VALORISATION OF SLAG IN CONSTRUCTION: SO MUCH MORE THAN JUST TECHNOLOGY

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Introduction

Much work has been published on the alkali activation of slags, mainly ground granulated blast furnace slag (GGBFS), and coal fly ash, with studies on the activation of other industrial wastes and natural pozzolans being more limited.[1-3] Some proponents of a specific class of activation chemistry have gone to great lengths to distinguish their terminology from alkali-activation, and to claim that their methods are superior. It is not the aim here to enter into this debate, nor to present an analysis of cementitious phase formation, alkali activation, or geopolymer chemistry. Here, the inclusive term *activated cement* (AC) or *activation chemistry* will be used to capture all types of reactions of supplementary cementitious materials (SCM) caused by the addition of reagents, including Portland Cement (PC). Here, alkalis, acids and neutral salts are all considered to be *activators*. The aim is to minimise the use of both PC and activators and maximise the use of SCM, so as to reduce the CO_2 emissions of the resulting cement and at the same time optimise the production cost.

Instead of having a technical focus, the aim of this paper is to outline the commercial challenges facing the adoption of activated slag into the construction market, and to suggest ways to overcome hurdles. It will be shown how an innovative combination of activation technology with a distributed grinding system can facilitate the valorisation of smaller quantities of locally available SCM, including metallurgical slags. It will be shown how an activation mix design protocol based on a deep understanding of phase evolution has been used successfully in large scale construction projects.

Drivers for Commercial Adoption

Concrete based on PC blended with GGBFS and/or coal fly ash is widely accepted in construction and conforms to the standards and design codes. Therefore, there must be a strong commercial or technical driver for the adoption of AC as a PC replacement. Such drivers may be:

1. Ultra-low CO_2 emissions (80% to 90%) of AC compared with PC;
2. Valorisation of waste materials, including metallurgical slags and natural pozzolans not currently blended with PC;

3. By using high levels of indigenous materials in remote locations, the transportation of PC can be minimised when using AC;
4. High chloride resistance of AC, hence excellent in a marine environment, resulting from low permeability, immobilisation of chloride at pore surfaces, and elimination of portlandite;
5. High sulphate resistance of AC, as the binding phases do not degrade as in the case of PC;
6. High acid resistance of AC due to the absence of portlandite;
7. High fire resistance of AC resulting from the absence of portlandite and the pore structure morphology;
8. AC concrete can be formulated to give ultra-low shrinkage by balancing chemical shrinkage and expansive reactions;
9. Low heat of hydration of AC, which is beneficial at high ambient temperatures and when large volumes of concrete are poured;
10. GGBFS is usually white in colour, almost like expensive white cement. By using proprietary technology, it is possible that the metal content in metallurgical slags could be removed and the slags atomised to become a white cementitious powder, like GGBFS. Therefore, ultra-high levels of such slags can be combined with a small amount of white cement in AC to produce a white binder with high reflectance, which is increasingly sought after to reduce the heat absorption of urban roads.

Limitations of Existing Cement Technology

Contemporary cement technology does not allow ultra-high replacement of PC by slag or fly ash owing to their low reactivity, hence slow strength development. The dissolution of gypsum initially and subsequently cement clinker by water causes the formation of portlandite that acts as an activator for dissolution of the glassy phases in slag and fly ash. The early strength of the concrete results mainly from binding phases formed from the PC, with the slag and fly ash dissolving more gradually when sufficient portlandite has been formed by the PC. Increased levels of slag also cause higher water demand, which means that excessive levels of superplasticiser are required to reduce water demand, as in normal concrete technology a higher water addition results in higher permeability and hence decreased durability. Consequently, the high admixture requirement of high slag concrete could lead to high cost mix designs.

An alternative approach followed by some suppliers of “geopolymer” technology is to accelerate the dissolution of fly ash or slag by the addition of high levels of strong alkalis like sodium silicate and sodium hydroxide, which accelerate the dissolution reaction. Such high level of strong alkalis equates to using a “sledge hammer” to address the problem of low reactivity of slag or fly ash. Moreover, it increases the cost of the mix design, sometimes to uncompetitive levels. Unless one is careful to control chemical balances, this approach may lead to the formation of undesirable phases,

which will result in poor durability. At the same time, conventional superplasticisers are not effective in the high soluble silicate environment, hence workability of the wet concrete is reduced. Proprietary superplasticisers have been developed for this chemistry, but are not yet commercially available. For these reasons, classic "geopolymer" technology has found only limited application in large structures.

Different Approach to Activated Cement

Zeobond's E-Crete™ technology uses a series of proprietary activators and catalysts to suit the reaction profile of any SCM in order to accelerate dissolution reactions and at the same time catalyse the formation of binding phases. This methodology is based on a thorough microscopic and kinetic characterisation of the starting materials, as shown in Figure 1. A system of equations is then solved to predict the evolution of phase development, and validated using quantitative microscopy; if required, the model predictions are refined. This predictive approach ensures that desirable phases are formed at the right time along the reaction pathway, while the formation of deleterious phases is avoided. The data generated are sufficient that the setting time and slump of the concrete can be designed at different operating temperatures.

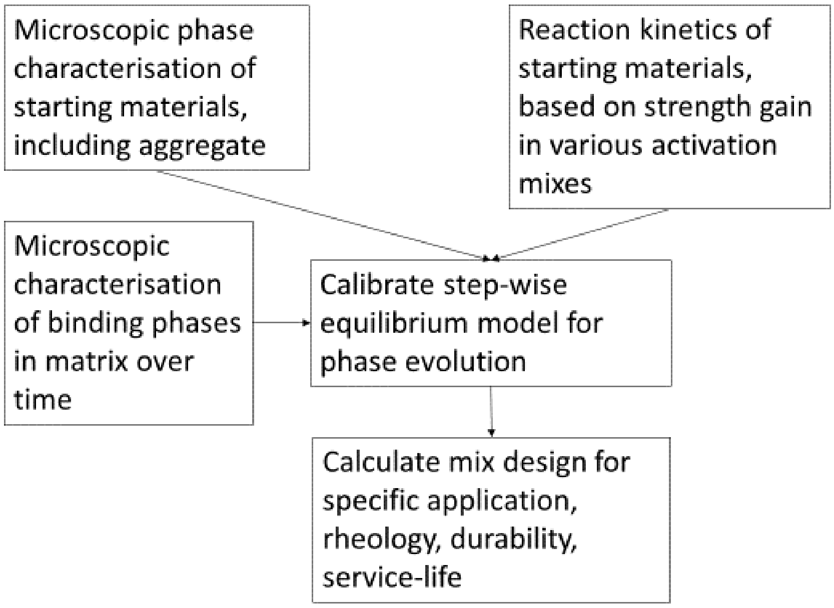

Figure 1: Methodology for concrete mix design based on activation chemistry

Although it is possible to use zero PC when activating many SCMs, a small portion (5 to 10%) PC is often used. This is often an efficient way to introduce calcium into the system, PC is always available, and structural engineers and customers feel more confident if the AC contains some PC. Only "mild" reagents that are safe for manual handling are used. The technology also exploits the reaction of binding gel with

aggregate particles, and takes the latter into account in phase calculations. Depending on the phase assemblage possible with certain starting materials, a high water/binder ratio may sometimes be beneficial for ongoing crystalline phase development, in contrast with what is taught conventionally.

Geographically Distributed Processing of Indigenous Materials

PC clinker and GBFS granules are usually ground in large, vertical roller mills (Figure 2a) that are capital intensive and located in association with PC operations. It is not practical to use such equipment in smaller markets or in a geographically distributed manner to exploit smaller waste streams such as metallurgical or steel slag, or virgin materials like volcanic ash or rock. This limitation on grinding practice has consolidated the position of PC interests in smaller and remote markets, even when local material could be used as SCM.

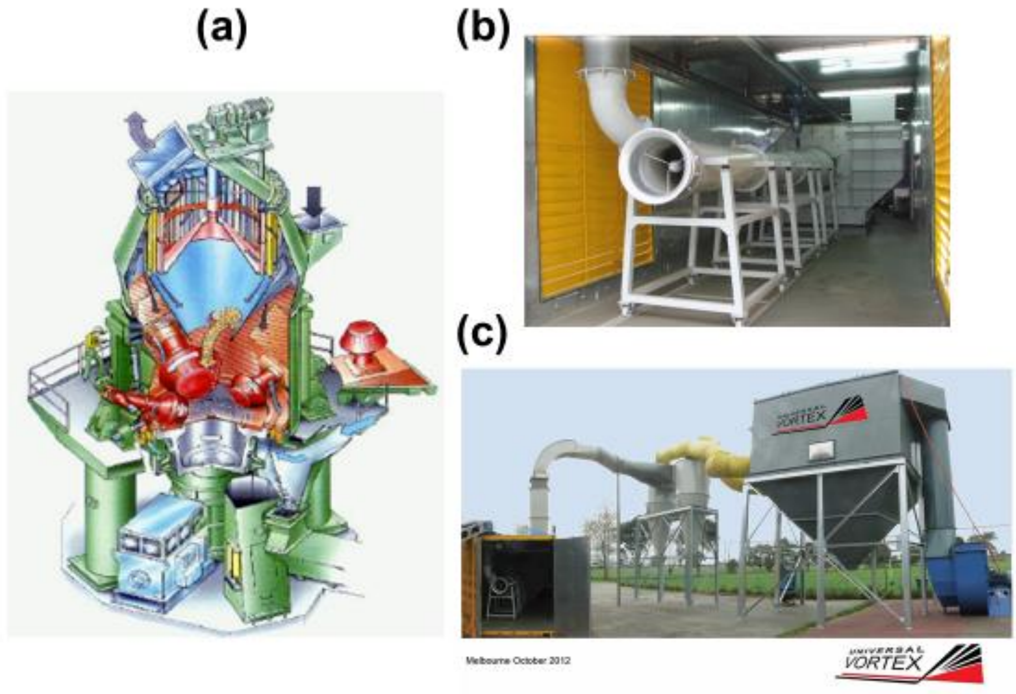

Figure 2: (a) Schematic diagram of vertical roller mill, (b) Universal Vortex acoustic grinder in a shipping container, and (c) with dust collection system

Loesche[4] in Germany has recognised this limitation and now has a compact vertical roller mill available for remote locations where a customer will grind PC clinker and/or GBFS granules in smaller volumes. IMPTEC[5] in South Australia has also recently developed and successfully trialled an innovative gyratory crusher with excellent capability for cementitious materials. The IMPTEC fine-crusher has been shown to work for metallurgical slags and fly ash. The Universal Vortex acoustic grinder produces a shock wave generated in a precisely designed geometry to shatter brittle materials and has been used at demonstration scale for PC clinker and GBFS granules. The

advantage of the Universal Vortex is that it fits into a shipping container (Figure 2b and 2c) so it is mobile and can be deployed easily in remote locations for the grinding of indigenous material (Figure 3), and also for one off construction projects, when using AC.

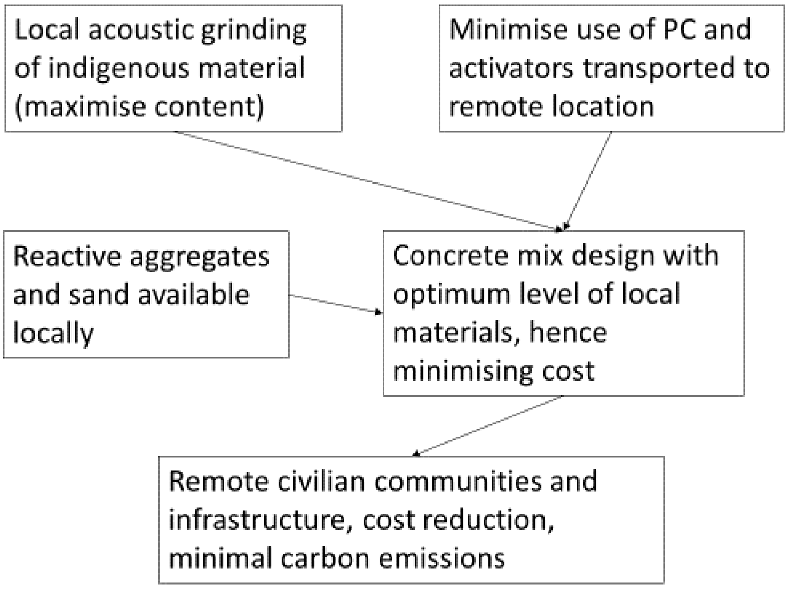

Figure 3: Geographically distributed grinding and activation of indigenous material

Performance-Based Versus Prescriptive Standards

Obstacles implicit in the standards framework

In view of the low reactivity of slag and ash relative to PC, the regulatory framework for cement and concrete in most jurisdictions has become prescriptive, even when it is claimed superficially that such standards are performance-based. The committees drafting such standards usually have good intentions to ensure quality of concrete, but in the process, may not be aware of the constraints they place on innovation by basing their assumptions on PC chemistry. In essence, the standards frameworks restrict the use of GGBFS and coal fly ash, and hence prescribes concrete compositions. Based on the existing status of concrete technology, these restrictions are understandable, but at the same time they prevent the introduction of a higher level of proven concrete technology such as Zeobond's E-Crete into the market. Usually, the underlying assumptions in existing regulatory frameworks are:

1. For higher strength concrete, the addition of slag or fly ash must be restricted as their reactivity is too slow to give adequate strength development; it is assumed that such reactivity cannot be enhanced.

2. Ironically, for more aggressive exposure conditions, including to overcome alkali silica reactions (ASR), a higher level of ash or slag addition is prescribed.
3. It is assumed that the main binding phases result from PC, hence the specification of minimum PC levels for different strength grades.
4. A minimum cementitious content per m3 concrete is prescribed, which assumes that binding phases do not result from the aggregate particles. This is a result of the practice in existing concrete technology to use inert aggregates, as it is (incorrectly) assumed that binding phase generation from reactions at the aggregate are necessarily deleterious.
5. A maximum water/cement ratio is prescribed, which assumes that too much water leads to higher permeability and hence low durability. The underlying assumption is that only a certain fraction of the water can be bonded in crystal formation.
6. Only coal fly ash and GGBFS are normally approved as supplementary cementitious materials (SCM), with some standards allowing a restricted content of natural pozzolans and calcined clays. This restricted definition of SCM prevents the use of other waste materials such as biomass ash and reactive metallurgical slags not produced by an iron blast furnace.

Standards and codes committees in most jurisdictions have membership from the relevant industry groups, including cement and concrete interests, some researchers and key government representatives. In view of their composition, it rarely happens that a standard is introduced or revised that will benefit a new market entrant and disadvantage dominant industry incumbents. Unfortunately, few academic members of a standards committee, who are often in the minority, will push hard against the interests of the incumbent industry in fear of losing research funding. This prejudice will not be admitted by members but is implicitly a result of human nature.

The need for performance-based standards

In order to enable the wide adoption of advanced concrete technologies like Zeobond's E-Crete, it is essential that a performance-based standards framework be adopted instead of the current prescriptive system. At the least, such a performance-based framework should apply to concretes containing above the maximum SCM currently specified. There should be no restriction on the type of components used, either as cementitious material, aggregates or admixtures/activators. The amount of cementitious material and the water/cement ratio should also not be restricted. Suppliers should report the content of PC and other SCM, but for commercial reasons the specific nature of the admixtures/activators do not need to be specified. A Material Safety Data Sheet (MSDS) should of course be supplied for all admixtures and activators, or combinations thereof. For a dry one-part activated cement mix it may be required to specify only the main components such as an XRF analysis, plus an MSDS.
It is important to ask which performance and durability testing methods should be used in order to specify performance criteria. The discussion above shows the challenge of developing testing methods for durability that are independent of initial

binder phase assemblage. In a critical review of performance-based approaches[6] it was explained that it is possible to relate service-life prediction models to durability testing, even when it is known that the diffusion parameters in concrete are complicated by several factors, including interaction between the diffusing species and the matrix, and the reduction of diffusion coefficients with age. It is noteworthy that South Africa[6] has developed a suite of durability index tests – oxygen permeability, sorptivity, and chloride conductivity – and these are linked to service-life models for the relevant deterioration mechanisms in reinforced concrete structures. In addition, the slump and setting time must be specified per application, and for certain exposure conditions resistance to freeze-thaw, salt scaling, sulphate, acids and ASR[7] may be added to the performance criteria.

Unfortunately, few engineers taking decisions on the approval or not of a concrete mix have sufficient insight to relate microstructure to durability and service-life prediction. Even concrete researchers struggle with this concept. Therefore, it is not so easy to convince decision-makers that a concrete will be durable if it is possible to predict phase assemblage over time, so that deleterious phases like expansive alkali-silica gel does not form, even when a high level of silica is present. There remains a need to publish in-depth research on these questions, as that will help to instil confidence in AC. Unfortunately, many of the academic studies focus on either artificial conditions, or present mix designs that are far from industrial reality, so that the conclusions have little practical relevance. By using spin-polarised Density Functional Theory (DFT), Özçelik and White[8] recently showed that activated binder phases can be even more stable than PC-generated phases provided that alkali cations are accompanied by a bridging Al site and the proper amount of H atoms for charge balancing. This provides an example where in-depth theoretical work has a direct implication for mix design using AC.

Commercialisation strategy and Applications

Despite the regulatory hurdles described above, it is possible to penetrate the construction market with a new AC binder if innovative commercial strategies are used. For example, bulk products such as rendering mortar, grouts and screeds that are not subjected to cement standards can be developed and marketed, provided there is a cost or performance benefit, such as reduced shrinkage. There are indeed applications with a high requirement for durability, in which case AC could be used, provided that a convincing argument can be made for competitive cost and an extended service life; often this must be done on a case by case basis. Many precast products like building blocks and even large paving for road concrete road construction have largely a performance and durability specification, which is suitable for AC. In order to make progress with standards committees and build confidence with key customers it is often necessary to obtain special approval for iconic projects; this is challenging and requires special skills of negotiation. Wherever possible, it should be attempted to comply with existing cement and concrete standards, even if it means

that a higher level of PC is added than necessary technically. As an initial strategy, this facilitates adoption of AC as it conveys a message of similarity in a conservative market. The pathway towards commercial adoption will be smoother through vertical integration of control over the materials supply chain, concrete production, and control over construction projects, so that approvals are internalised.

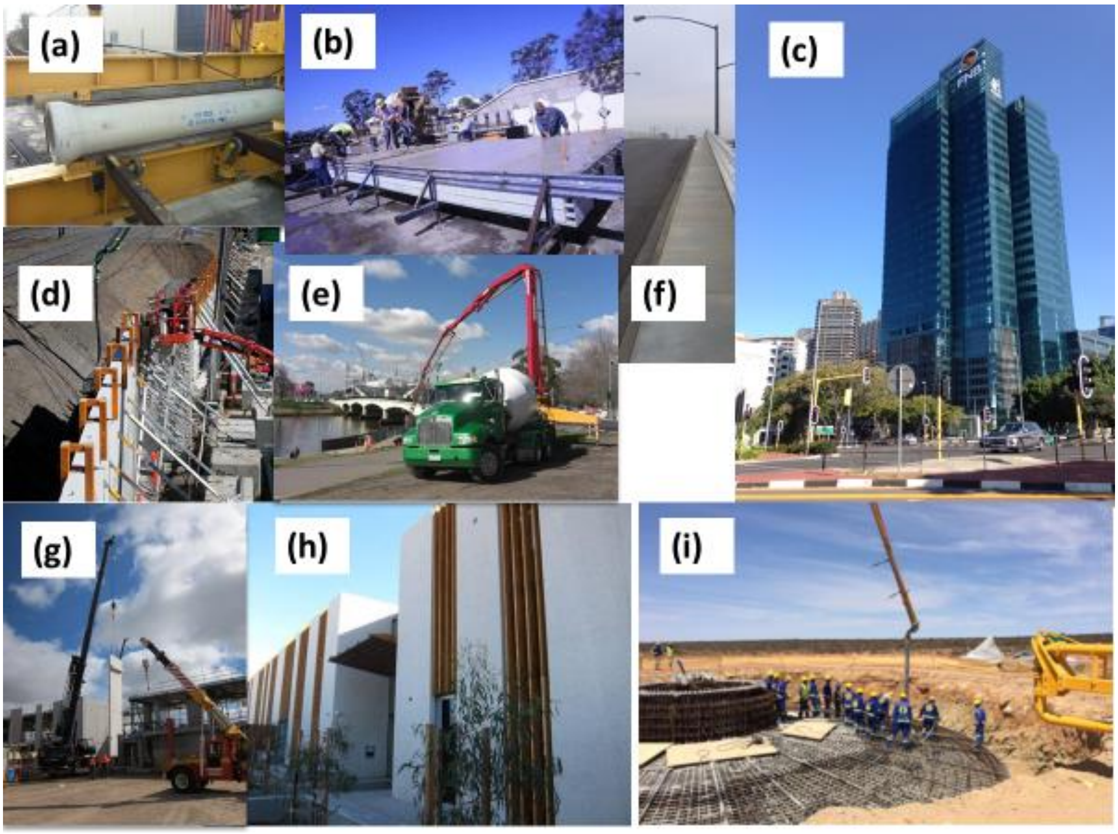

Figure 4: Selected examples of AC projects in Australia and South Africa: (a) Pipes produced by Reinforced Concrete Pipes of Australia (RCPA), (b) Bridge deck cast in Queensland, (c) Portside building in Cape Town, South Africa constructed by Murray & Roberts, (d) Retainer wall for Regional Rail Link project in Melbourne, (e) Embankment for Swan Street Bridge in Melbourne, (f) Bridge deck panels for Salmon Street Bridge in Port Melbourne, (g) and (h) Precast panels and general concrete works for Melton Library, Melbourne, (i) Foundations for windfarms at west coast of South Africa constructed by Murray & Roberts

Figure 4 shows that AC technology has been applied in a large number of pre-mixed and precast projects in Australia and South Africa. VicRoads, the roads authority in Victoria, Australia, has changed its specifications to recognise AC concrete as equivalent to PC. Also, the E-Crete produced by Zeobond meets the Australian standard AS3600 for structural grade concrete, as it prescribes only a low content of PC. In South Africa, pioneering work[6] to promote performance-based standards has been instrumental in getting acceptance for ultra-low PC concrete. Consequently, Murray & Roberts has constructed the main container terminal in Johannesburg, high-

rise buildings in Cape Town and Sandton, and multiple wind farms using this approach, where about 90% of the PC has been replaced by Corex slag and fly ash. In Australia, the driver for adoption of AC technology has been reduced CO_2 emissions, while in South Africa the drivers have been both low CO_2 emissions and significant cost reduction.

Carbon Emissions

CO_2 emissions from cement production arise from the consumption of fossil fuels, the use of electricity and the chemical decomposition of limestone during clinker formation at around 1400°C. The decarbonation of limestone to give the calcium required to form silicates and aluminates in clinker releases roughly 0.53 tonnes CO_2 per tonne of clinker.[9] In 2005, cement production (total cementitious sales including PC and blended cement) had an average emission intensity of 0.89 with a range of 0.65 to 0.92 tonnes CO_2 per tonne of cement binder.[10] Therefore, the decarbonation of limestone contributes about 60% of the carbon emissions of PC, with the remaining 40% attributed to energy consumption. In contrast, if energetic materials such as fly ash, slag or natural pozzolans are activated, it is mainly the CO_2 intensity of the activators that determine the CO_2 intensity of the AC. A commercial Life Cycle Analysis (LCA) on Zeobond's activation technology has shown before that CO_2 savings in excess of 80% are possible relative to a PC blend containing about 30% ash or slag.[11] An independent analysis of the Zeobond patent for a one-part geopolymer type cement showed CO_2 emissions of only 5% of that of 100% PC.[12]

Different activators have vastly different CO_2 intensity, and the source of activators has an equally significant impact. Zeobond usually seeks to use waste material as an activator, as it incurs no penalty in an LCA. The production of sodium silicate, which is widely used as an activator, is based on Na_2CO_3, which can be obtained by furnace or hydrothermal routes, with CO_2 emissions varying by a factor of 2 to 3, while other emission categories in a complete LCA could vary by a factor of 800.[13] The case of NaOH, which is not preferred as an activator, but still used, is similar, as its production uses different processes in different parts of the world which will also change the LCA substantially. Therefore, the published LCA of AC show very different outcomes, from more than 80% CO_2 reduction to nil.[14]

Many of the published mix designs for AC involve high activator addition, usually in an attempt to accelerate dissolution and binding phase formation. In contrast, Zeobond's proprietary mix designs used at commercial scale have involved very low levels of activator, and where such activator has been sourced from industrial waste streams, with negligible CO_2 emissions. This has been made possible by using proprietary reagents to accelerate dissolution and phase formation reactions interactively. The resultant cement then results in a CO_2 saving of 80 to 90% compared with most PC blends. These commercial mix designs using low activator addition have also resulted

in substantial cost reduction compared with PC blends, which has been the key driver for their adoption, rather than just CO_2 reduction.

Final Remarks

AC has progressed from a laboratory research phase to industrial application in various structures and in different countries. Although further work is required to introduce a wider variety of precursors into the cementitious supply chain, and confidence building in the market will be ongoing, AC now offers a high-volume, affordable, and low-CO_2 alternative to PC. Although methods for accelerated durability testing and prediction of service-life can always be improved, existing methods for any cement including AC are adequate to underpin the adoption of a performance-based standards framework, which is essential for the utilisation of various precursors, including metallurgical slags, in AC. Such a framework will greatly enhance market adoption as it will simplify specification of AC by structural engineers and reduce perceived risk, which will expand the scale of the supply chain, reduce costs and justify more expenditure on research, leading to further improvements in the technology. An effective way to overcome the obstacles to the adoption of AC is to vertically integrate the production of AC into construction projects and internalise the approvals process.

Substantial progress has been made on the analytical characterisation and phase modelling of AC. Nevertheless, as is the case with PC, the link between nano-structure, microstructure and macroscopic/engineering behaviour of AC requires further work. There is a need to generate more data to describe the engineering behaviour of AC under different exposure conditions, so that existing structural design methods can be recalibrated. For this to happen in a productive manner, it is essential that structural engineers and materials researchers collaborate more closely.

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