MATERIALS ENGINEERING

Alkali-activated materials: cementing a sustainable future

INGENIERÍA MATERIALES

Materiales de activación alcalina: cementando un futuro sostenible

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Abstract

This paper presents an overview examining the microstructural and macrostructural properties of alkali-activated binders based on granulated blast furnace slags, metakaolin and their blends, developed by the Composite Materials Group of Universidad del Valle over the past decade. Durability results of activated binders when exposed to aggressive agents such as chlorides, and carbon dioxide are reported. The results of this research have elucidated the great feasibility of adopting alkali-activation technology in Colombia for producing high strength concretes based on industrial by-products, with a wide range of properties that can be suitable for different civil infrastructure applications, and contribute to the valorization of low-cost industrial by products through production of more environmentally friendly building materials. Our research highlights the fact that a deep understanding of the chemistry of these systems allows the manipulation of the microstructure and therefore the performance of the final products, toward the production of sustainable and versatile materials.

Keyrwords: *Alkali-Activation, blast furnace slag, Metakaolin, compressive strength, durability*

Resumen

En este documento se presenta una revisión de las propiedades microestructurales y macroestructurales de cementantes de activación alcalina basados en escorias granuladas de alto horno, metacaolín y sus mezclas, desarrollados por el Grupo Materiales Compuestos de la Universidad del Valle durante la última década. Resultados de durabilidad de cementos activados cuando son expuestos para agentes agresivos tales como cloruros y dióxido de carbono son reportados. Los resultados de esta investigación han elucidado la gran viabilidad de la adopción de la tecnología de activación alcalina en Colombia para la producción de concretos de alto desempeño basados en sub-productos industriales, con un rango amplio de propiedades que puedan ser adecuadas para diferentes aplicaciones de infraestructura civil, y contribuye a la valorización de sub-productos industriales de bajo costo a través de la producción de materiales de construcción más amigables con el medio ambiente. Nuestros resultados resaltan el hecho que un entendimiento profundo de la química de estos sistemas permite la manipulación de la microestructura y por lo tanto el desempeño de los productos finales hacia la producción de materiales sostenibles y versátiles.

Palabras Claves: *Activación Alcalina, escoria de alto horno, Metacaolín, resistencia mecánica, durabilidad*

1. Introduction

Alkali-activation is a globally growing technology that involves the chemical reaction between a solid aluminosilicate precursor and an alkaline activator, at room temperatures, giving a hardened product (Shi *et al.* 2006). These materials can be used in clinker-free high performance concretes and in particle-fiber reinforced ceramics, with properties comparable or even superior to what is expected of conventional Portland cement-based materials, or ceramic materials produced through conventional methods. As main precursors for producing alkali-activated materials industrial by-products such as granulated blast furnace slag (derived from the steel making industry), fly-ash (derived from coal combustion), and natural clays (metakaolin) are used, among others (Duxson & Provis 2008). These materials were first produced on a significant scale by Purdon in the 1940s (Purdon 1940), but the worldwide awareness of this technology started to develop in 1950s with the work developed by Glukhovsky in Eastern Europe, who investigated the binders used in ancient Roman and Egyptian structures (Glukhovsky 1994), discovering the possibility of producing binders using low basic calcium or calcium-free aluminosilicates (clays) and solutions containing alkali metals (Glukhovsky 1959). He called the binders "soil cements" and the corresponding concretes "soil silicates". Since the 1960s, the Glukhovsky Research Institute in Ukraine has developed this technology to a sufficient extent that railway sleepers, road sections, pipes, drainage and irrigation channels, flooring for dairy farms, pre-cast slabs and blocks, have been produced and put in service for more than 40 years using alkali activated blast furnace slag as the sole binder (Shi *et al.* 2006), on a scale of hundreds of thousands of tons of material.

In Instituto Eduardo Torroja, Spain, since the early 1990s, Palomo and Puertas have studied the alkali activation of fly ash and blast furnace slag, respectively. Both groups have aimed to establish the effect of the factors involved in activation, identify the mechanisms governing the process on chemical and microstructural levels, and characterize the nature of the hydration products (Fernández-Jiménez *et al.* 1999, Fernández-Jiménez *et al.* 2005). These studies have also assessed the effect of formulation conditions on the strength and durability of activated binders. In 2000, the first collaborative project between Universidad del Valle and Instituto Eduardo Torroja was developed, focused on the development of alkali-activated materials using Spanish and Colombian by-products, specifically alkali-activated slags. The early work derived from this collaboration demonstrated the high chemical stability of activated slag mortars when exposed to sulfates and seawater (Puertas *et al.* 2002) and the high retention of mechanical strength exhibited by these materials when exposed to high temperatures (Mejía de Gutiérrez *et al.* 2004).

Since then, the Composite Materials Group (Universidad del Valle) led by Professor R. Mejía de Gutiérrez has published pioneering work, in Colombia and the world, in the development and assessment of alkali-activated materials derived from Colombian wastes and industrial by-products, specifically granulated blast furnace slag and metakaolin (derived from the calcination of kaolinite), and more recently fly ash (Mejía 2010) and other industrial by products including spent fluid catalytic cracking catalysts (Trochez *et al.* 2013). This research program, with world-leading collaboration across Australia, the United States, Spain and England, is one of the most active research groups working in this area in Latin-America. This work has led to the development of alkali-activated slag (Bernal *et al.* 2011a), and activated slag/metakaolin blends (Bernal *et al.* 2011b), using commercial activators and alternative alkaline activators derived from chemically modified industrial wastes such as rice husk ashes (Bernal *et al.* 2012a). The formulation and preparation of these materials are described in a recently granted Colombian patent '*Procedimiento para la obtención de un cemento inorgánico no Portland para usos estructurales y no estructurales y producto cementante obtenido", approved by Resolution Nº 10585*'. Other activated systems have been also developed with

Colombian raw materials including metakaolin-based geopolymers (Rodríguez *et al.* 2009), with a diversity of properties allowing their application in the production of high-performance concretes (Rodríguez *et al.* 2008, Bernal *et al.* 2011c, Bernal *et al.* 2012e), high-temperature resistant concretes (Bernal *et al.* 2012f) and binders with high stability when exposed to acid environments (Bernal *et al.* 2012b). Detailed characterization of these products has been conducted through the application of high resolution synchrotron based analytical techniques such as X-ray diffraction and fluorescence microscopy (Bernal *et al.* 2013a), along with other techniques including infrared spectroscopy, thermogravimetry, and nuclear magnetic resonance spectroscopy (Bernal *et al.* 2011b), providing a deep understanding of the structural evolution of the binders, which can then be tailored in order to achieve desired mechanical and durability performance.

2. Methodology

2.1 Materials and samples preparation

The primary raw material used in this study was a Colombian granulated blast furnace slag (GBFS) from the factory Acerías Paz del Río, and metakaolin produced in the laboratory by calcination of Colombian kaolin containing minor traces of quartz and dickite. Chemical composition along with physical properties of these raw materials are given elsewhere (Bernal *et al.* 2012e). The alkaline activating solutions were formulated by blending a commercial sodium silicate solution with 32.4 wt.% SiO_2, 13.5 wt.% Na_2O and 54.1 wt.% H_2O, and 50 wt.% NaOH solution, to reach the desired activation conditions, which are specified throughout the paper. Binders were prepared at activator concentrations of 4 wt.% Na_2O and 5 wt.% Na_2O, expressed relative to the mass of slag. For the production of concrete, crushed gravel and river sand were used as coarse and fine aggregates. Detailed formulation information for the concretes can be found in Rodríguez *et al.* (2008), Bernal *et al.* (2011c), Bernal *et al.* (2012e).

2.2 Tests conducted on concretes

Concrete samples were tested to determine compressive strength following the standard procedure ASTM C39/C39M-09a. Flexural strength was assessed in prismatic samples with dimensions 0.076×0.076×0.28m, in accordance with the standard procedure ASTM C 293-08. Total porosity and absorption were calculated according to the standard procedure ASTM C642-06. A measure of the resistance to chloride ion penetration was obtained by testing in accordance with the standard procedure ASTM C1202-05 using a PROOVE'it instrument supplied by Germann Instruments.

3. Results and discussion

3.1 Setting time and calorimetric measurements

The effect of the nature and concentration of activation in the setting times (hardening) of activated Colombian slag sources, evaluated by Vicat test, is presented in Figure 1, where it is identified that the increment of the concentration of activation reduces the setting time, and this is more significant in binders produced with NaOH as an activator. Changes in the solution modulus (Ms = molar ratio SiO_2/Na_2O) of silicate-based activators ("waterglass") also affect the setting times of Colombian activated slag, so that an activator with Ms = 1.3 (waterglass in Figure 1) promoted shorter setting times than the activator with Ms = 2.0 ($Na_2O.rSiO_2$ in Figure 1) at increased concentrations of activation. The alkaline activator is one of the most important factors controlling setting time and compressive strength development in any alkali-activated binder material (Fernández-Jiménez & Puertas 2001). The key role of the alkaline solution in alkali-activated slag is to accelerate the dissolution of the slag into small structural units, which then polycondense with the progress of the reaction to form a short-range ordered gel structure, mainly composed of calcium silicate hydrates (C-S-H) along with other reaction products (Shi & Day 1996, Fernández-Jiménez & Puertas 2003).

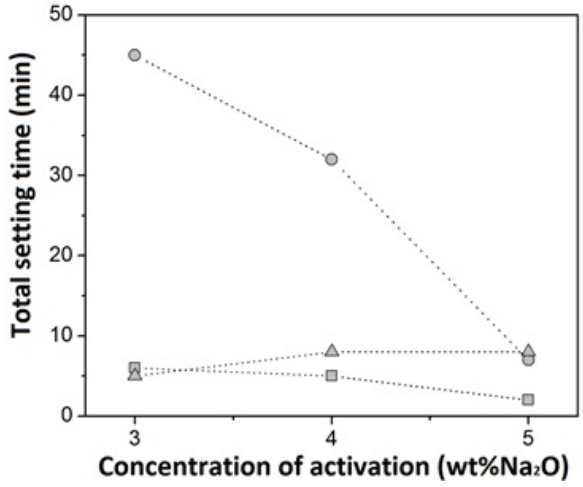


Figure 1. *Setting time of alkali-activated slag binders as a function of the nature of the alkaline activator and the concentration of activation, expressed as wt.% of total slag in the mix. (●) NaOH, (▲) $Na_2O.rSiO_2$, (■) waterglass.*

The setting times identified for these binders are very low compared with what is specified for Portland cement, which is generally required to have a minimum initial setting time of 45 min (Hewlett 1998). However, calorimetric measurement of the heat evolution from the reaction taking place during setting of silicate-activated slags (Bernal *et al.* 2011a) revealed that there is not a direct correlation between the measurements of setting times via the Vicat test (Hewlett 1998) and the formation and precipitation of reaction products in activated slag binders, as shown in Figure 2. This suggests that the Vicat test is not a reliable measurement for determining the hardening time of activated slag binders.

3.2 Determination of reaction products via analytical techniques

Detailed structural evolution of silicate-activated slag binders was also studied via X-ray diffraction (Bernal *et al.* 2010, Bernal *et al.* 2011a). X-ray diffractometry was carried out using a high-resolution high-throughput synchrotron powder X-ray diffractometer with a system of twelve simultaneous analyzer/detectors at beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory, USA. The formation of calcium silicate hydrate (C-S-H) is identified (Figure 3(a)), as the main reaction product in silicate-activated slags, in good agreement with the reported in other studies (Wang & Scrivener 1995, Fernández-Jiménez & Puertas 2003). Formation of the aluminosilicate zeolite gismondine is also observed. No crystalline hydrotalcite-type phases were observed in any of the samples studied, due to the very low Mg content of the slag used. This is one of the key differences between the Colombian activated slag binders and those produced and assessed in Europe and Australia, where the slags contain higher levels of Mg and such phases are usually identified.

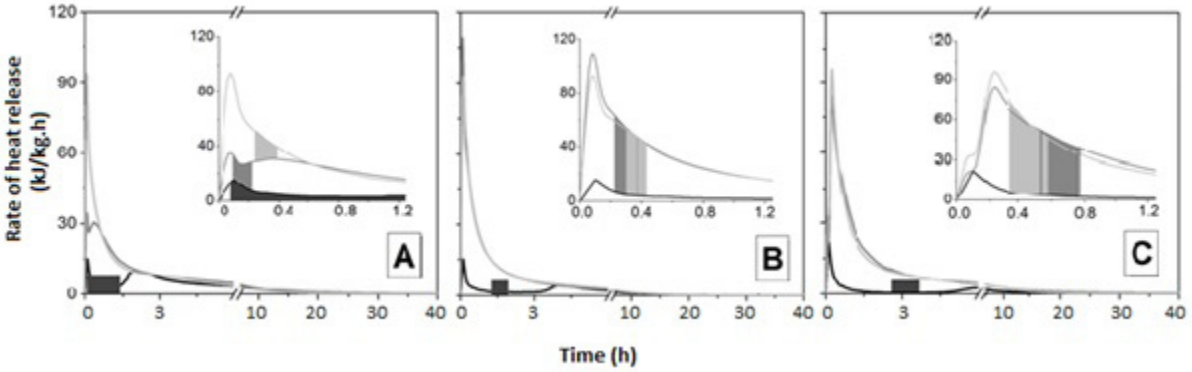


Figure 2. *Isothermal calorimetry (25 °C) curves showing heat release from alkali-activated slag (GBFS)/metakaolin (MK) blends with GBFS/(GBFS+MK) ratios of (A) 1.0, (B) 0.9 and (C) 0.8. The highlighted areas in the inset panels correspond to the setting period (from initial set to final set) determined for each mix by the Vicat test. Data from (Bernal et al. 2011a). (—) Ms 2.4, (—) Ms 2.0, and (—) Ms 1.6.*

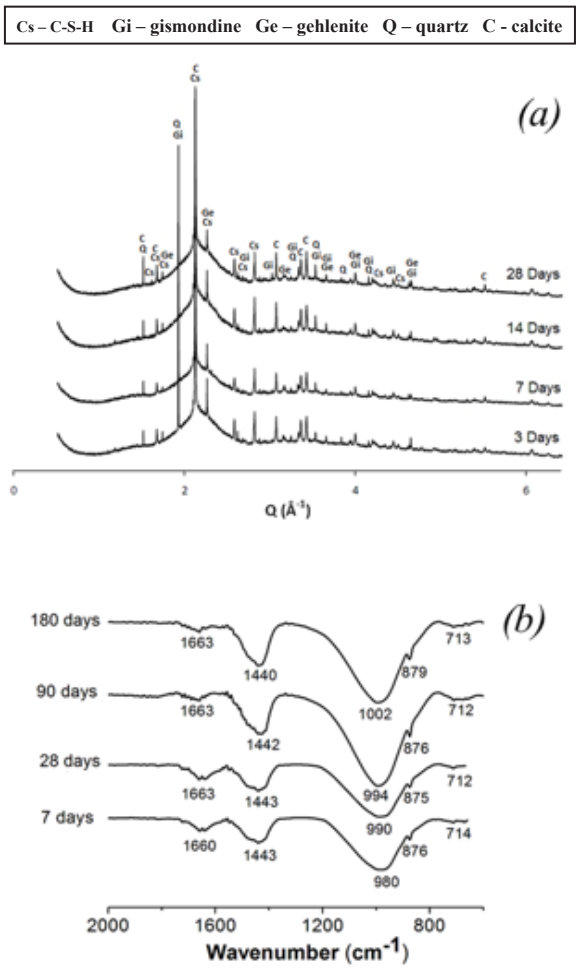


Figure 3. *(a) High resolution synchrotron X-ray diffraction patterns of pastes (= 0.401738 Å) based on alkali-activated GBFS with Ms = 2.4, at different times of curing; (b) Fourier transform infrared spectra of pastes of silicate activated slag with Ms = 2.4 as a function of the curing time. Data from (Bernal et al. 2011a).*

Fourier transform infrared (FTIR) spectrometry was conducted via the KBr pellet technique, using a Shimadzu FTIR 8400 instrument. Assessment of these specimens through FTIR (Figure 3(b)) showed that extended times of curing mainly affects the band at around 1000 cm^{-1}, assigned to the asymmetric stretching mode of the Si-O-T (T = tetrahedral Si or Al) bonds within the reaction products (Gadsden 1975). A broad band at 980 cm^{-1} is associated with a highly depolymerized silica network and attributed mainly to the contribution of the unreacted slag at earlier ages. After 28, 90 and 180 days a progressive shift in this band to 990 cm^{-1}, 994 cm^{-1} and then 1002 cm^{-1} was observed, indicating an increased polymerization degree of the C-S-H products (Yu *et al.* 1999). The higher intensity of the bands after 90 and 180 days of curing (Figure 3(b)) also shows a greater extent of reaction product formation at these ages of curing.

Preliminary results from production of binary activated slag/metakaolin blends revealed that adopting similar activation conditions to those used solely slag-based materials do not provide sufficient alkalinity to favor the dissolution of the metakaolin. Therefore, its incorporation hinders the kinetics of reaction of activated slag binders (Bernal *et al.* 2011a), reducing the mechanical strength and increasing the susceptibility of these materials to degradation phenomena such as carbonation (Bernal *et al.* 2010).

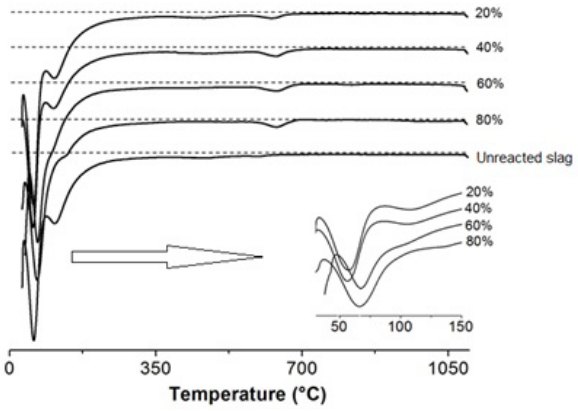


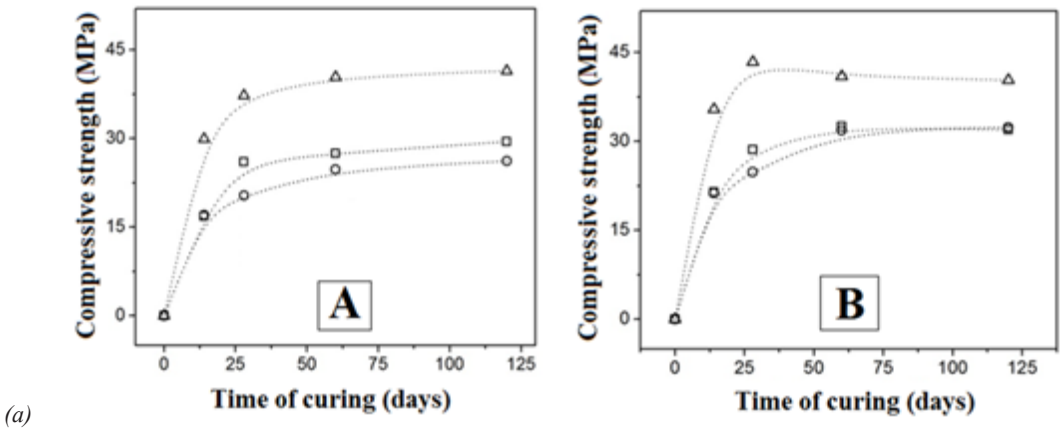
Figure 4. *Differential thermograms (mass loss downwards, dashed lines represent zero for each data set) indicating the content of slag in alkali silicate-activated metakaolin/slag blends. Data from (Bernal et al. 2011b).*

However, modifications in the criteria of formulation of these binders, considering the chemical composition of the whole system (i.e. binder design according to desired overall oxide ratios), promoted the formation of stable and strong binders (Bernal *et al.* 2011b). Under these activation conditions, the microstructure of these binders is dominated by a C-S-H type gel when slag percentages of up to 60% are included, shown by the first mass loss peak in Figure 4 appearing

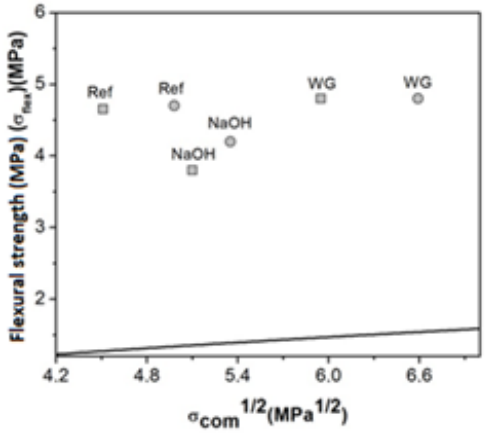
at higher temperatures for C-S-H type gels. Replacement of some of the slag by metakaolin favored the formation of an aluminosilicate type gel ('geopolymer gel'), seen by the first mass loss peak at lower temperatures in Figure 4. This was identified via thermogravimetry, using a thermogravimeter SDT-Q600, by considering that the water is more tightly bonded in C-S-H type products than in aluminosilicate type gels. The mechanical strength of blended activated binders is strongly dependent on the activation conditions, as this modifies the availability of silicate species in the system during the early stages of the activation reaction (Bernal *et al.* 2011b).

3.3 Engineering properties of alkali-activated concretes

The compressive strength development of activated slag concretes as a function of the activator used is presented in Figure 5(a). Reference samples of Portland cement were produced using a similar content of binder in the concretes, and a constant water/binder ratio (w/b) of 0.42. The waterglass used here is a sodium silicate solution with Ms of 1.3. Detailed information regarding sample formulation and preparation is given in (Bernal & Rodríguez 2004). All concretes exhibit an increase in mechanical strength over the time of curing,



(a)



(b)

Figure 5. *(a) Compressive strength of 28-days cured activated slag concretes formulated with (A) 300 kg/m³ and (B) 400 kg/m³ of binder, as a function of the nature of the alkaline activator. (□) reference, (△) NaOH, (○) waterglass; (b) Relationship between flexural and compressive performance of concretes produced with different activators and contents of binder, with the relationships specified for Portland cement concrete (AS3600) plotted for comparison. (■) concretes with 300 kg of binder, (●) concretes with 400 kg of binder and (—) AS 3600.*

and with the inclusion of higher contents of slag in the concrete. NaOH-activated slag concretes show a strength development comparable with the Portland cement reference samples; however, remarkable increments in the strength are identified in silicate activated concretes (labeled as waterglass in Figure 5(a)) as the extra silicate supplied by the activator favors the formation of additional C-S-H type products (Fernández-Jiménez & Puertas 2003).

Slight variations in the flexural strength are identified in activated concretes using different activation solutions and comparable modulus of rupture are obtained in slag activated concretes produced with a type of activator but increased contents of slag (Bernal & Rodríguez 2004). The correlation between compressive and flexural strength of these concretes is reported in Figure 5(b). The relationship between flexural and compressive strength of the concretes assessed is higher than the recommendation of ACI 318-08 and the Australian standard AS3600 (Bernal *et al.* 2012e), suggesting that adopting design criteria used for Portland cement-based concretes when using alkali-activated slag concrete leads to a conservative design; these alkali-activated concretes show higher flexural strengths than expected for conventional concretes, for the same compressive strength. This is in good agreement with the trends identified by Sofi *et al.* (2007) and Diaz-Loya *et al.* (2011) in activated fly ash and fly ash/slag concretes. The relationship between compressive and flexural strength of activated slag concretes including minor percentages of metakaolin has been also studied (Bernal *et al.* 2012e). The concretes assessed had a very high alkali activator content, which favored the reaction of metakaolin and promoted good compressive strength (>50 MPa) after 180 days. In order to determine a correlation between formulation conditions and mechanical strength developed for these binary activated systems, statistical modeling using a response surface methodology (Bernal *et al.* 2009) and Bayesian probability (Gordillo 2011) have been applied.

4. Durability performance of alkali-activated materials

4.1 Water absorption and chloride permeability

The durability of cementitious materials is strongly dependent on the ability of an aggressive agent to penetrate the material to react with either the reaction products forming the matrix or embedded steel reinforcing, modifying the original concrete microstructure and leading to increasing permeability and reduced loading capacity. The volumes of permeable voids of 60-day and 120-day cured concretes are reported in Figure 6(a). The results reveal that the nature of the alkaline activator, the content of binder and the time of curing strongly influence the permeability of these concretes. This is consistent with the formation of a refined pore structure when using silicate-based activators (Brough & Atkinson 2002). It has been reported that when applying this test, total porosity values of 10% indicate concretes with good durability, which suggests that the activated slag concretes have the potential to be highly durable.

In alkali-activated slag, the presence of Na^+ and OH^- in the pore solution is likely to be affecting the results of the chloride test (ASTM C 1202), as Na^+ will be expected to counter-diffuse as the Cl^- ions are electrically driven into the pore network, leading to an increased charge transfer during the test, so the fact that Figure 6(b) shows a lower charge passed value for alkali-activated slags than the Portland cement reference can be taken to indicate that the actual chloride movement through the materials is likely to be much slower. It has been reported that well-cured alkali-activated slag concretes report a reduced permeability to chlorides when compared with Portland cement based concretes (Shi 2004), as a consequence of the refined pore structure of the activated binding matrix. When testing activated materials, the results of the ASTM C 1202 test need to be considered as an indicator for quality control when comparing concretes with similar binder chemistry, rather than as an absolute measure of durability (Bernal *et al.* 2011c).

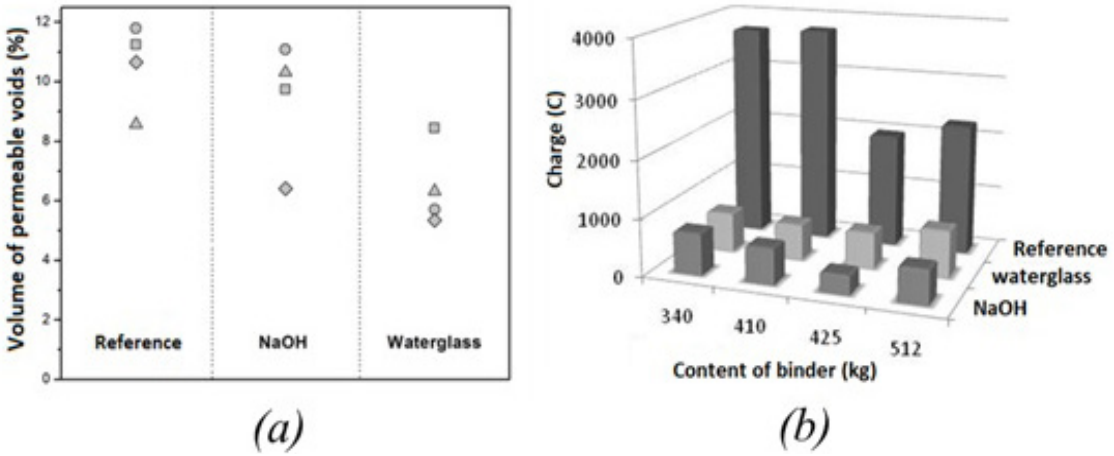


Figure 6. *(a) Effect of the nature of the alkaline activator, curing duration and the content of binder in the volume of permeable voids of alkali-activated slag concrete, (■)300kg/ 60days, (▲) 400kg/60 days, (●) 300kg/ 120 days and (◆) 400kg/ 120 days. (b) Charge passed (as an indicator of chloride permeability) of 28-day cured activated slag concretes determined according to ASTM C 1202.*

4.2 Natural and accelerated carbonation testing

There is limited existing knowledge about the long-term in-service stability of alkali-activated concretes when interacting with CO_2, where concretes will in general undergo a series of phenomena referred to as carbonation. Laboratory studies of pastes and mortars of alkali-activated slag, and slag/metakaolin blends (Palacios & Puertas 2006, Puertas *et al.* 2006, Xu *et al.* 2008, Bernal *et al.* 2010), have shown potentially higher susceptibility to carbonation in these materials compared with conventional cements when assessed under accelerated conditions. However, this has been shown to be a consequence of the pore solution alkalinity (Bernal *et al.* 2012d) and binder chemistry under the specific conditions of the test, rather than in service, especially related to the absence of portlandite as a reaction product in these binders.

The carbonation depths of activated slag concretes, cured for 28 days and then exposed to an urban atmosphere for 180 days, as a function of the nature of the activator and content of binder, are presented in Figure 7. A detailed study of the effect of the binder content on the performance of activated slag concretes (Bernal *et al.* 2011c) revealed that carbonation in these materials is initially a chemically controlled process followed by a diffusion controlled process, and is more intense in those concretes where microcracking problems can be identified. This is in good agreement with a recent proposed mechanism of reaction where carbonation of activated binders is likely to be taking place in a two-step process: first the carbonation of the pore solution leading to the formation of sodium carbonate reaction products, followed by the decalcification of the C-S-H type products and consequent decay of the mechanical strength (Bernal *et al.* 2012d). The effect of the composition of the cement binder and incorporation of metakaolin in activated slag binders and concretes has also been assessed (Bernal *et al.* 2010), where it has been identified that the inclusion of metakaolin as a secondary precursor in activated slag materials increases the susceptibility to carbonation, and that the accelerated carbonation testing conditions have a remarkable impact on the carbonation rates identified for different activated concretes. At higher concentration of CO_2 and moderate relative humidity (65%), a larger carbonation extent is detected in these materials, whose trends do not match well what is identified in concretes with similar formulations carbonated under natural exposure conditions (Bernal 2009). Accelerated

carbonation testing of activated slag concretes should not be conducted at CO_2 concentrations beyond 1% CO_2, as higher CO_2 concentrations completely modify the pore network, and so misleading results can be obtained under such testing conditions (Bernal 2009).

In order to reconcile the results between natural and accelerated carbonation of silicate-activated slag concretes, assessment of 7-year old concrete specimens exposed to a Colombian urban atmosphere has been conducted (Bernal *et al.* 2013b). In these materials, relatively low carbonation depths have been identified (<15 mm) in all the concrete formulations assessed, and formation of the mixed Na-Ca carbonate phase nyerereite is observed, indicating the development of a highly self-desiccating environment within the material, consistent with the increased scope for water ingress and increased carbonation depth identified in those concretes.

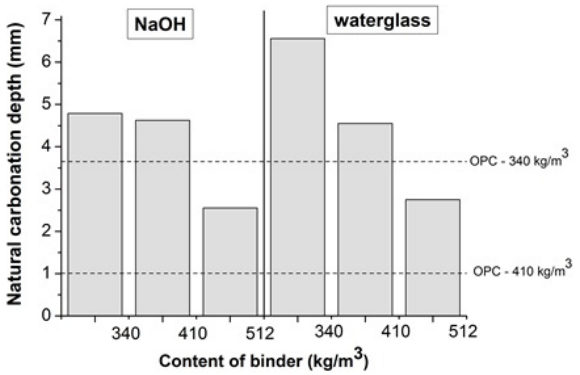


Figure 7. *Carbonation depth of 28-days cured activated slag concretes exposed to an urban atmosphere for 180 days, as a function of the nature of the activator and content of binder. Data from (Rodríguez et al. 2008).*

4.3 Performance after exposure to high temperatures and acids

The performance of activated slag binders when exposed to high temperatures has been also assessed (Bernal *et al.* 2011b, Bernal *et al.* 2012c, Bernal *et al.* 2012f). Evaluation of activated slag pastes produced using commercial silicate activators or chemically modified silica fume (silica fume + NaOH) revealed that exposure to temperatures up to 200ºC enhances mechanical strength, and good strength was retained when exposed to temperatures up to 600 ºC, where conventional Portland cement materials usually report complete decay. However, exposure to higher temperatures (>800ºC) leads to a reduction of the compressive strength associated with the dehydration/decomposition of the reaction products, leading to shrinkage of the matrix and the consequent collapse of some parts of the microstructure. However, it is important to note that the residual strengths after high temperature exposure of activated specimens are still much higher than those obtained in Portland cement specimens.

Alkali-activated slags have shown high stability when exposed to acidic attack (Bernal *et al.* 2012b), retaining 75% of their initial strength (58 MPa) after 150 days of exposure. Conversely, Portland cement specimens are completely destroyed after testing 150 days of exposure. This high residual strength of activated slag binders is associated with the absence of acid soluble phases, such as $Ca(OH)_2$, as a reaction product and the formation of a residual aluminosilicate type gel in the affected area, which is less soluble and more mechanically sound than the silicate gel formed in Portland cement binders, and delays the ingress of the acid inside the specimens.

5. Conclusions

Colombian granulated blast furnace slag, and metakaolin obtained through thermal treatment of kaolin clay, are suitable precursors for the production of alkali-activated materials that can perform as sole binder in the production of mortars and concretes. These materials can show high strength, low permeability, high resistance to acidic attack and good retention of mechanical strength when exposed to high temperature, with a performance that is comparable or even superior to what has been identified for reference materials based on Portland cements. Considering all of the

durability testing results presented, it is possible to elucidate that alkali-activated materials perform extremely well when subjected to many types of severe conditions, as a consequence of their distinct chemistry when compared with Portland cements. However, it has been identified that accelerated testing methods sometimes modify the mechanism of degradation taking place in these materials, such as in the case of carbonation, and therefore the careful assessment of the test methods adopted for determining the durability of alkali-activated binders needs to be undertaken in order to have a truly accurate idea of how these materials are going to behave in service conditions.

Even though it is clear that Colombia is provided with adequate raw materials for producing these novel cements, it is important to bear in mind that for the adoption of these materials at an industrial scale it must be accepted that they are part of the 'tool-kit' of a series of alternative building materials that will help to mitigate the current environmental impact associated with the cement producing industry, and will contribute to fulfilling the growing infrastructure needs of our society, but they will not be the sole solution to fully replace Portland cement in all possible applications.

The development of a good understanding of the chemistry of activated binders, especially when exposed to aggressive environments, and the existing correlation with their macroscopic properties, is essential for the production of materials designed to fulfill the long-term performance expected for high-quality building materials. It is important to note that different raw materials or by-products produced under the same activation conditions will develop different microstructures and therefore different mechanical and durability properties, and so care must be taken in transferring knowledge between systems based on different precursors. This is of great importance in generating the necessary confidence in the long-term performance of these materials and to give them a real chance to be adopted at an industrial scale in Colombia and the world.

6. Acknowledgments

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