

Alkaline activation of different aluminosilicates as an alternative to Portland cement: alkali activated cements or geopolymers

La activación alcalina de diferentes aluminosilicatos como una alternativa al Cemento Portland: cementos activados alcalinamente o geopolímeros

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Abstract

Portland cement is considered an excellence building material. This is due mainly to its high performance, its good quality/price ratio and the raw materials from which it is made can be found almost everywhere in the world. However, the development of alternative Portland cements obtained through processes involves lower emission of CO₂ into the atmosphere is a priority research and great interest worldwide. Alkaline activation constitutes an alternative to Portland cement, preferably amorphous or vitreous aluminosilicates and alkaline activator (such as NaOH, Na₂CO₃ or sodium silicates hydrates). The aluminosilicates may be natural products such as metakaolin or industrial by-products such as blast furnace slag or aluminosiliceous fly ash. These cements and concretes obtained by alkali-activating aluminosilicates are characterised by high mechanical strength, low heat of hydration and high impermeability, as well as resistance to high and low temperatures and sulphate, seawater and acid attacks. Moreover, the preparation of these alkaline cements requires lower energy than in the manufacturing process of Portland cement. However, we still cannot say or establish that alkaline cements (alkali activated materials or geopolymers) are based on a clean chemical to the environment, due to production processes of alkaline solutions such as sodium silicates emit large amounts of CO₂ into the atmosphere. This article aims to make a trip back in time to the origins of the alkali activation to explain the most characteristic and important chemical concepts.

Keywords: Alkali activation, geopolymers, slags, fly ash, activators

Resumen

El cemento Portland es considerado el material de construcción por excelencia ya que, a día de hoy, no hay ningún conglomerante que posea la aceptación que posee este material. Esto es debido, principalmente, a sus buenas prestaciones, a su buena relación calidad/precio y a que las materias primas a partir de las cuales se fabrica pueden encontrarse prácticamente en todo el mundo. Sin embargo, el desarrollo de cementos alternativos al cemento Portland que se obtengan a través de procesos que supongan menores emisiones de gases contaminantes a la atmósfera y con un apreciado ahorro energético, constituye una línea de investigación prioritaria y de gran interés a escala mundial. Dentro de estos materiales alternativos se encuentran aquellos que proceden de la activación alcalina de aluminosilicatos naturales (arcillas) y/o subproductos industriales, como son las escorias de alto horno o las cenizas volantes. Estos cementos y hormigones activados alcalinamente se caracterizan por presentar bajos calores de hidratación, elevadas prestaciones mecánicas y buena durabilidad frente a diferentes agresivos químicos y físicos, además de no requerir en su elaboración los elevados consumos energéticos que son inherentes al proceso de fabricación de los cementos Portland. Sin embargo, aún no se puede decir o establecer que los cementos alcalinos se basan en una química limpia con el medioambiente, ya que los procesos de producción de las disoluciones alcalinas tales como los silicatos sódicos, emiten grandes cantidades de CO₂ a la atmósfera además de ser un proceso costoso. El objetivo de éste trabajo es realizar un viaje en el tiempo hacia los orígenes de la activación alcalina para tratar de explicar mejor sus conceptos y características más importantes.

Palabras clave: Activación alcalina, geopolímeros, escorias, cenizas volantes, activadores

1. Introduction

The study and development of new cementitious materials that are an alternative to Portland cement is a priority line of research and of great interest worldwide. The purpose of developing these new materials is to minimize as much as possible the emission of contaminant gases to the atmosphere, as well as to obtain a significant energy saving.

The cement industry taps natural resources (quarries) and discharges contaminant gases to the atmosphere (CO₂, SO₂, NO_x). The CO₂ emissions are mainly associated to the

decarbonization of limestone, which is the main component of the raw materials for cement manufacture (accounting for more than 60% of total emissions). At global level, between 5% and 7% of the CO₂ emissions come from the cement industry, which also consumes primary energy, estimated around 3% of the global consumption.

Therefore, it is necessary to develop new cementitious materials whose manufacturing process discharges less contaminant gases and achieves a significant energy saving. Among these alternative materials are those coming from the alkaline activation of aluminosilicates, either as natural products (clays) (Chen et al., 2016) or industrial byproducts, such as blast furnace vitreous slags and/or fly ash (Neupane, 2016), where different binders are obtained following the

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activation of these materials with alkaline solutions. These alkaline cements and concretes are characterized by low heats of hydration, high mechanical strength, and good durability in the presence of different chemical attacks (acid environments, sulfate attacks, fire, etc.); and its manufacturing process requires less energy consumptions than in Portland cement.

The aim of this paper is to briefly discuss the timeline of the evolution of the alkaline activation, in order to explain the most characteristic and important concepts regarding its chemistry. However, we still cannot say that alkaline cements (alkali-activated materials or geopolymers) are based on an environmentally friendly chemistry, because the production processes of alkaline solutions, such as sodium silicates, emit large amounts of CO₂ to the atmosphere, and it is also an expensive process. Therefore, further researches should be made about the reuse of alternative materials that provide the characteristics and properties that are closest to the commercial solutions that have been used in the last years for preparing these systems.

2. Why the alkaline activation?

There are many reasons that explain the different origins of the alkaline activation of aluminosilicates. The main ones are related to the search for alternatives to the conventional manufacturing process of Portland cement, which has a strong environmental impact and high greenhouse gas emissions (mainly CO₂) coming from different generation sources during the production process, etc.

Since the decade of 1990, the alkaline activation research has significantly grown all over the world, with more

than 100 active research centers (academic and commercial ones) operating worldwide, as well as detailed studies taking place in all continents. Many of these papers are based on the development of materials with an acceptable performance, using specific raw materials that are locally available.

A large number of names applied to the description of these materials have been established. However, the terms “alkali-activated materials” and “geopolymers” are, in our opinion, the most adequate and those used herein to refer to these types of cements and concretes.

- **Alkali-activated material** is the broadest classification, which essentially embraces any binder obtained by a reaction between a source of alkaline metal (solid or soluble) and a silicate powder (Deventer et al., 2010). These solids can be calcium-rich or calcium-poor aluminosilicates, such as blast furnace slags or fly ash, respectively. Alkaline sources may include alkali hydroxides, silicates, carbonates, sulfates, aluminates or oxides, basically any soluble substance that can provide alkali metal cations, increase the pH of the reaction mixture and accelerate the solution of the solid precursor.

The word **geopolymer** often refers to a subgroup of alkali-activated materials. Fly ash with a low content of calcium and calcined clays (e.g., metakaolin) are the most common precursors used in the geopolymer synthesis. It should be highlighted that the term geopolymer was coined in the 1970's by the French scientist and engineer Joseph Davidovits (Davidovits, 1991; Davidovits, 1982; Davidovits, 2008).

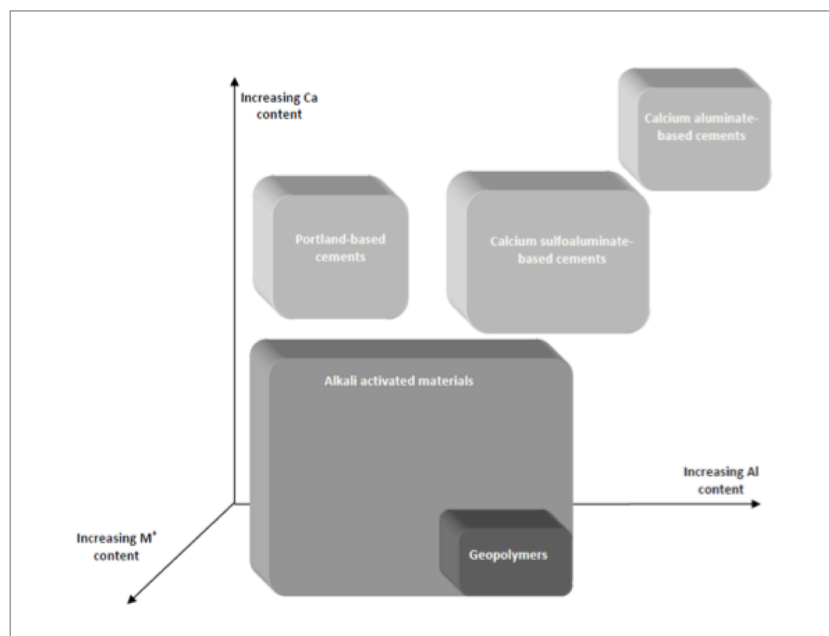


Figure 1. Classification of alkali-activated materials, with comparisons between OPC and calcium sulfoaluminates. The shading indicates the approximate content of alkali, where the darkest shading corresponds to higher concentrations of Na and/or K (I. Beleña) (Provis and van Deventer, 2014)

Figure 1 shows a diagram of the distinction between these classifications (Provis, 2014). This is a very simplified view of the chemistry of the cementitious systems, based mainly on $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-M}_2\text{O-Fe}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$ systems. The purpose of this graph is to illustrate the classification of alkali-activated materials and their position with regard to that of Ordinary Portland Cement (OPC) and cementitious systems based on sulfoaluminates. Geopolymers are shown here as a subgroup of alkali-activated materials, with high concentrations of aluminum, silicon and alkali.

During the last two decades, alkaline cements and concretes have aroused great interest among the scientific community and the construction industry, due to the following reasons (Ruiz-Santaquiteria, 2013):

- a) Good mechanical performances from very early ages. After the first 20 hours of curing, these materials can develop mechanical strengths comparable to those of the Portland cement concrete after 28 days of curing.
- b) Carbon dioxide emissions and energy spending in the production process of these alkaline cements are significantly lower than those required in the Portland cement manufacture; some authors estimate that these reductions are around 60-70%.
- c) On many occasions, the manufacture of this type of cements offers the possibility to use, as the sole "raw material", industrial waste that would otherwise accumulate in the corresponding landfill sites, thereby contributing to the environmental contamination: used FCC catalysts (Caicedo Casso et al., 2015), demolition waste (Asensio et al., 2016), glass waste (Torres-Carrasco et al., 2014); Puertas and Torres-Carrasco, 2014; Torres-Carrasco and Puertas, 2015), rice husk ash (J. M. Mejía et al., 2013), etc.
- d) Concretes made of activated slags and ash present very good mechanical strengths. For example, concretes made of alkali-activated slags with sodium silicate solutions (waterglass) can reach 68 MPA at one day of curing and 96 MPA at 3 days.
- e) In most cases, these materials offer durable behaviors similar or even better than those of traditional Portland cements: good resistance to sulfate attacks (Fernández-Jiménez et al., 2006; Bakharev, 2005a; Puertas et al., 2002), acid environments (Fernández-Jiménez et al., 2006; Bakharev, 2005b), less expansion problems derived from the "aggregate-alkali" reaction produced, under certain conditions, in the case of Portland cement mortars and concretes (Fernández-Jiménez et al., 2006; García-Lodeiro et al., 2007; Puertas et al., 2009). Furthermore, recent studies have evidenced that these materials maintain their good properties at high temperatures and can act as immobilizers of certain toxic and/or hazardous waste, and even radioactive waste (Donatello et al., 2012; Shi and Fernández-Jiménez, 2006).

There is currently a group of RILEM experts ("Durability Testing of Alkali-activated Materials-Technical Committee 247-DTA"), led by Prof. John L. Provis, who are trying to make an exhaustive study about different durability tests to which these alkali-activated materials can be subjected to, so as to set specific standards for these materials. Many of these tests, with materials that are an alternative to Portland cement, demonstrated an optimal behavior; but it is also true that many of these standards are sometimes not adjusted to the study and characterization of alkaline materials, mainly due to the difference in the chemical composition between Portland cement-based systems and alkali-activated aluminosilicates systems.

3. Alkaline activation: a new perspective

3.1 Components in the alkaline activation

The raw materials most used as precursors in the preparation of alkali-activated cements are blast furnace vitreous slags (calcium-rich components), fly ash from coal combustion (calcium-poor) and thermally activated clays (mostly metakaolin); or a mixture of some or several of these precursors. Figure 2 shows the composition of these materials in the ternary graph for $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$.

Por lo general, las sales de álcalis o los hidróxidos alcalinos son los que se utilizan como activadores alcalinos de los cementos y hormigones activados alcalinamente. Se clasificaron en seis grupos de acuerdo a su composición química (Shi et al., 2006):

1. Alkali hydroxides: MOH
2. Salts of weak acids: M_2CO_3 , M_2SO_3 , M_3PO_4 , MF, etc.
3. Silicates: $\text{M}_2\text{O}\cdot n\text{H}_2\text{O}$
4. Aluminates: $\text{M}_2\text{O}\cdot n\text{Al}_2\text{O}_3$
5. Aluminosilicates: $\text{M}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot(2-6)\text{SiO}_2$
6. Salts of strong acids: M_2SO_4

From all these activators, NaOH, Na_2CO_3 , $\text{Na}_2\text{O}\cdot n\text{SiO}_2$ y Na_2SO_4 are the most widely available chemical products. Some potassium components have been used in laboratory studies. Nevertheless, their possible applications would be very limited due to their availability and cost. On the other hand, sodium and potassium components have very similar properties. These alkaline activators can be used in liquid or solid state. Usually, cements incorporating the precursor and activator are preferred (in solid state), and water as mixing liquid.



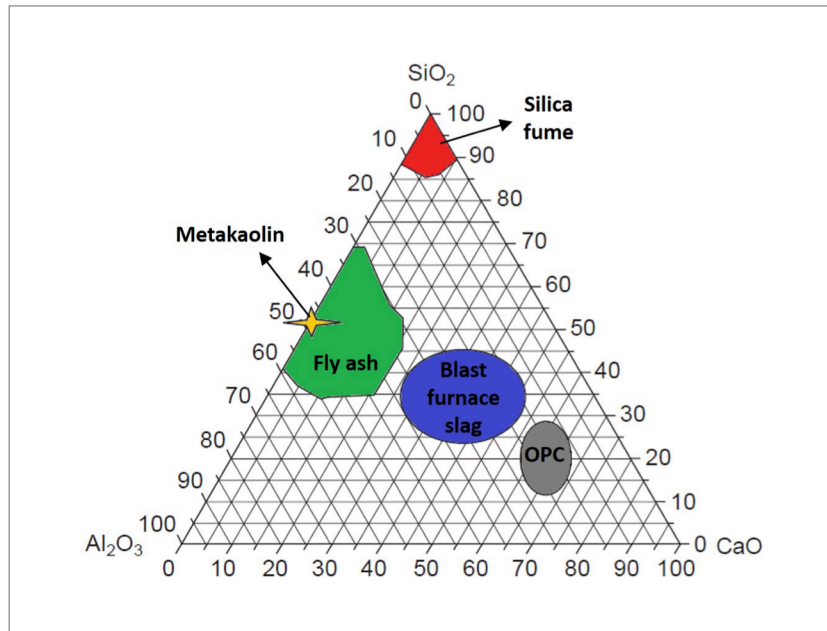


Figure 2. Ternary Graph for CaO-SiO₂-Al₂O₃

3.2 Alkali-activated materials with high Ca contents: blast furnace vitreous slags

The structure of gels formed by slag activation strongly depends on different chemical factors controlling the reaction mechanism and, therefore, the development of resistances and durability as well. These factors can be classified in two categories: those associated to the characteristics of raw materials or precursors, and those related to the activator used.

The main product generated in the activation of blast furnace slags is a calcium aluminosilicate hydrate gel (C-A-S-H), similar to the gel generated in the OPC hydrate (C-S-H gel), but with lower proportions of CaO/SiO₂, which generally range between 0.9 and 1.2, in relation to the CaO/SiO₂ ratios of the C-S-H gel, ranging between 1.5 and 2.2. This reaction product goes along with the formation of byproducts, such as the hydrotalcite (Mg₆Al₂CO₃(OH)₁₆·4H₂O) (identified in alkali-activated slag systems with high MgO contents) (Haha et al., 2011) and zeolites, such as the gismondine (formed in blast furnace slag systems with high Al₂O₃ contents and low MgO contents (< 5%)) (Bernal et al., 2010; Bernal et al., 2011).

The structure and composition of the C-A-S-H gel formed after the slag activation highly depends on the nature of the activator used (Aydin and Baradan, 2014). The product formed after using NaOH as an activator presents a greater CaO/SiO₂ ratio and a more organized structure than the type of C-A-S-H gel formed by activators based on sodium silicate hydrates (Fernández-Jiménez and Puertas, 2003; Escalante-García et al., 2003). Puertas et al. (Puertas et al., 2011) identified that C-A-S-H gels obtained after the sodium silicate activation had a structure comparable to the tobermorites (11 nm (14 links) and 14 nm (5 links)) (see Figure 3a). Myers et al. (Myers et al., 2013) developed a structural model to describe these gels based on the limitations inherit to cross linked and non-crossed linked structures of different tobermorite units (see Figure 3b), which allow calculating the chain length, the Al/Si ratio and the linking degree for these more complex structures that cannot be completely described through standard models of non-crossed linked C-D-H gels of similar tobermorites.

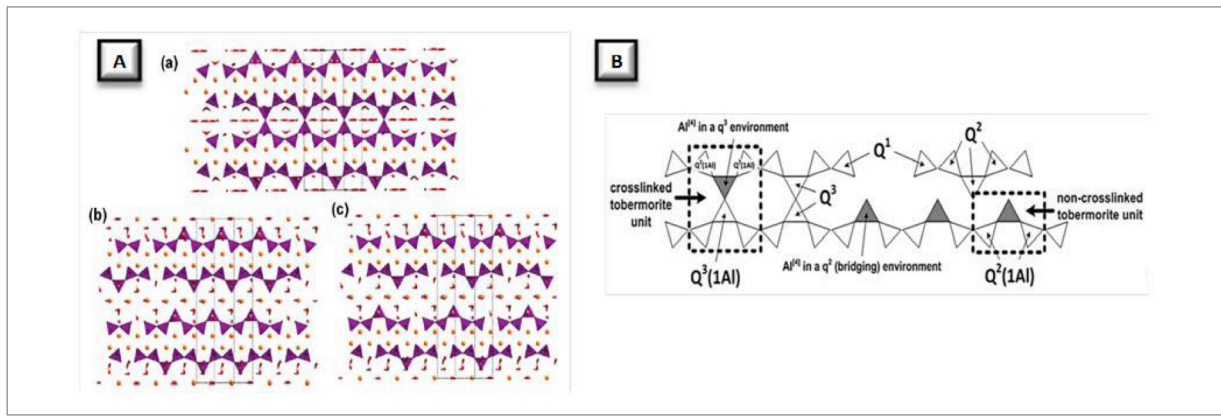


Figure 3. A) Structural models for: a) T11, b) T14 and c) T14(5); B) Structural model of C-A-S-H gels (Myers et al., 2013)

3.3 Alkali-activated materials with low Ca contents: fly ash

There are a large number of researches focused on fly ash as precursor of these cements, due to their low cost and easy availability. However, the nature of fly ash, as well as their chemical and mineral compositions, affect the final behavior of the geopolymers obtained. In the same way as in the alkali-activated slag systems, the influence of the activator is a variable that should be taken into account.

The main reaction product derived from the alkaline activation of fly ash or metakaolin is an amorphous alkali aluminosilicate (N-A-S-H gel) (Garcia-Lodeiro et al., 2014), which contains silica and aluminum tetrahedrons randomly distributed along cross linked polymeric chains forming a tridimensional structure. The chains' cross linking provides adequate cavities to accommodate alkali cations, thus compensating the charge deficit generated when replacing a silica (IV) by an aluminum (III). Moreover, there are terminal hydroxyl groups on the gel's surface, although its presence is not significant in the context of the material's structure (see

Figure 4). The byproducts of the reaction in this type of systems are zeolites, such as hydroxy sodalite, zeolite type P, sodium-dominating chabazite, zeolite Y and faujasite.

A large number of studies have demonstrated that the curing temperature and the type of reaction kinetics, based on the used activator, are factors that should be strongly considered, since the nature of the generated products (N-A-S-H gel) can be different (Görhan et al., 2016). Long curing times give origin to the formation of silica-rich products, thus favoring the development of the material's final resistances.

On the other hand, the raw material is not the only origin nor the reason for the formation of the N-A-S-H gel as the main reaction product; the alkaline activator plays an important role too (Torres-Carrasco and Puertas, 2015). For example, the silica from the sodium silicate normally used as alkaline activator is highly soluble and, therefore, it is an integral part of the N-A-S-H gel. The polymerization degree of this sodium silicate, which directly depends on its $\text{SiO}_2/\text{Na}_2\text{O}$ ratio, conditions the structure of the gels that precipitate in the different formation stages of the $\text{SiO}_2/\text{Na}_2\text{O}$.

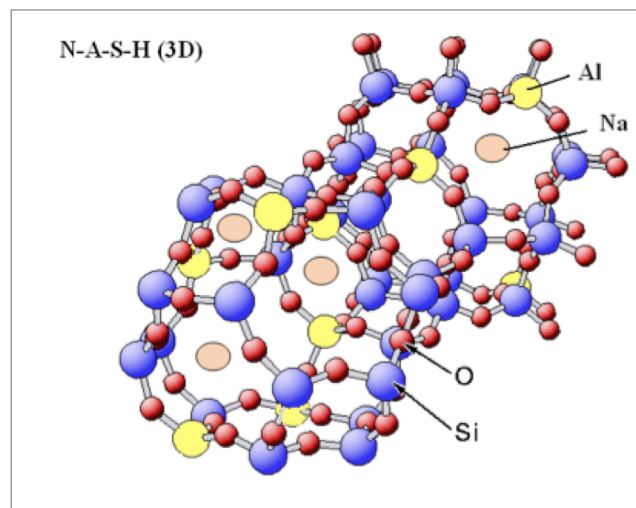


Figure 4. View of the tridimensional structure of the N-A-S-H gel (Garcia-Lodeiro et al., 2014)



3.4 Alkaline Activators

Alkaline activators are the second essential component for the development of alkaline cements. These activators are usually included in the mixture as a solution, although they can also be incorporated in a solid state, either mixed or integrated with the slag and/or ash.

Generally, the most used activators are alkali hydroxides and silicates. However, the nature of the activators plays a crucial role in the activation process, both in slags and fly ash, where the effect of the pH and the influence of the cations-anions are parameters to be considered.

- The pH effect

The most critical role of the alkaline activator in an alkali-activated material is to dissolve the aluminosilicate and accelerate the reaction, which is obtained by generating a high pH. Alkali silicates and hydroxides generate the highest pH values, while carbonates and sulfates create moderately alkaline conditions and generate free hydroxide for the activation process through reactions involving the slag calcium.

In general terms, the pH of the activating solutions has to be over 11.5. The optimal values for the activation of blast furnace vitreous slags are around 13-13.6. Additionally, the effect of the pH on the activation of the slags is highly dependent upon the type of activator, since the solubility of calcium decreases at higher pH, while the silica and alumina increase their solubilities. Although the activating solutions of NaOH have a higher pH value than the sodium silicate solutions in similar alkali concentrations, comparable amounts of slag reacting in the presence of each type of activator cause the silicate to develop a greater mechanical strength than in the systems activated with NaOH. This is a consequence of the additional silicate source in the systems reacting with the Ca^{2+} cations from the dissolved slag, thereby forming dense reaction products (C-S-H gel).

The optimal activators usually employed in the activation of aluminosilicates with low calcium contents (fly ash) are those with pH values similar to a NaOH 8M solution. A lower alkalinity adversely affects the cements' mechanical properties, because the ionic bond generated in the activator-binder system is not sufficiently high to satisfactorily hydrolyze the silica and the aluminum in the initial material.

- The silicates effect

Criado et al. (Criado et al., 2008) studied the effect of the activator's different polymerization degrees (in proportions of $\text{SiO}_2/\text{Na}_2\text{O} = 0.17, 0.60$ y 1.90) on the intermediate reaction products generated during the fly ash activation. They observed that this parameter played an essential role in the kinetics, the structure and the composition of the initial gel formed, and that the addition of soluble silica affected the intermediate reaction products, but not the final one. They indicated that the Si/Al ratio did not increase indefinitely in the N-A-S-H gel; and they found that the optimal values were around 2, towards which the systems tends to regardless of the initial conditions, possibly due to thermodynamic stability reasons. Furthermore, they proposed that the effect of a highly polymerized silica in the formation of the N-A-S-H gel could influence the kinetics of the reaction, provoking a delay thereof and the crystallization of zeolites.

- Alternative activators

Currently, there are several ways of reusing different wastes as potential alkaline activators, and as an alternative for commercial sodium silicates, which are associated to relevant economic and environmental issues.

The use of urban and industrial glass waste in the activation of aluminosilicates is a pioneer research undertaken by the group led by Prof. Francisca Puertas at the Instituto Eduardo Torroja (Puertas et al., 2012; Torres-Carrasco et al., 2014; Puertas and Torres-Carrasco, 2014; Torres-Carrasco and Puertas, 2015; Torres-Carrasco et al., 2015). Based mainly on its chemical composition, formed by SiO_2 , Na_2O , Al_2O_3 y CaO , it is possible to obtain alternative solutions that can partially or totally replace the traditional solutions, such as the commercial sodium silicate. Therefore, an alternative recycling solution for these glass materials is created, mostly for those that are not reused again in the production of new glass bottles, thereby minimizing the environmental issue caused by the fact that this waste will otherwise end up in the landfills.

There are other alternative sources of activators that can provide advantages in terms of price and/or ecological footprint, such as rice husk ashes (J. M. Mejía et al., 2013) and nano-silica (Rodríguez et al., 2013), which have been also evaluated as a replacement silica source for these alternative activators.

4. Applications of alkaline cements

Since the discovery of alkali-activated cements and concretes in 1958, they have been produced and used in a variety of construction projects in the old Soviet Union, China and other countries. During the last 40 years, a broad experience has been gained from the design, production and application perspectives, which is useful for the development and application of these alkali-activated materials.

During the period of 1999-2000, a group of scientists in Ukraine examined several concrete structures built with alkali-activated slag cement, among which it is worth highlighting different constructions such as silage pits, railway embankments, buildings up to 15 floors, etc. In all these cases, alkali-activated slag cements and concretes were still operating well and exceeded the performance of the Portland cement concrete used in the same region.

More recently, a group of Spanish and Australian scientists developed different types of applications with alkali-activated fly ash concretes: railroad ties and channeling pipes (Palomo et al., 2004; Hardjito et al., 2004). An interesting fact is that these new concretes, manufactured with activated fly ash, not only present higher mechanical strengths than ordinary Portland cement concretes (OPC), but also show an excellent bonding behavior with the steel reinforcements, and additionally, an excellent dimensional stability (Jiménez-Fernández et al., 2004; Palomo et al., 2007).

This year, the United Kingdom adopted the PAS 8820:2016 standard, "Construction Materials. Alkali-activated Cementitious Material and Concrete Specification", which gives rise to immense perspectives for these new construction materials.

5. Conclusions

The development of cements that are an alternative to Portland cements, obtained by processes involving lower CO₂ emissions to the atmosphere and a significant energy saving, is a priority line of research of great interest worldwide. Although great progress and research have been made regarding these alternative materials, there is still much work ahead to get a better knowledge of their behavior. This would imply to overcome additional problems concerning the full use of these materials; however, these geopolymers show that they are suited for a large number of high-technology applications that are currently being used. Nevertheless, their interesting chemistry, as well as their physical properties, should be subject to further studies leading to the

development of materials with new functionalities from the point of view of the mechanical strength and durability.

In short, new geopolymer-based materials offer excellent perspectives for the future; they should not be regarded as competitive materials for Portland cement, which has been the reference construction material for so long, but as alternative materials with a series of important advantages to be considered.

6. Acknowledgements

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