability challenges posed by each specific application to be met by the most appropriate technology option.

The advantages of alkali activation over Portland cement technology are largely based around the ability to valorise high-volume industrial waste streams into high-performance concretes with a highly significant reduction in CO_2 emissions.[6] Alkali activation is the process of reacting a solid aluminosilicate-based precursor with an alkaline solution, most commonly sodium silicate, carbonate or hydroxide, although sulphate solutions are also effective in combination with specific classes of solid precursor.[7,8] The most widely used precursors are ground granulated blast furnace slag, fly ash from coal combustion, and calcined clays.[9,10] Fly ash and slag appear at present to be the most promising precursors for large-scale industrial production of alkali-activated binders due to the more favourable rheological properties and lower water demand of binders synthesised from them, when compared to calcined clays.[11] There are some international pressures on the supply of high-quality slag due to its widespread use as a supplementary cementitious material in Portland cement concretes, and fly ash is not available in some parts of the world where coal-fired electricity generation is not used, which is leading to a push for the development and study of alternative precursors for AAM binder production. However, the main focus of research and development in Australia remains on the use of fly ash and slag, which are available in sufficient quantities in this country – in particular, Australian fly ash production is almost equal to the total national cement demand at present, and there exist large stockpiles of unutilised fly ash, which have in effect (or in practice) been sent to landfill.

The key hurdles to widespread commercial adoption

Standards

Portland cement has been the primary binder in construction materials for the entirety of the modern age. This is significant because the use of Portland cement basically pre-dates any development of standards, meaning that there has never had to be a new building material accredited or approved for use in many building applications in which cement is almost universally used. This is unlike much of the construction industry which surrounds us today, such as plumbing, electrical systems, doors, windows, glass and so on, where there has been significant change in the materials and methods of construction in the past century. This is not to say that there are no alternative binder systems used in the construction industry, but rather that these systems have not been commercialised at anywhere near the scale of Portland cement, or (importantly) during the modern era of standards and the global nature of the construction community.

Today, there are very specific standards for what is considered acceptable performance for a cementitious binder in every manner of application. Such standards have been developed over many years, with input from representatives of the entire construction industry including Portland cement manufacturing companies, contractors and asset owners – and with, due to the absence of significant alternatives, the chemistry and behaviour of Portland-based concretes intrinsically in mind. The dominant presence of Portland cement is most evident via the widespread use of prescriptive standards containing constraints such as "minimum cement content". Even for Portland-based concrete such standards are increasingly being viewed as prohibitive, and products with high levels of cement substitution by supplementary cementitious materials (SCMs) are now no longer seen as technological oddities. The change from prescriptive to performance-based standards has been the subject of a significant debate in the construction industry for many years, and gives the reader an insight to the level of challenge to have standards for different binder chemistries developed and accepted.

Products such as geopolymer or AAM concrete, other non-Portland binders, and even high-performance cement-based systems, may not simply be an evolution of existing Portland technology, but instead may require an entirely different chemical paradigm to understand their behaviour, and may perform entirely acceptably but without conforming exactly to the established regulatory standards – particularly with regard to rheology and chemical composition.[12] The fact that these aspects of the binder systems fall outside the existing standards is a significant hindrance to the acceptance of geopolymer technology. It is understandable that without the imprimatur of a form of government or association, and given the enormous scale and diversity of the concrete industry, that it is effectively impossible for the public, technically less-sophisticated producers or users to have confidence in the technology. However, by their very nature the committees and associations that develop and maintain standards are extremely slow-moving and inherently not incentivised to encourage or easily accept change. After all, standards only have meaning if they provide a relatively static datum point representing a minimum acceptable level of performance over a long period of time.

The necessary preconditions for the writing of such standards therefore include:

- A quorum of industrially and academically recognised experts in a field;

- Sufficient fundamental technical knowledge to convince those skilled in the field that performance can be measured in a short period of time (<90 days in general);
- A minimum performance standard utilising the aforementioned measures;
- Real world structures and examples to validate the minimum performance standard.

Therefore, the geopolymer community determined several years ago that new standards would need to be developed to meet the performance and chemical criteria of the system, and some of the outcomes of this discussion are covered later in this paper.

Durability

The question of whether geopolymer or AAM concretes are durable remains the other key obstacle to broader commercial adoption. This is to say that it is the question, rather than the answer, that remains the obstacle. Some would say that alkali-activated materials have been subjected to detailed investigation only recently and cannot possibly have the decades of durability data to prove long-term stability, yet this is plainly not the case.[8,13-15] It can equally well be asked what evidence, other than structures that have existed in service for long periods of time, do existing binder systems have to prove their fundamental durability? The answer is that there is very little - but the durability of Portland cement is not questioned, even though recent analytical studies show significant changes in the nature of the hydrated Portland cement binder and cement-slag blends over a period of 20 years.[16] Against this background, alkali-activated systems have the unenviable task of proving themselves durable when the ultimate measure, the presence of decades-old structures, is in the end the only verification tool accepted.

Most standard methods of testing cement and concrete durability involve exposing small samples to very extreme conditions – such as highly concentrated acid or salt solutions – for short periods of time. These results are then used to predict how the material will perform in normal environmental conditions over a period of decades or more. Predictive models rely on concepts including mass transport through porous media, reaction kinetics and particle packing. A shortcoming of this approach to attempting to “prove” durability is that it can only provide indications of the expected performance under actual environmental conditions, rather than any sort of definitive proof. Furthermore, the structure of the research community is based fundamentally around the timescale of graduate research projects, 3-6 years. This inherently leads to the problem that what is considered ‘long-term’ testing is at least an order of magnitude shorter period of time than the predicted service life of most concrete structures. Where projects are conducted over longer periods of time there needs to be strong project stewardship and focus, which is rarely seen. Therefore, the reality is that durability tests mean little in the absence of real world validation. Thus, the adoption of new materials at scale is intrinsically very slow, as periods of 20-30 years are required for verification of test results, and this is clearly not a timescale on which commercialisation efforts can be based.

Therefore, there are two approaches possible, which are now being undertaken in parallel: linking durability of alkali-activated materials to chemical structure using cutting edge scientific techniques, and putting as many real world structures with very well documented mix designs into use as soon as possible, so that they can achieve the required ages of decades or more, as soon as possible.

The role of chemical research

Quite plainly, it is due to the many decades of work in the area since 1940[17] that alkali-activated technology is now at the point of commercial utilisation. The quorum of interest from industry and academia required to provide a broad acceptance of the technology, as outlined above, has been best embodied in the formation of the RILEM Technical Committee 224-AAM, investigating alkali-activated materials. The core challenge of such committees in this field is to provide simple measures for determining performance characteristics for alkali-activated materials, particularly where such measures are intrinsic to AAM chemistry. Measurement of mechanical performance measures such as shrinkage, compressive strength, creep and moduli of elasticity, on the other hand, is material-independent. The areas in which consensus is difficult to reach include measures of porosity, permeability and penetrability of materials, where a deep understanding of the nature of the material is required.

AAM technology is not likely to be accepted at scale until there is industry-wide acceptance of AAM durability, and the ability to accurately measure it in a short period of time. Therefore, in essence the challenge of understanding the durability of alkali-activated materials is a sub-set of the standards discussion, but deserves heightened status due to its importance. There are many such tests for OPC-based concrete, and here a case-study is provided as an example of the challenges ahead for the industry. The Victorian Roads Authority puts significant weight on the measurement of the “volume of permeable voids” (VPV), which is in effect a measure of the total voids (air and pore water) in concrete cores. This is fundamentally related to four main factors; the extent of hydration of cement and SCM’s, compaction, porosity of aggregates and water content of the mix design. The intent of the measure is sensible; to make ‘acceptable’ concrete you need to have ‘enough cement’, not ‘too much water’, ‘good compaction’ and ‘good aggregate’. The principle is that a single parameter is used to provide an overall durability prediction, similar to the manner in which the ASTM rapid chloride permeability test is often used. For the VPV test, analysis of thousands of mix-designs over decades shows excellent correlation of this method with acceptable outcomes for Portland cement. The problem, however, is that alkali-activated materials do not hydrate. Therefore, the basis of this methodology no longer covers the concept of extent of reaction in the case of alkali activation. Additionally, one can make similarly performing mix-designs of alkali-activated concrete with either high or low water content. Therefore, half of the principles of this durability measure do not apply well to AAM's.

While commercial producers play a critical role in putting alkali-activated materials in service for real-world verification, and regulatory authorities are prepared to undertake trial and verification programs over long time horizons as anticipated above, there have been significant advances recently in fundamental chemical analysis that point to a rapid pathway to make progress in understanding durability with short time-horizon analysis. Specifically, recent research using X-ray tomography[18] has shown the potential for direct, three-dimensional characterisation of AAM pore networks as a function of mix design and curing duration. The porosity of AAM binders decreases with increasing slag/fly ash ratios, and with increasing curing time in the slag-rich systems which are expected to generate space-filling hydrate binder phases (but not to anywhere near the same extent in low-calcium systems which do not form a hydrated binder).[18] Pore network tortuosity, which is just as critical as total porosity in terms of durability performance, can also be measured by this technique, and increases dramatically for low-porosity, slag-rich, well-cured samples. By understanding the nature of the porosity and tortuosity of geopolymer and alkali-activated gels it thus becomes possible for the first time to describe how gels synthesised by different processing routes, while exhibiting similar physical and mechanical properties, may have dramatically differing prospects in terms of durability.

Conclusions

From the very brief discussion presented here, it is clear that significant progress in the commercialisation of alkali-activated materials has only occurred due to chemical research completed and published around the world by academic and industrial workers for more than 70 years. This has resulted in a quorum of interest in the technology, which is required to gain the industrial credibility and impetus to form new standards. These standards can then govern adoption and provide incentive for authorities to put in place long term trial project for real-world monitoring. Alkali-activated materials are generally well-served by the existing standards relating to OPC products describing material performance characteristics that are not chemistry-specific. The remaining challenges lie now in identifying aspects of chemistry related to standards, and completing the necessary research to provide equivalent rapid tests for performance and durability validation. This challenge ties directly the fortunes of the technology to fundamental chemical research.

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