

A short review on alkali-activated binders and geopolymer binders

Vishojit Bahadur Thapa¹, Danièle Waldmann¹

¹ Laboratory of Solid Structures, University of Luxembourg, Luxembourg
6, rue Coudenhove Kalergi, L-1359 Luxembourg
daniele.waldmann@uni.lu

ABSTRACT

In the recent years, the trend for reusing waste products or industrial by-products to reduce the amount of Ordinary Portland Cement (OPC) in concrete constructions has become an important task for industries and research institutions. OPC is the second most used material in the world after water and statistics confirm that the life cycle of OPC contributes to the generation of up to 5% of the annual CO₂ emissions worldwide. Mostly responsible for this negative environmental performance of OPC are the high CO₂ emissions related to the cement production processes, namely the deacidification of limestone and the burning of the clinker raw materials at high temperatures above 1400°C. The current demand for cementitious binder is higher than ever whereas the incentive of building sustainable and robust constructions is gaining increasingly in importance. There is a need for development of new more durable and environmental friendly binders as an alternative to OPC binders. Therefore, the research on cement alternatives has risen over the last decades and a lot of research work has been carried out to fulfil the requirements of the market. In this work, the concepts of alkali activated materials and geopolymers are presented, and their properties are compared and discussed. A short historical review is given. Furthermore, the reaction mechanisms and hydration products of these binders are characterized and explained by referring to literature. Finally, novel binders based on waste materials are presented before closing with a short outlook on remaining questions and future challenges.

1 Introduction

Concrete, which mainly consists of cement clinker, figures among the most widely used construction materials in the world. In fact, cement is known as the second most consumed element in the world after water. In 2015 [Web-1], the cement industry produced around 4.1 billion tonnes of cementitious material and the estimated annual growth rate was 2-3 %. However, the production of such large quantities is related to high quantities of CO₂ emissions during the manufacturing process. Statistics point out that up to 5-6 % of the annual anthropogenic CO₂ emissions worldwide result from the cement industries.

The production of cement clinker involves high CO₂-emitting processes like deacidification of limestone, thermal activation of clinker raw materials by calcination at temperatures above 1400°C and combustion of fuels in the kiln, as well as from power generation. As these processes generate high polluting emissions, the cement industry and the government make effort to find reliable and sustainable alternatives. Actually, it has been estimated that the production of 1 tonne of cement clinker corresponds to the generation of 1 tonne CO₂ emission. Therefore, in the future, the demand for cement alternatives will increase.

Structures build of OPC binders few decades ago currently show deterioration problems, as these structures tend to decompose due to various reasons and clearly highlight the limitations of OPC structures. The main reasons for concrete deterioration are exposure to chlorides, carbonation, freeze-thaw deterioration, chemical attacks from acids, salts, alkalis or sulphates, aggregate reactivity, abrasion of the surfaces, deterioration due to high temperatures and overload damage [Web-2, 2-4].

In general, these apparent deteriorating issues can be related to the properties of concrete. Its permeability, porosity and presence of calcium hydroxide form an exposed target for aggressive components to penetrate into the concrete, leading to its decomposition. The unfavourable environmental impact of cement production and the intrinsic properties of concrete promote the development of new, durable and environmental friendly binders. One of the most promising developments are alkali-activated binders and geopolymer cements which have shown great potential to be developed as OPC replacement and have been extensively investigated over the last decades. Alkali-activated binders or geopolymer binders are hardened

compounds which acquire their strength and other properties by chemical reaction between an alkaline soluble source and aluminate-rich raw materials.

Before discussing details about the potential and the structure of these novel binders, it is necessary to point out that even if the geopolymer technology and the concepts of alkali-activated materials are researched since last mid-century, there is still confusion and no overall accepted consensus considering the terminology of these materials. The most common descriptions, which are found in literature, are “alkali-activated materials”, “inorganic polymers” and “geopolymer”. There are also many other nomenclatures which are formed by combinations of these terms. It is complicated to give a complete overview as some experts use the notions and denomination based on the OPC hydration chemistry, whereas others ask for an adapted terminology due to the differences in the chemical processes, structures and properties of the final products. Furthermore, this demand for proper terminology is justified by some authors, who claim that the expressions “alkaline cement” or “alkali-activated cement” are irritating and are not accurate because OPC hardens in alkaline conditions and, thus, it can be considered as an alkali-activated calcium silicate [10]. The generally accepted classification of alkali-activated materials is illustrated in **Fig. 1**. However, still today, there is a disagreement in the research community, whether “geopolymer” can be considered as a subset of “alkali activated binders”. In order to understand these discussions, it is essential to understand the historical background and the mechanisms of the different systems to have a clearer overview [5, 15].

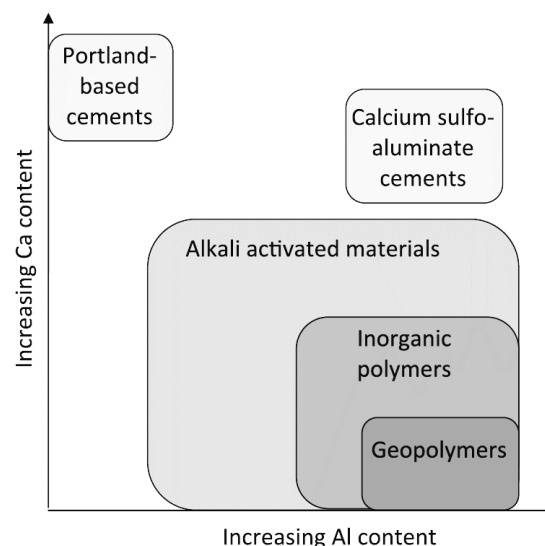


Fig. 1: Classification of different subsets of alkali-activated binders with comparisons to OPC and calcium sulfoaluminate cements [11]

There were already references to alkali activated materials before the 1940s [6-8], however, Glukhovskiy [9] was the first researcher who extensively studied the presence of analcime phases in the binders of ancient constructions and later developed binders made from aluminosilicates in reaction with alkaline industrial wastes, which he named “soil silicate concrete” and “soil cements”. The early investigations on alkali-activated binders mainly focused on the activation of blast furnace slag, a by-product of the metallurgical industry. The next wave of interest rose after the results of Davidovits [10, 12], who developed and patented a novel binder [13-14] which he named “geopolymer cement”. The first geopolymer binder was a slag-based geopolymer cement which consisted of metakaolin, blast furnace slag and alkali silicate. The benefit of this technology compared to OPC technology is that it hardened faster while reaching the maximal strength at early hours and provided a durable and compact microstructure. Subsequent studies have been carried out based on these original structures and different authors have done important research on the understanding of the chemical mechanism and the development of alkaline binders [17, 18, 20-36]. For example, Palomo et al. [18] proposed two models of alkali-activation: The first one is the activation of blast furnace slag with a moderate alkaline solution leading to C-S-H-like phases as final products. The second model consists of an alkaline activation of metakaolin with high alkaline solutions. The reaction products are characterized by zeolite-like phases and a polymeric model.

Today, after several decades of development and the occasional application of alkali activated materials, the interest has once again increased due to the high potential of reducing the carbon dioxide footprint of constructions by replacing OPC by alkali-activated binders or geopolymer cements. In order to create a binder with lower carbon footprint, not only the intrinsic

properties of the main raw materials, but the whole design concept and the choice of the right chemical mechanism need to be considered separately for each application. Moreover, in the past decades, there has been some progress in the conflict of definition of alkali-activated materials and geopolymer. A clear division has been made between alkali-activated materials based on calcium-rich raw materials and alkali-activated materials based on low-calcium raw materials. High-calcium precursors are mainly blast furnace slag and other calcium-rich industrial by-products. Low-calcium or calcium-free (“geopolymer”) precursors are mainly fly ash or clay-based raw materials which allow to develop strong and durable binder systems. However, the reaction mechanism of alkali-activated compounds is still not completely understood because the solidification and setting mechanisms are very dependent on the raw materials and the used alkaline solution. In the following sections, the mechanism of alkali-activated binders and geopolymers are discussed using different research works, followed by recent works dealing with application of these concepts to other industrial by-products and waste products.

2 Alkali activated binders/cements

Most of the works on alkali-activated binders have been carried out for the activation of granulated blast furnace slags by an alkaline solution. Blast furnace slag is a calcium-rich by-product of the metallurgical industry and can achieve high compression strengths after activation with an alkali solution. Shi et al. [16] succeeded in reaching compression strengths of about 160 MPa after 90 days of curing at ambient temperature by alkali-activation of blast furnace slag with sodium silicate. Before, Glukhovskiy [17] already did valuable work on “alkali-activated slag cement” and defined the reaction mechanism of alkaline binders which is a synthesis process occurring in a solution and is very much dependent on the raw material and the alkaline solution. It involves the dissolution of the aluminosilicate material in the alkaline medium, transportation of the dissolved units, followed by a condensation process into a polymeric network of aluminosilicates units and finally hardening. During the exothermic process of dissolution phase, due to the increased alkalinity (pH rises) in the system, the aluminosilicate solids are disintegrated into unstable, reactive units consisting of covalently bond Si-O-Si and Al-O-Si units. After, new phases are formed by penetration of the Al atoms into the Si-O-Si compounds leading to the formation of a coagulated structure, the aluminosilicate gels (colloid phase) [5]. Then, there is the generation of a condensed structure and crystallization.

In general, two types of reaction mechanism of alkali-activated binders can be established [18]. The first system involves the activation of calcium-rich raw materials like blast furnace slags, with high content of Si, Al and Ca atoms. The activation is realised using moderate alkaline solutions leading to calcium silicate hydrates-like phases as reaction products. The second mechanism involves the alkali activation of low-calcium, respectively calcium-free prime materials using medium to high alkaline solutions, leading to a polymeric network with formation of amorphous zeolite-like phases and high mechanical strength similar to OPC.

Provis [19] presented an approximated schematic representation (**Fig. 2**) of the phases formed within alkali-activated binders depending on the Si/Al ratio related to the content of calcium and magnesium. It is difficult to determine the exact phases formed because of the high chemical complexity of the systems due to varying parameters like the chemical compositions of the prime materials, the alkaline activating solutions, the used liquid/solid ratio and the curing conditions. High content of calcium-rich aluminosilicates leads to the formation of calcium aluminosilicate hydrate (C-A-S-H) gels. The use of precursors with high content of magnesium will lead to the assemblage of hydrotalcite phases, instead of zeolites which would be the case for low calcium and magnesium contents. The alkali-activation of low calcium aluminosilicates leads to formation of so-called N-A-S-H gels. Furthermore, in high pH conditions, the presence of aqueous aluminate and aqueous calcium modifies N-A-S-H gels leading to the partial substitution of sodium with calcium to form “C-(N)-A-S-H gels”.

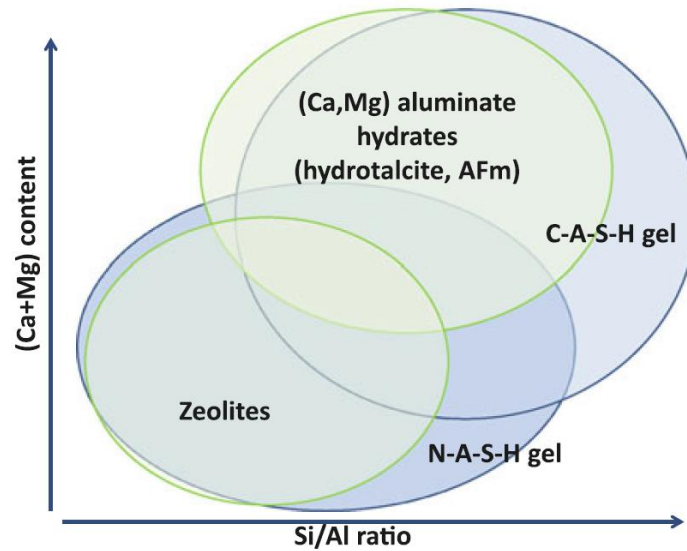


Fig. 2: Schematic representation of phase formation within alkali-activated binders; green: ordered products; blue: disordered products [19]

In case of calcium-rich raw materials, blast furnace slag is the more reactive raw material used for alkali-activation and therefore can be processed using a larger range of activators like hydroxides, silicates, alkali carbonates or sulphate solutions. However, usually higher alkaline solutions are used as these promote faster setting and better strength development at ambient curing temperatures. The binder formed by alkaline activation form aluminium-rich secondary phases like hydrotalcites and zeolites, and C-A-S-H phases depending on the aluminium and magnesium content of the raw material [20-27]. Song et al. [28] reported similar reaction product after alkali activation of blast furnace slag. He observed the formation of C-S-H gels with traces of hydroalcite phases by x-ray diffraction. Puertas et al. [29] investigated the reaction of blast furnace slag with activation by sodium hydroxide solutions and observed the presence of C-S-H gel phases, hydroalcite and calcite by XRD analysis.

The low-calcium alkali-activated material technology can be divided in low-calcium alkali-activated binders based on fly ash as a precursor and calcium-free alkali-activated binders formed by alkali activation of clay-based raw materials, mainly metakaolin. These precursors are most commonly activated with hydroxide or silicate solutions. Even if there are confusions on the terminology and the notions of alkali-activated binders, there is no doubt that the first development of low-calcium alkali-activated binders was conducted by the Joseph Davidovits [10]. The initial purpose was to develop fire-resistant inorganic polymeric binders using clay-based raw materials.

In case of "low-calcium" raw materials, fly ash or metakaolin are the more reactive raw materials used for alkali-activation and commonly is processed using strong alkaline activators like hydroxides and silicates. The final hydration products are strongly dependent on the prime materials. Xie and Xi [30] studied the reaction products of fly ashes alkali activated with mixed solutions of sodium hydroxides and sodium silicates and noticed the presence of crystals, mainly unreacted sodium silicate phases. Furthermore, the XRD analysis led to the detection of only small reaction products. Similar studies were conducted by Krivenko and Kovalchuk [31] and they reported the formation of zeolite phases like hydroxysodalite and analcime. Other authors [32, 33] reported the formation of hydroxysodalite and heschlite as final hydration products.

Phair and Deventer [34] reported that at pH of 12, the dissolution of metakaolin in form of Si and Al species is very high. The aluminium of metakaolin disintegrates ten times higher and the silica dissolves two times higher than its uncalcined raw material (kaolin). Yunsheng et al. [35] investigated on three key parameters ($\text{SiO}_2/\text{Al}_2\text{O}_3$, $\text{M}_2\text{O}/\text{Al}_2\text{O}_3$ and $\text{H}_2\text{O}/\text{M}_2\text{O}$) composition design method based on chemical characteristics analysis of calcined kaolin-based geopolymer cement. The results showed that the hardened binder had the best mechanical performance at $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$, $\text{H}_2\text{O}/\text{Na}_2\text{O} = 7.0$ and the highest compressive strength achieved was 34.9 MPa. Furthermore, the analysis of the IR spectra indicated that cement with the highest strength was the most fully reacted one and possessed the largest amount of geopolymers. According to Rowles et al. [36], in the production of the inorganic polymer, the amounts of OH^- and Na^+ are coupled, as the ions of the NaOH are their only source in the activating solution. In samples with low sodium content, there would be both insufficient OH^- to completely dissolve Si^{4+} and Al^{3+} from the metakaolinite, and insufficient Na^+ to allow complete polymerisation of the network. This content leads to unreacted metakaolinite which results in a lower strength material. In samples with high sodium

content, an excess of OH^- allows a complete dissolution of Si^{4+} and Al^{3+} from the metakaolinite. However, an excess of sodium in the network would weaken the structure.

Table 1 lists the compressive strengths of different binders based on literature. It can be considered that in terms of mechanical performance alkali-activated binders based on industrial by-products or waste material already fulfil or even outperform the standard strength requirements for OPC. Therefore, it is essential to continue the research work on alkali-activated binders to entirely understand their behaviour in structural systems and harmful environments to confirm it as a valid alternative to OPC.

Table 1: Comparison of compressive strength of different binders

Compressive strength after 28 days cured at ambient temperature		
Type of binder	Strength [MPa]	Reference
Ordinary Portland Cement		
CEMI 32.5	$32.5 \leq x \leq 52.5$	According to EN 197-1 [42]
CEMI 42.5	$42.5 \leq x \leq 62.5$	
CEMI 52.5	≥ 52.5	
Alkali-activated binder based on		
Ground granulated blast-furnace slag	40.0	[43]
Fly ash	59.0	[44]
Metakaolin	38.5	[44]
Alkali-activated binder based on waste		
Waste ceramics	71.1	[38]
Calcined reservoir sludge	56.2	[39]
Tungsten mine waste mud	60 -75	[40]
Waste treatment sludge & Rice husk ash	16.0	[41]

3 Are “Geopolymers” a subclass of alkali-activated materials?

The term “geopolymer” was mentioned for the first time by the chemist Joseph Davidovits in 1975 to classify all forms of inorganic polymeric material synthesized by chemical reaction of alumina silicates and a low alkaline activating solution. Initially, the term defines silicon-based polymers, which use raw materials from mainly rock-forming minerals of geological origin. A geopolymer is realised by activation of an aluminosilicate prime material having a low calcium content with an alkaline solution at room temperature.

Regarding kaolinite-based raw materials, the production of geopolymer cement comprises in two main procedures: calcination and geopolymerisation. The calcination process consists in the thermal treatment of the raw material, which leads to dehydroxylation of clay mineral into a high-energy and nearly amorphous meta-state. One of the main reason to use clay-based geopolymer binders as cement alternative is the fact that the dehydroxylation process occurs at lower temperatures than the burning of cement clinkers. After the addition of the alkaline solution to the meta-clay, the geopolymerisation is initiated and is based on three complementary processes, namely, the depolymerisation of the minerals into monomers by condensation of the alkaline component, the formation of oligomers and the polycondensation into a geopolymer ribbon by combination of the oligomers into a covalently bonded network. The synthesized geopolymers show interesting characteristics like good mechanical properties, high strength and good durability [Web-3]. Davidovits presented in [10] the example of an aluminosilicate geopolymeric cement based on calcined kaolinite clays, blast furnace slag and silica fume which were activated using alkali-silicates. The resulting cement hardened at ambient temperature with early compressive strength of around 20 MPa (after 4 hours). The final 28-day compressive strength range from 70 to 100 MPa.

However, in the last decades, the term “geopolymer” has been “misused” to describe all sorts of alkali-activated materials based on low-calcium precursors, which does not suit to the initial definition of geopolymer. Therefore, Davidovits [10, 37]

reminds the scientific community and points out in his speeches and writings that it is a scientific mistake to use alkaline activated materials and geopolymer as synonyms because, according to him, not all alkali-activated materials are polymers considering their chemistry and therefore cannot be considered as geopolymers. Furthermore, his main issue is that the scientific community applies the concept of geopolymer cement as a derivative of the calcium silicate hydrates from OPC hydration leading to wrong formulation like NASH and KASH depending on the alkaline solution. According to Davidovits, during geopolymerisation, there is never the formation of a hydrate nor a gel, but the formation of a polymer by polycondensation of reactive ortho-sialate units.

According to [37], “geopolymer cements” are binding systems which solidify at ambient temperature and if heat treatment is required for hardening then the geopolymer compound is called “geopolymer binder”. Geopolymer cements can be considered as a valid alternative to Ordinary Portland cement for different applications from fast hardening to durable compounds for infrastructure and construction. Furthermore, geopolymer cement requires mild alkaline soluble silicates or hydroxides and therefore the geopolymeric alkaline reagents can be classified as “user-friendly”, opposed to strong alkaline solutions required for alkali-activated binders.

Fig. 3 schematically illustrates the general differences between “alkali-activated binders” and “geopolymers”. As previously explained, alkali-activated binder are calcium-rich raw materials activated with high alkaline solutions. After the dissolution of the precursors, a binder paste with hydraulic potential is build leading to simultaneous formation of C-S-H gels and aluminosilicate polymers. Geopolymers is structured around tetrahedral co-ordinated Si^{4+} and Al^{3+} , forming a polymer chain. There is chemical bonding of geopolymer precursors into oligomers leading to the formation of aluminosilicate polymers.

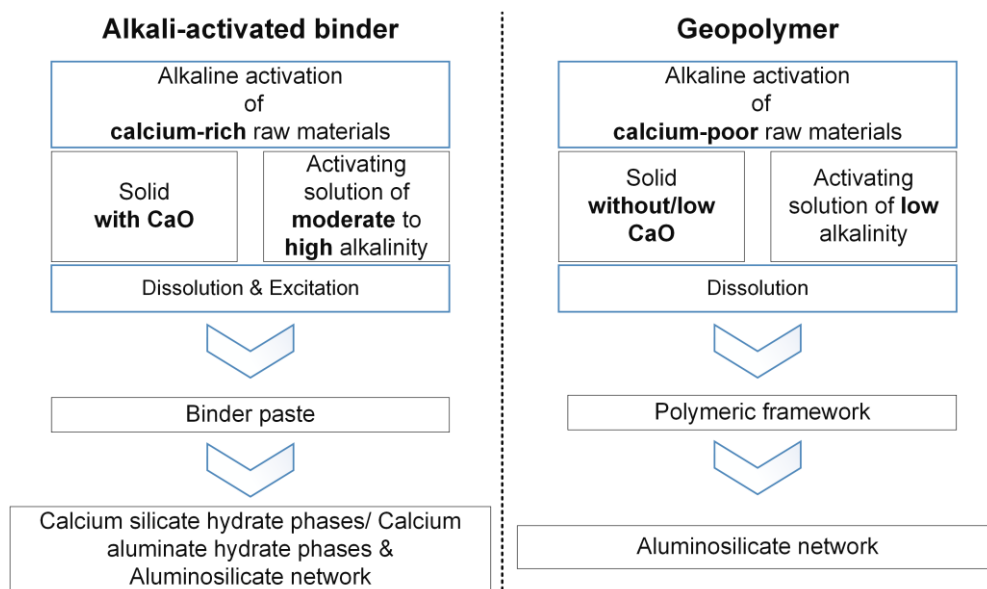


Fig. 3: Overview of the general reaction mechanisms of alkali-activated binder and geopolymer

4 Alkali-activated binders from waste products

Most of previous investigations used pure metakaolin or slag-based prime materials with high content of reactive SiO_2 and Al_2O_3 as raw materials for cement substitution. However, the application of inorganic polymers as construction materials is unfavourable due to the high price of commercially available raw materials. For example, the price of metakaolin has risen during the last years due to its high demand. Therefore, in the recent year, there is a trend to investigate on alternative prime materials to be revalorised for development of alkali-activated binders. In recent literature, other raw materials than metakaolin, mainly waste products from different industrial origins, are increasingly studied to being processed to synthesise an alkali-activated binder or geopolymer binder and very promising results have been found, but also indicate that further research is needed. Zengqing Sun et al. [38] investigated on the synthesis of geopolymers out of waste ceramics which were activated by alkali hydroxides and/or sodium/potassium silicate solutions. The maximal compressive strength measured after 28 days was 71.1 MPa and favourable thermodynamically stable properties were observed. The results approve the approach of recycling ceramic wastes for production of value-added alkali-activated composites. Chen et al. [39] studied the practicability of calcined sludge from a drainage basin of a water reservoir as a precursor for alkaline activation into an inorganic polymer. The raw material consisted of a sludge containing fractions of silts and smectite clays with high content of

aluminosilicates (around 85%) and some impurities. The maximal compressive strength measured after 28 days was 56.2 MPa using raw material calcined at 850°C. Further research of this material could approve its adequacy for OPC replacement as a high compressive strength and low cost alkali-activated binder. Pacheco-Torgal [40] investigated on an alternative to OPC using tungsten mine waste mud as prime material. The mineralogical analysis indicated the presence of muscovite and quartz minerals. After activation with a mix of sodium hydroxide and sodium silicate, different fine aggregates were added and the formed binders showed very high strength at early ages. The compressive strengths for the different mixtures measured after 28 days ranged from about 60 to 75 MPa and thus, show even higher mechanical performance than alkali-activated mixtures with more reactive aluminosilicates like metakaolin. Poowancum et al. [41] developed a geopolymer binder using water-treatment-sludge and rice husk ash as raw material. The alkaline activator used was a mixture of sodium hydroxide and sodium silicate and the resulting maximal strengths were around 16 MPa for a rice husk content of 30%. These strengths are clearly lower than that of the minimum requirement of OPC and therefore only usable for lightweight structures. Furthermore, recent works like from Thapa et al. [45] performed investigations on the suitability of a promising waste product (gravel wash mud) as raw material for synthesis of a novel geopolymer binder and reported early indications about its performance without addition of further strengthening components

The revalorisation of waste products has become subject of intense study for development of novel alkali-activated binders or geopolymer cements. Some of the results seem to be very promising; however, the exact reaction processes and reaction products are not yet quite understood. Furthermore, these results are mostly valid for specific raw materials, mostly available at regional level under given specific conditions and therefore the interest for research on these materials is mainly of local or regional interest.

5 Concluding remarks

Alkali-activated binders or geopolymer cements are now gaining great interest for their high potential of great mechanical and environmental performance. Therefore, the understanding about the chemical reactions, structure and durability of these systems must be developed in order to improve the properties of the binders. From this writing, it can be deduced that already extensive research has already been carried out in this field. However, the exact reaction mechanism of alkali-activated binders is still not completely understood because of its strong dependency on the compatibility of raw materials and the alkalinity of the activator. Fortunately, there is a consensus in the scientific community that the reaction mechanism of alkaline activation of materials undergoes three main stages, namely dissolution and restructuration on molecular level and finally hardening. In general, the final reaction products can be determined as C-S-H-like gel for alkali activation of calcium-rich precursors and zeolite-like polymers for alkali activation of low-calcium precursors. The right terminology of the different binders must be solved considering that the more "commercial" term "geopolymer" is already widely accepted for low-calcium, respectively calcium-free alkali activated materials. Even if lots of research are carried out in this field, there are remaining unknowns related to the use of these binders as mentioned in [34]:

- Standards: As alkali-activated binders, like OPC, have varying properties like strength, elasticity, hardness, and workability depending upon the mixture, the development of performance-based standards becomes indispensable. Standards would prescribe evaluation criteria and procedures to facilitate the comparison of different binders. Furthermore, the verification of the consistency and the conformity of raw materials and activating solution would be defined.
- Development of database: A global database with the mineralogical and chemical compositions of different raw materials and their performance after alkaline activation would allow to better predict the performance of new raw materials.
- Reactivity and reaction mechanisms: Greater understanding of the reactivity and reaction mechanisms is required. In addition, it is necessary to define better the activation effectiveness of different types of alkalis [34].
- Characterization: New methods are required to characterize the complex mineralogical systems of alkali-activated binders, as the understanding of complex solid phases is essential to analyse their effects on the long-term behaviour of alkali-activated binders.
- Processing of raw materials: Further studies are required to determine the influence on the binder properties of different processing parameters of the raw materials like material preparation, granulometry, temperature, concentration of alkalis hydration conditions, etc.

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