Alkali Activated fly Ash based geopolymer concrete for infrastructure applications

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Abstract

Geopolymer is an inorganic aluminosilicate binder that can be used as an alternative to Ordinary Portland Cement. This alternative inorganic binder chemistry has been investigated extensively in the laboratory to develop geopolymer matrices and concrete materials laid on scientifically sound basis. Significant progress has been made in the development and applications of geopolymers during the recent decades. An overview of advances in geopolymers formed by the alkaline activation of aluminosilicatesis presented in this paper. The technological and commercial potentials and opportunitieswere also outlined in the paper. The challenges faced in the up scaling and implementation of the geopolymer concrete in construction and other various less well known niches of applications are described briefly. The research and development carried at CSIR-CBRI, Roorkee is presented with developed various products using geopolymer concrete at the Institute with pilot scale trials.

INTRODUCTION

The use of alternative binders in place of ordinary Portland cement (OPC) have gained strong basis recently due to the increasing focus on global climate change, the public and consumer preferences for "green" products, and the associated markets in carbon credits. These alternative binding systems can provide a viable direct opportunity for near term and substantial CO_2 emissions reduction. There are a variety of binder systems available that deliver the potential for high performance and environmental savings, while representing a significant departure from the traditional chemistry of OPC. The demand of green concrete in construction industry is driven by increased regulations to reduce carbon footprint, limit greenhouse gas emission and shortage of landfill sites. Increasing emphasis on energy conservation and environmental protection has led to investigationson alternatives to conventional building materials. In this regard, a potential alternative to Portland cement is geopolymer. The term "geopolymer" is generically used to describe the amorphous to crystalline reaction products from the synthesis of alkali aluminosilicates with alkali hydroxide/alkali silicate solution. There are several advantages of geopolymer materials over OPC, namely potential environmental benefits, high compressive strength, rapid setting and hardening, fire resistance, and acid and salt solution resistance reported in the literatures. One of the most important benefits of geopolymers lies in the utilization of industrial wastes as resourceraw materials. In terms of their environmental impact, geopolymers are reported to generate nearly 80% less CO_2 than OPC.

However, this green binder constrained from full scale application because of the key gaps in one or more of the following areas: (a) validated long term durability data (b) appropriate regulatory standards and accompanying awareness from regulatory authorities regarding the state of technological maturity (c) industrial and commercial experience in materials design, production, quality control and placement; (d) raw materials supply chain [1].

The national and global geopolymer market is projected to witness robust growth throughout the upcoming period. The rising focus of key players on technological developments and innovations is one of the vital factors estimated to encourage the growth of global geopolymer market in the next few years. In addition, the expansion of application base is expected to generate promising opportunities for the key players operating in the geopolymer market. With the help of these drivers, the geopolymer market is expected to register an impressive growth.

The commercial future of alkali activated geopolymer materials, similar to the case of many other alternative binders for concretes, depends not only on technical readiness, but also on the economic and social readiness. Standardization is an important component of commercialization, but in fact (and contrary to the assumptions of many researchers) represents only a small part of the whole commercialization process.

The aim of this paper is to provide a comprehensive review on the process of synthesis of geopolymer binder and to briefly describe the research studies reported on the geopolymer concrete in construction. Various possible applications of geopolymer concrete have been presented along with thechallenges faced by the promoters and commercialization agencies for large scale construction and implementation.

GEOPOLYMER SYNTHESIS

Geopolymers are the subset of alkali activated materials (AAM), where the binding phase is almost exclusively aluminosilicate and highly coordinated [2]. To form such a gel as the primary binding phase, the available calcium content of the reacting components is usually low, to enable formation of a pseudo-zeolitic network structure rather than the chains characteristic of calcium silicate hydrates[3]. The activators are usually alkali metal hydroxide or/and silicate. Low-calcium fly ashes and calcined clays are the most prevalent precursors used in geopolymer synthesis [4]. The fundamental binder structure in low-calcium alkali-activated systems is known to be a highly disordered, highly cross-linked aluminosilicate gel. Both Si and Al are present in tetrahedral coordination, with the charges associated with tetrahedral Al sites balanced through the association of alkali cations with the gel framework. Similarities between this gel structure and the structure of zeolites have been cited in numerous publications. This includes the early research work of Glukhovskyet al. [5], who used zeolitic structures to draw an analogy between alkali-activated binders and ancient Roman concretes. Davidovits [6], who sketched molecular structure fragments based on the zeolitic or similar structures (analcime, sodalite, phillipsite, leucite, kalsilite). Later, itwas proposedthe similarity between hydrothermal zeolite synthesis and the synthesis of alkali aluminosilicatebinders [7]. This leads to generation of nanosized zeolite-like structural units throughout the AAM gel in addition to crystalline zeolites, which are widely observed, embedded within the disordered gel, particularly at higher curing temperatures [8].

The geopolymerizationprocess involves three separate processes and during initialmixing, the alkaline solution dissolves silicon and aluminiumions in the raw material (fly ash, slag, silica fume, bentonite,etc.). It is also understood that the silicon or aluminiumhydroxidemolecules undergo a condensation reaction whereadjacent hydroxyl ions from these near neighbours condenseto form an oxygen bond linking the water molecule, andit is seen that each oxygen bond is formed because of acondensation reaction and thereby bonds the neighboring Sior Al tetra-hedra [9].Fig. 1 presents a highly simplified reaction mechanism for geopolymerization.

Thisoutlines the key processes occurring in the transformation of a solid alumino-silicate source into a synthetic alkali aluminosilicate [4].

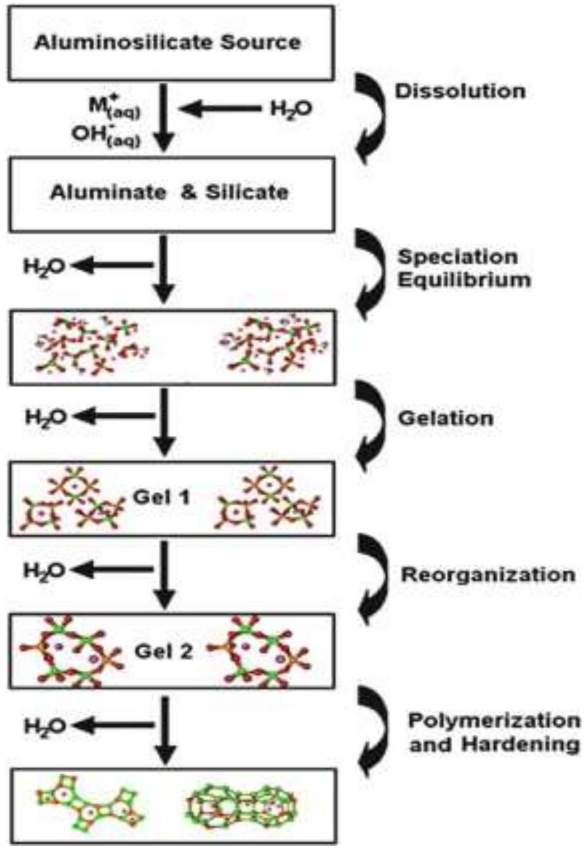

Fig. 1. Synthesis of geopolymer binder by hydroxide activation of an aluminosilicate source [4].

The of geopolymerization mechanism composed of conjoined reactions of destruction/dissolution–coagulation–condensation–crystallization.The first step consists of a breakdown of the covalent bonds Si–O–Siand Al–O–Si, which happens when the pH of the alkaline solution rises,so those groups are transformed into a colloid phase.The dissolution step is affected by several factors which includes temperature, pH and thepossible pretreatments of the aluminosilicate source. An accumulationof the destroyed products occurs, which interacts among them to form a coagulated structure, leading in a third phase to the generation of a condensed structure and crystallized.

APPLICATIONS/ PRODUCTS DEVELOPMENT

Early research in the developments of geopolymer (low-calcium including calcium-free) binders were led by Davidovits in France. These materials were initially envisaged as a fire-resistant replacement for organic polymeric materials, with identification of potential applications as a possible binder for concrete production [10]. However, developments in the area of concrete production soon led back to more calcium-rich systems, including the hybrid binders, leaving work based on the use of low-calcium systems predominantly aimed at high-temperature applications and other scenarios where the ceramic-like nature of clay-derived alkali- activated pastes was beneficial. Geopolymer cement is an innovative material and a real alternative to conventional Portlandcement for use in construction,transportation infrastructure and offshore applications.

Application as structural members

The applicability and suitability of geopolymer concreteas structural element, design aspects such as loadcarrying, flexural strength and bond-slip were studied and assessed. Therefore, applications of geopolymer concrete were extended to structural elementssuch as beams, columns and slabs. The structural behaviour of fly ash-based geopolymer concrete beam similar to the ordinary reinforcedconcrete beams [11]. Ng et al. [12] found better performance of geopolymer concrete beams with steel fibers. The shear cracks were delayed due to addition of fiber. It was reported that lower post-peak ductility wasobserved when ground granulated blast furnace slag (ggbfs) were added in geopolymer concrete [13]. Failure mode offly ash basedgeopolymer concrete column wasobservedsimilar to conventional concrete column [14]. Brittle failure was reported of geopolymer concrete columns [11]. To increase the load carrying capacity andthe ductility of steel fibers and confinement canbe used.While in geopolymer concrete slabs, it was found that the ductilityand energy absorption are better compared to ferrocement slabs [15,16].

Application as porous/insulating material

Research studieswere carried out on the development of porous geopolymer particularly as insulating materials for potential building applications. Thefoamed agents includes air foaming generator, sodium perborate, hydrogen peroxide,aluminum powder, and biomass materials were used [17- 21]. Abdollahnejad et al. [17] investigated thejoint effect of several mix parameters on the properties of fly ash-based foam geopolymers andobserved a better result with sodium perborate compared to hydrogen peroxide as a foamingagent. A mixture with a low thermal conductivity of 0.1 W(m K)$^{-1}$ and compressivestrength of 6 MPa was obtained, suggesting the potential use of the foamed fly ash geopolymeras insulating materials for building applications [17].In addition to insulating applications, porous or absorbent geopolymers were alsodeveloped with or without foaming agents, for potential application in purification [22,23].Pilot-scale production of autoclaved foamed alkali-activated ggbfs concrete was initiated in 1978 in Berezovo, Russia, using a waste mixed-alkali hydroxide solution as an activator[24]. Later, in Kiev the development of autoclaved aerated concretes by alkaline activation of metakaolins and fly ashes were carried out [25,26].

Applications as fire resistant/ protection materials

Several researchers [27-30] carried out the development of geopolymers for fire resistant lining / coating applications. Reflective heat insulation coating was prepared using a geopolymer, which wasmainly made of sodium silicate solutions and metakaolin as the primary film forming materialbefore adding, after screening their functions, sericite powder, talcum powder, titanium dioxideand hollow glass microspheres as fillers. This coating presented many capabilities, such as goodwater-retention, simple spraying, high durability and dirt resistance, with a reflectivity above90% and a thermal insulation temperature difference reaching 24ºC, suggesting its potential usein buildings to conserve energy [28]. Geopolymer coating can also be applied as surfaceprotection to concrete structures in order to extend their service life [29,30].

For fire resistant applications there are two distinct product types: those that are to be used as structural components (tunnels, walls, etc.), and those that will be used as coatings to insulate structural steel beams or other items. The first type requires high compressive strength over a wide temperature range so the structure is not compromised, while the second type needs high adhesion to a substrate and must be lightweight. Wear resistance rather than mechanical strength is important in coating applications [1]. Extensive research hasbeen carried out on the assessment of thermal properties of geopolymer materials.Kong and Sanjayan [31] showed that fly ash-based geopolymer is consolidated further whenexposed to elevated temperatures up to 800 °C. Metakaolin geopolymers prepared with sodiumor potassium alkaline reagents were reported to be fire resistant, with thermal stability up toabout 900 °C [32,33]. Geopolymer concrete have been observed to offer an advantage over OPC of significantly reduced spalling and superior mechanical strength retention after exposure to fire [34]. Applications for fire-resistant products include tunnel linings, high rise buildings, lift doors and marine structures/coatings [35].

Specializedgeopolymer formulations are also suitable for refractory applications, where their low cost and acceptable performance at moderately hightemperatures can provide advantages over other available materials [36–38]. Low water content and high-purity geopolymer suits industrial refractory applications where the material may be subjected to temperatures in excess of 1,200 °C.

A number of authors have also made use of the foaming tendencies of partially-polymerisedaluminosilicate gels at elevated temperature to develop geopolymer materials which expand into a foam at elevated temperature [39–41]. This property has been noted to be of value in passive fire prevention applications [42], as it is endothermic and also leads to the generation of a space-filling incombustible foam material.

Application as pre-cast members

The Melton Library in Melbourne consists of 3,500 m^2 of floor space over two levels and has been madefrom 40 MPa geopolymer concrete designed for high early strength with focus on sustainable construction. 35 precast panels of 9 m long of geopolymer concrete were installed in 2012 as exterior façade of the building as shown in Fig. 2. Another obvious civil infrastructure-related application for geopolymer concrete are in precast applications as shown in Fig. 3. In addition, prestressedrailways sleepers meeting the national standards of Japan have been produced on a laboratory scale by alkali-silicate activation of fly ash [43]. Alkali-activated slag sleepers were also developed in Poland, reaching the required 70 MPa strength through the use of finely ground slag [44], and providing performance reported as being equivalent to that of Portland cement sleepers during a 5-year service period [45]. A pilot-scale research and development program in Spain [46, 47] led to the development of pre-stressed steam-cured sleepers based on alkali hydroxide-activated fly ash, which were able to meet the requirements of Spanish and European specifications for such products.

Fig. 2: Precast geopolymer concrete panels for Melton Library, Melbourne, Australia

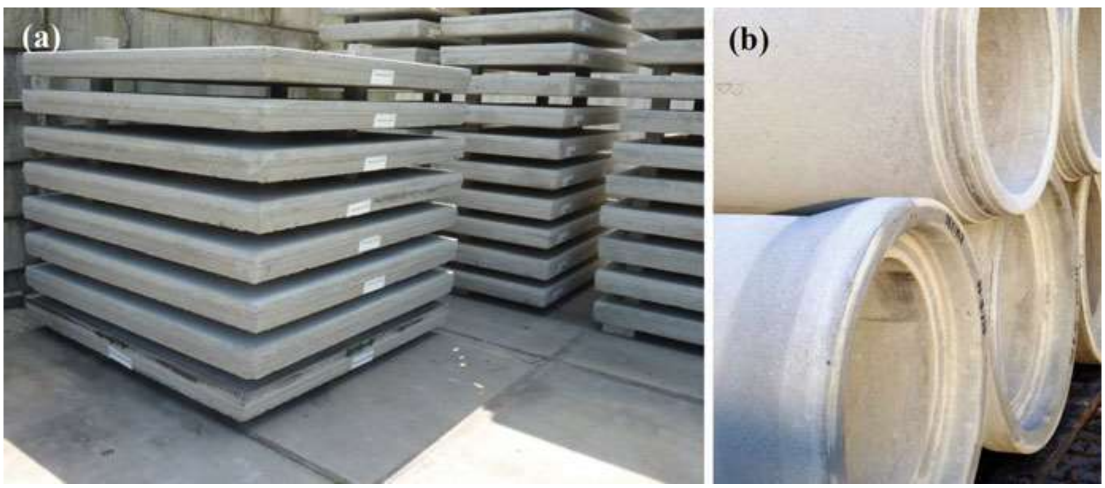

Fig. 4. Precast Geopolymer concrete products (a) slabs; (b) pipes

In addition to the civil infrastructure-related applications, there are a number of areas in which geopolymer chemistry has been shown to provide the potential for utilization in niche applications in various areas of civil and materials engineering. It is unlikely that any specific binder formulation will show all of the properties. It is also possible to tailor materials for applications in lightweight materials production, as a well for underground construction, for high-temperature applications, as a stabilisation/solidification matrix for hazardous or radioactive wastes.

Zeobond Group in Melbourne, Australia commercialized geopolymer concretesince 2006. It has developed a geopolymer binder branded as the E-Crete^{TM}, whichis generally produced from blends of fly ash, slag and alkaline activators. This is mixed with sand and aggregate in similar proportions to traditional cement binders to form concrete. The life cycle analysis of geopolymer binder were compared to the standard OPC blends which showed an 80 % reduction in CO_2 emissions, whereas the comparison on a concrete-to-concrete basis showed slightly greater than 60 % [1]. Several applications are shown in Fig. 4 and Fig. 5.

Fig. 4:E-Crete pre-cast footpath at Salmon Street bridge in PortMelbourne, Australia

Fig. 5:E-Crete retaining wall at the Swan Street bridge in Melbourne, Australia

RESEARCH AND DEVELOPMENT AT CSIR-CBRI

CSIR-CBRI, Roorkee has pioneered in study on fly ash based geopolymer in India. The R&D work has been focused on developing geopolymer concrete and building products. The research work carried out to study the effect of various parameters that influences the properties of geopolymer in fresh as well as hardened state. Systematic study on geopolymer paste, mortar and then on concrete has been carried out. Geopolymer with different binder composition, activator type and doses, curing conditions etc. were produced. For large scale in-situ application, an ambient cured geopolymer concrete has been designed with compressive strength ranging from 25 MPa to 60 MPa. Different mechanical and engineering properties were evaluated. Performance of geopolymer concrete was assessed by durability studies under different aggressive environment (acid and sulphate). Alkali-silica reaction test was also carried out to know potential resistance of aggregate in geopolymeric environment. Several building elements like bricks, blocks (solid and hollow), light weight geopolymer foam, sandwich composite and insulation concrete were prepared as shown in Fig. 6. Structural behaviour of the geopolymer concrete beams were also evaluated and compared with Portland cement concrete based on existing design guidelines and was found satisfactory. Indian patent has been filed on this development and process know-how has been licensed to the industry.

(a) (b)

(c)

Fig. 6: Geopolymer products (a) bricks (b) solid blocks (c) reinforced beams

Self-compacting geopolymer concrete is also developed and a pilot scale trial was carried out using concrete pump and mini batching plant as shown in Fig. 7. The concrete was pumped through 150 mm dia. pipe for a length of 100 m. The fresh concrete properties complied the EFNARC guidelines. In-situ strength of the casted column was assessed using NDT through rebound hammer and UPV test was performed to know the quality of cured concrete.

Fig. 7. Self-compacting geopolymer concrete and its casted column

The implementation of the geopolymer technology was done at CSIR-CBRI, Roorkee by laying a 50 m road stretch designed as per IRC/MoRTH specifications. The road stretch was designed for an axial load of 18 tonnes using geotechnical data of the site. Instrumentation of constructed road was also carried out to know temperature differential in top and bottom layer of the geopolymer concrete pavement. The pavement was casted in form of slabs of 4.5 m length jointed through dowel bars for load transfer. The road was tested during casting and also after its construction and found satisfactory. No cracks were observed in the slab. Based on this experience, similar geopolymer road stretch of 100 m length has been constructed as an implementation of the developed technology at NTPC, Dadri. The constructed road is operational and performing well as shown in Fig. 8.

Fig. 8. Geopolymer concrete roads(a) 50 m at CSIR-CBRI, Roorkee (b) 100 m at NTPC Dadri

CURRENT CHALLENGES

The main challenges faced in the wide application and scaled up utilization of geopolymer concrete are as under:

1) *Variability inconstituent raw materials and its sources:* Both quality and quantity of material required vary from place to place and as a result the geopolymer concrete properties differ with the same constituent material.Quality from a single source and most critically, consistency of quality also changes. Not only the base aluminosilicate materials, but also the alkali activators, need to be sourced via a stable and dependable supply chain for a relatively long-time span, to provide a return on the investment required to establish a production facility.

2) *Cost economics:*Geopolymer materials could become very economically attractive if CO_2taxation, or other pollution-related financial charges are implemented in an effective (global and/or regional) manner, and thus become a serious issue for the building materials industry. The raw materials costs, including slag, fly ash, other natural aluminosilicates and alkali activators, may then be lower than those of OPC clinker if CO_2 taxation is imposed on top of the conventional OPC production cost.

3) *Quality control (QC) and quality assurance (QA):*Geopolymer concrete productions QA & QC are the most crucial and challenging steps. As most of the operations personnel in

a concrete manufacturing facility are accustomed to following certain procedures for QC and QA during OPC based concrete production, it will be an important educational step to change mindsets regarding management of the consistent quality and uniformity of incoming raw materials and output products. Technical operators must understand the strong dependence of product quality on the entire production processes, as there is no clinkerisation process as the "gate-keeper" of product quality.

4) *Performance of geopolymer concrete in long term:* The main issue in establishing a standard for performance assessment of geopolymer concrete is the acceptance of the accelerated testing methods and data evaluation processes. Most of the accelerated methods to assess durability are mainly designed for OPC based materials, with implicit assumptions regarding binder and pore solution chemistry, and are not always suitable for alternative materials such as geopolymers. There is often a conflict between the desire to innovate and develop a large scale project built with new materials, and the need for prior certification for new materials to realise a large scale project. In some jurisdictions (e.g. Japan, Austria), governments or authorities can provide special permits enabling practitioners to demonstrate long term behaviour of materials. However, in many other areas, this is a very challenging step.

5) *Standardisation:* In many markets, without the existence of specific standards and certification, new cement or concrete products may face great obstacles to market entry. To draft a new cement standard is not an easy process, as final consensus must be reached by the majority of the stakeholders who are participating in the standardisation committee. These stakeholders include industrial manufacturers, trade associations (industry), professional institutions, government, consumer bodies, academia, education bodies, customers, and certification bodies. These various groups are interested not only in the use of standards to guarantee the quality and performance of their products or services, and to increase the safety of products and foster the protection of environment and health, but also to improve the competitiveness of their business through ensuring that their own systems comply with all legal obligations. As soon as a business advantage can be delivered by the suppliers to the customers, technical barriers to achieving final consensus will be readily removed. Thus, it is essential that the participants in this process are able to see the potential commercial (as well as environmental) benefits of geopolymer technology.

6) *Acceptance from the customers:* To win the acceptance of customers, sufficient convincing facts comparing an alternative material to OPC must be presented. These facts can either be opportunities or threats, such as economic benefits, better performance (e.g. strength, durability), or environmental competitiveness (e.g. green labelling, LEED credits). Education efforts can be focused on local councils, government authorities, corporations, project developers and architects, to highlight CO_2 emissions benefits and alleviate concerns or potential misconceptions held by the market stakeholders. Successful product education builds confidence in product performance, and in turn, creates project and technology advocates who further raise awareness within the specifier/user community. It is increasingly seen in the market that an additional "green advantage" for the end user can be the key element in achieving product differentiation.

DISCUSSIONS

It is noted that not every commercial endeavour related to geopolymer concrete has been with market success, and there are known complications related to water sensitivity, curing conditions and workability which are more challenging in the application of geopolymer concretethan for Portland cement concretes. However, there is a growing body of evidence which speaks in favour of the usability, durability and marketability of geopolymer concrete under service conditions in civil infrastructure applications. Moreover, there have been at least pilot-scale or demonstration projects in each of the areas discussed here, and each provides scope for future development and potentially profitable advances in science and technology.

Increasing efforts have been committed by leading practitioners from both academia and industry, to demonstrate the suitability of using geopolymer concrete in various applications, and to validate the long-term performance of this concretes. Customers in different market areas are becoming more and more aware of technical progress in the development of non-Portland binder systems, and geopolymer materials are ideally positioned to take advantage of this awareness. Although there are still great challenges facing geopolymer producers, concerted commercialisation efforts in parallel with ground-breaking research will be the only path forward to reach the final goal of large-scale deployment of this technology. Fundamental research should be targeted at improvement of the application and performance properties of geopolymer concrete, including development of chemical admixtures and analysis of durability, and remains pivotal to ongoing technical and commercial progress.

It has been recognised that innovative and non-conventional technology is difficult to transfer to practice, as existing standards do not allow for new technology, and new standards do not yet exist [48]. In the case of geopolymer concrete, it does not conform to most national and international cement standards, as they are mainly inherently based on the composition, chemistry and hydration products of OPC or OPC-blended cement. Existing cement standards therefore tend torule out non-traditional binders and its products.

CONCLUSIONS

The increasing demand for environmental friendly and sustainable construction materials has necessitated the identification of alternative materials for OPC. In this regard, geopolymer binder, involving the use of various industrial wastes and by-products, has the potential to be considered as a promising alternative to OPC in various applications.

The main reasons for the lack of industrial application of geopolymer materials, to date, have been identified as: (a) Vested interests and established practices in the construction materials industry; (b) The huge technological gap between laboratory and industrial scale concrete in terms of the handling of powders and wet concrete, and the engineering behaviour of wet and hardened concrete; (c) A lack of industrial and commercial experience of many researchers; (d) A lack of understanding of supply chain dynamics and control; (e) Limited experience of a small selection of source materials, instead of extensive experience of a wide variety of source materials used under different operating conditions in different climates and countries.

A more rigorous approach to environmental assessment must be applied if claims of sustainability are to be justified, including careful assessment of the currency and accuracy of the data used as inputs into life-cycle studies. The preference of many customers is to make their first use of geopolymer concretes in lower-risk applications; particularly, projects which have flexible timelines, are readily accessible, and where the consequences of a material falling short of defined performance targets are limited. Progression to the use of a new material in higher-risk applications then requires the engagement of regulatory authori- ties, engineers and specifiers. These parties typically prefer to take a step-wise approach towards the development of standards and commercial adoption.

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