ACTIVAREA ALCALINĂ A UNOR ALUMINOSILICAȚI CA ALTERNATIVĂ LA CIMENTUL PORTLAND : REVIEW
ALKALINE ACTIVATION OF ALUMINOSILICATES AS AN ALTERNATIVE TO PORTLAND CEMENT: A REVIEW

M. TORRES-CARRASCO∗, F. PUERTAS
Eduardo Torroja Institute for Construction Sciences (IETcc-CSIC), Madrid (Spain) C/Serrano Galvache 4, 28033

The study and development of new binders as alternatives to portland cement is a priority line of research the world over that aims to minimise the pollutant gas emissions and substantially reduce the energy consumption inherent in cement manufacture.

Cement manufacture has a heavy environmental footprint, for it exploits natural resources (quarries) and emits large quantities of polluting gas (CO_2, SO_2, NO_x) into the air. World-wide, around 5 % to 7 % of CO_2 emissions can be attributed to the cement industry. In addition, given the power consumed to heat kilns to the necessary temperatures and drive the mills that grind the clinker, cement manufacture has a high energy price tag.

This review traces the history and development of alkaline activation, explaining the most characteristic features of the chemistry involved and drawing a comparison between the economic and environmental data for these alternative materials and for portland cement. The findings show that alkaline-activated cements and concretes perform better in both respects. Nonetheless, alkaline cement chemistry cannot yet be said to be wholly eco-friendly, for large amounts of CO_2 are emitted in the production of alkaline solutions such as sodium silicates, which is, moreover, a costly process. For those reasons research should be ongoing on the valorisation of alternative materials with characteristics and properties similar to those of the commercial solutions used to date to prepare these systems.

Keywords: *alkali activation, geopoymers, slags, fly ash, durability*

1. Introduction: need for alternative cements and concretes

Portland cement is regarded as the construction material par excellence, for no other binder on the market today is so widely accepted. Its popularity is due primarily to its high performance, good price/quality ratio and the nearly universal availability of its raw materials. Nonetheless, the development of alternatives to portland cement obtained with processes involving lower polluting gas emissions and substantial energy savings constitutes a priority line of research and one of enormous interest world-wide.

Global cement consumption continues to rise. In 2014 it amounted to 4.3 Gt, up from 2.83 Gt just 6 years earlier, in 2008. For that reason, the cement industry is training its sights on reducing CO_2 emissions and complying with the sustainability targets defined at international conferences on the environment.

Today the notion that global warming is a real environmental and economic menace to our way of life is scanty challenged. According to studies by Mahlia [1] and Zhang et al. [2], the greenhouse gases generated by human activity are the primary cause of global warming, which will have catastrophic consequences if not controlled and mitigated.

The evidence supporting the plausibility of such consequences has encouraged industries and governments to study and implement promising strategies to stem the accumulation of greenhouse gas in the atmosphere. The 195 countries attending the latest UN climate change conference held in Paris (2015) adopted an agreement to halt global warming, christened by President François Hollande as the first universal deal 'in the history of climate negotiations'. The agreement sets a ceiling to greenhouse gas emissions and establishes a funding system. In light of the failure of the attempts to set individual country targets (the Kyoto Protocol, which opted for that formula, only managed to cover 11 % of worldwide emissions), the process has been reversed. The deal sets only one mandatory goal: to contain the mean temperature rise on Earth through the end of the century to 'much lower' than two degrees over pre-industrial levels and even attempt to hold it at 1.5 °C. Each country must then table its voluntary contributions to reduce national greenhouse gas emissions accordingly.

The cement industry is regarded as one of the major contributors to anthropogenic CO_2, accounting for approximately 5 % to 7 % of worldwide emissions [3]. Depending on the type of fuel used to produce clinker, 0.9 t to 1.0 t of CO_2 is released into the atmosphere per tonne of cement

---

Future emmisions, no measures   **Future emmisions, measures**

2.33   2.22   2.34
1.88   2.2
0.57
0.83
0.57   1.55

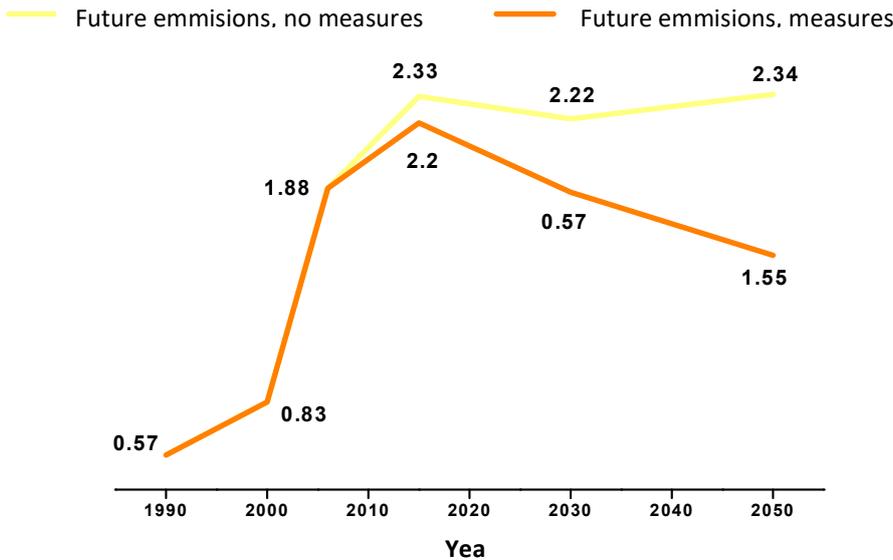1990   2000   2010   2020   2030   2040   2050

Yea

Fig. 1 - Global cement plant emissions of CO_2 from 1990 to 2050 (in Gt) [12].

produced [4-7]. Even in plants using the latest equipment and technology, Bosoaga et al. [8] confirmed that from 0.65 to 0.92 kg of CO_2 is emitted per kilogramme of cement manufactured.

Most of the CO_2 emitted by the cement industry is directly attributable to fossil fuel combustion and limestone calcination to calcium oxide. The source of some of the CO_2 computed is indirect, i.e., associated with the electricity generated to power the mills that grind the raw materials used to manufacture cement [6,9].

Worldwide cement production rose by 54 % between 2000 and 2006 (World Business Council for Sustainable development 2009). Fuelled by population growth and worldwide demand, from 2006 onward output is expected to grow by 0.8 % to 1.2 % yearly, reaching from 3.7 Gt to 4.4 Gt by 2050. This significant rise will induce brisk CO_2 emissions growth. Whereas global CO_2 cement plant emissions amounted to 576 Mt in 1990 [11], that value trebled to 1.88 Gt by 2006. If that tendency continues uncurbed, the CO_2 emitted to the atmosphere by the cement industry alone would amount to 2.34 Gt in 2050 (World Business Council for Sustainable development 2009).

One technological and environmental target is to reduce such emissions to just 1.55 Gt [10] by 2050 through the application of suitable strategies, such as the implementation of energy efficiency measures, the use of alternative fuels or the replacement of clinker [12]. The trend in global CO_2 emissions in the cement industry in 1990-2050 is shown in Figure 1.

The use of portland cement not only adds to CO_2 emissions, however, but also has other adverse effects. Firstly, it contributes to the depletion of mineral reserves, particularly in small European and East Asian countries where cement consumption is high and natural resources limited.

A second concern around cement production is associated with the hazardous

substances emitted into the atmosphere from cement kilns. Although recent developments have improved the capture and recycling of cement kiln dust and other potential emissions [13], non-negligible amounts of hazardous components may be emitted by flue gas.

Public and private institutes engaging in cement research, sensitised to these issues, have been pursuing the development and commercial scale application of systems with a minimum clinker content to further the implementation of environmental and safety policies in the industry.

Governments, in response to social pressure, are regulating the extraction of prime materials and waste stockpiling ever more strictly, for environmental, health and aesthetic reasons. Public and private institutes engaging in cement research, sensitised to these issues, have been pursuing the development and commercial scale application of systems with a minimum clinker content to further the implementation of environmental and safety policies in the industry. *One such group of systems, alkali-activated materials or hybrids, is a source of good binders.*

2. What is alkaline activation?

Alkaline cements are binders resulting from the chemical interaction between alkaline solutions and aluminosilicates (with low or high calcium contents). The latter may be sourced from natural materials (clays) or industrial by-products (blast furnace slag or fly ash) [14].

Since the 1990s, research on alkaline activation has seen spectacular growth around the world, with over 100 (academic and commercial) research institutions actively engaging in the field on all the inhabited continents. Many of the papers published report on the development of materials

with acceptable performance, based on locally available raw materials. The literature includes hosts of technical reports and books describing the basic physical or microstructural properties of the products generated when prime materials are activated with alkalis [15 – 18].

Many names have been proposed for these materials, including 'alkaline cements', 'geocements', 'hydrocements', 'mineral polymers', 'inorganic polymers', 'vitreous inorganic polymers' and 'activated ash materials', to name a few. All these names allude to one and the same type of material obtained from similar chemical procedures. The existence of such a proliferation of names to describe essentially the same material is an indication that researchers are still scanty familiar with the field. The terms 'alkali-activated materials' and 'geopolymers' are the ones used hereunder to refer to this type of cements and concretes.

- *Alkali-activated material* is the broadest category, covering essentially any binder obtained from the reaction between a (solid or dissolved) alkaline metal and a solid silicate powder [19]. These solid aluminosilicates may be calcium-high, such as blast furnace slag, or calcium-low, such as fly ash. The sources of the alkalis used may be alkaline hydroxides, silicates, carbonates, sulfates, aluminates or oxides, i.e., nearly any soluble substance that furnishes alkaline metals, raises the pH of the reaction mix and accelerates the dissolution of the solid precursor.

- The word *geopolymer* often refers to a subset of alkali-activated materials. Fly ash with a low calcium content and calcined clays (essentially metakaolin [20]) are the precursors most commonly used in geopolymer synthesis. The word geopolymer is also used commercially and in research much more broadly, however, particularly in connection with commercialisation. The term was coined in the nineteen seventies by French scientist and engineer Joseph Davidovits [18,21,22].

Over the last two decades, alkaline cements and concretes have roused considerable interest in the scientific community and the construction industry both, for the reasons listed below [23].

a) They exhibit high early age mechanical performance. Twenty-hour materials can develop mechanical strength comparable to the strength developed by portland cement in 28 days [24].

b) The carbon dioxide emissions and energy consumed to produce these alkaline cements are substantially lower than observed in portland cement manufacture [25, 26].

c) The sole 'raw material' (often) needed to manufacture these cements is industrial waste such as fly ash from coal-fired power plants [27 – 29] or blast furnace slag [17, 30-33] which would otherwise be stockpiled in landfills, adding to environmental pollution.

d) These materials usually perform as well as or better than ordinary portland cement. For instance, they exhibit higher resistance to sulfates [34-36] and acid [34, 37]; they pose fewer 'aggregate-alkali' reaction-induced expansion problems observed under certain conditions in portland cement mortars and concretes [34,38,39]; recent studies have shown that these materials retain their properties at high temperatures [40-42] and are able to immobilise some types of toxic or hazardous waste, including nuclear waste [43-45].

3. Components in alkaline activation: precursors and alkaline activators

Alkaline cements are primarily the result of a chemical reaction between *precursors* and *alkaline activators*. The former are normally aluminosilicates derived from natural sources (thermally activated clay or similar) or industrial by-products (such as blast furnace slag and fly ash). The latter are usually alkaline salts or solutions. Glukhovsky classified activators into six major groups on the grounds of their chemical composition:

1. alkaline hydroxides: MOH
2. weakly acidic salts: M_2CO_3, M_2SO_3, M_3PO_4, MF
3. silicates: $M_2O \cdot nH_2O$
4. aluminates: $M_2O \cdot nAl_2O_3$
5. aluminosilicates: $M_2O \cdot Al_2O_3 \cdot (2\text{-}6)SiO_2$
6. strongly acidic salts: M_2SO_4

Of all these chemical compounds, $NaOH$, Na_2CO_3, $Na_2O \cdot nSiO_2$ and Na_2SO_4 are the ones most widely available. Whilst some potassium compounds have been used in laboratory studies, their scant availability and high cost limit their commercial application. Moreover, they afford no particular advantage over sodium compounds. Both can be used in liquid or solid form, although the current tendency is to prepare cements containing the precursor and a solid activator, with water as the mixing liquid.

The characteristics and properties of these alkaline cements are discussed below, divided into two major groups, depending on whether their precursors have high (vitreous blast furnace slag) or low (type F fly ash) CaO contents.

3.1. High calcium content alkali-activated materials: blast furnace slag

High calcium cementitious materials such as blast furnace slag have been studied, developed and assessed for over a century [29,46]. The renewed interest in the microstructure of these materials in recent years has induced a need for scientific methods to optimise activation conditions that ensure the strength and stability of

these binders based on a given starting material [19,46].

The basic chemistry of alkali-activated blast furnace slag-based binders has been discussed in detail in the literature [30, 47 – 56]. The structure of the gels formed in slag activation and hence strength development and durability depend heavily on the chemical factors that govern the reaction mechanism. These factors can be classified in two categories: those associated with the raw materials (precursors) and those associated with the activator used.

3.1.1. Activation, reaction products and microstructure

The structural development of alkali-activated blast furnace slag systems depends on a very heterogeneous reaction governed primarily by four mechanisms: dissolution of the vitreous precursor particles, nucleation and growth of the initial solid phases, mechanical interactions and bonds on the boundaries of the phases formed and reactions involving chemical equilibrium and diffusion of the reactive species through the reaction products formed after long curing times [57-59].

The main product of blast furnace slag activation is a calcium aluminosilicate hydrate (C-A-S-H) gel, similar to the gel generated in ordinary portland cement hydration (C-S-H), but with a lower Ca/Si ratio, which generally ranges from 0.9 to 1.2[54,60-63]. Secondary reaction products include hydrotalcite ($Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$), identified in alkali-activated slag systems with high MgO contents [64-66] and zeolites such as gismondine, which forms in blast furnace slag systems with high Al_2O_3 and low MgO (< 5 %) contents [59,67,68].

Reaction kinetics in this type of aluminosilicates depend heavily on the type of activator used and the activation process. The primary role of an alkaline activator in an alkali-activated material is to hasten the reaction, which is attained by raising the pH significantly. Alkaline silicates and hydroxides are the compounds that generate the highest pH, whereas carbonates and sulfates generate mildly alkaline conditions and free hydroxide for activation in reactions involving the calcium in the slag.

The kinetics of the first part of the reaction (first 24-48 hours) in systems activated with silicates, carbonates or hydroxides have been assessed using isothermal calorimetric techniques. Five stages of structural behaviour have been identified: induction, pre-induction, acceleration, deceleration and finalisation, with a heat flow curve that closely resembles the curve for conventional portland cement [69]. That notwithstanding, the duration and intensity of the heat released in the early hours of slag alkaline activation have been found to depend on the activator used [70].

The consensus reached by the many authors who have researched the characteristics of heat release in alkali-activated slag cements is that slag characteristics and the nature and dose (concentration) of the activators play a crucial role in the heat curve for these materials [17,71].

Activator efficiency depends heavily on the pH value, which governs the initial dissolution of the precursor and subsequent condensation reactions [72]. Slag solubility is low at pH = 3-11, but rises significantly at very acid (pH<3) and very basic (pH>11) values. In acid media, however, the hydrates formed are very unstable, whereas in basic media they are stable and compactly structured. The effect of the pH also depends heavily on the type of activator, since calcium solubility declines at high pH, while silica and alumina solubility rises. Although NaOH solutions have a higher pH than sodium silicate solutions at similar alkali concentrations, silicates sourced from a comparable amount of slag develop greater mechanical strength in the latter [31,73-75]. This is because the additional silicate reacts with the Ca^{2+} cations dissolving out of the slag to form dense reaction products (C-S-H gel) [61].

The structure and composition of the C-A-S-H gel formed after slag activation is highly dependent upon the nature of the activator used. The product that forms when NaOH is the activator has a higher Ca/Si ratio and a more orderly structure than the C-A-S-H gel generated with silicate activators [61,76] due to the greater availability of silicate species in the pore solution in the latter systems. Puertas et al. [62] found that the structure of the C-A-S-H gels obtained in sodium silicate activation resembled tobermorite-11 nm (14 links) and tobermorite-14 nm (5 links) (see Figure 2). A model developed by Myers et al.[63] describes these gels based on the limitations inherent in reticular and non-reticular structures in different tobermorite units (see Figure 3). It can be used to calculate chain length, the Al/Si ratio and degree of reticulation for these more complex structures that cannot be fully described with the standard non-reticular C-S-H gel models for similar tobermorites.
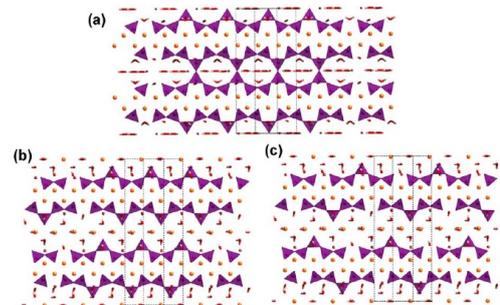

Fig. 2 - Structural models for: a) T11 (14), b) T14 (11) and c) T14 (5) [62].
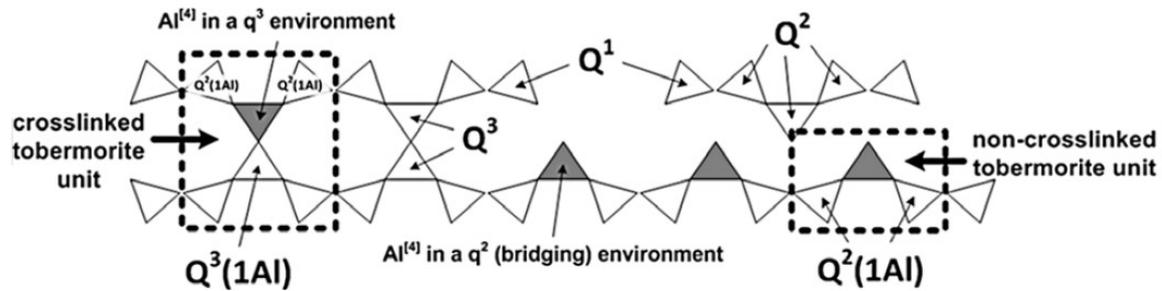
Fig. 3 - Structural model for C-A-S-H gels [63].

Recent studies [73] have also shown that some of the Ca^{2+} ions chemically bonded to C-A-S-H gel may be replaced by Na^+, giving rise to a C-(N)-A-S-H gel when activated with NaOH and sodium silicate solutions. Such C-(N)-A-S-H gels have also been observed in the interfacial transition zone between siliceous aggregate and alkali-activated slag with a low Ca/Si ratio [77].

3.2. Materials alkali-activated with Ca-low materials: fly ash

Fly ash from coal-fuelled steam power plants is the typical Ca-low precursor in alkaline activation. The nature of fly ash and its chemical and mineralogical composition affect the performance of the geopolymers obtained, however. Fly ash with CaO contents of under 5 wt% (ASTM type F) is normally used in these cements. As in alkali-activated slag systems, the activator is a key variable.

3.2.1. Activation, reaction mechanisms and microstructure

Glukhovsky [78] proposed a general mechanism for the activation reactions in these materials, consisting of three stages: a) destruction-coagulation; b) coagulation-condensation; and c) condensation-crystallisation. The composition of the products depends on the mineralogy and chemistry of the raw materials, the alkaline activator used and the curing conditions.

Palomo et al. [79] proposed a model to describe the process based on zeolite synthesis. In that model the reaction takes place in two stages: a) nucleation, with the dissolution of the aluminates present in the ash and the formation, through polymerisation, of complex ionic species (this stage is highly dependent on thermodynamic and kinetic parameters and encompasses Glukhovsky's first two steps); b) growth, when the nuclei reach a critical size and the crystals begin to grow. This stage is very slow due to experimental conditions.

The Palomo et al. [79] model was later revised by several authors [29,79,80]. Further to the revised model, N-A-S-H gel formation would include a series of steps that can be summarised

as follows. When the solution reaches saturation an aluminosilicate gel, N-A-S-H gel, precipitates. This initially aluminium-high gel, called gel 1, is an intermediate, metastable reaction product [29]. Its formation can be explained by the high Al^{3+} ion content in the alkaline medium in the early stages of the reaction, for reactive aluminium dissolves more quickly than silicon because Al-O bonds are weaker than Si-O bonds. As the reaction progresses, more Si-O groups dissolve out of the original source of aluminosilicates, raising the concentration of silicon in the reaction medium and its proportion in the N-A-S-H gel (gel 2) [29].

The main reaction product (N-A-S-H gel) [81] contains silicon and aluminium tetrahedra distributed at random across cross-linked polymeric chains that form a three-dimensional structure [24,27]. The cavities created by the interlinking chains can accommodate alkaline cations to compensate the charge imbalance resulting from the replacement of a silicon (IV) by an aluminium (III). Terminal hydroxyl groups are also found on the gel surface, although their presence has little bearing on the structure of the material.

The alkaline activator used plays an important role in the formation of the main reaction product. For instance, the silica from the sodium silicate normally used as an alkaline activator is highly soluble and therefore forms part of the N-A-S-H gel. The degree of polymerisation of the sodium silicate, which depends directly on its SiO_2/Na_2O ratio, conditions the structure of the gels precipitating in the various stages of N-A-S-H gel formation [82]. Criado et al. studied the effect of different degrees of activator polymerisation (with SiO_2/Na_2O ratios of 0.17, 0.60 and 1.90) on the intermediate reaction products of fly ash activation. They found this parameter to be instrumental in the kinetics, structure and composition of the initial gel formed and noted that the addition of soluble silica affected the intermediate but not the final reaction products. They reported that the Si/Al ratio did not rise indefinitely in N-A-S-H gel and observed the optimal values to be on the order of 2, toward which the system tended irrespective of the initial conditions, possibly for thermodynamic stability-

related reasons. They also proposed that the effect of a highly polymerised silica on N-A-S-H gel formation could retard reaction kinetics and zeolite crystallisation [77].

3.3. Alkali-activated cement and concrete durability

As a rule, alkali-activated concretes exhibit higher resistance to corrosion [83], acids and high temperatures[37,84-86], as well as better freeze-thaw performance [87,88], than portland cement. They nevertheless have some drawbacks, including more intensive shrinkage and microcracking (particularly in alkali-activated slag systems) and greater efflorescence [89, 90].

At this time, a RILEM Technical Committee (TC 247-DTA: Durability testing of alkali-activated materials), under the leadership of Prof. John L. Provis (Sheffield, United Kingdom), is conducting an exhaustive study of the durability tests to which these alkali-activated aluminosilicates can be subjected to establish specific standards for these materials. To date, the durability tests conducted on alkali-activated slag and fly ash pastes, mortars and concretes were the ones laid down in standards written for portland cements. While these alternative materials have performed better in many of these tests than portland cement, not all these standards are well suited for use in alkaline materials, due primarily to the difference in chemical composition between portland cements and alkali-activated aluminosilicate systems.

Alkaline cement and concrete resistance to chemical and physical aggressive agents is reviewed below.

3.3.1. Sulfate and acid resistance

Alkali-slag cements and concretes are more stable when exposed to aggressive sulfates than the respective Portland cement. Bakharev et al. [91] explored sulfate resistance in activated slag and portland cement concrete specimens as per ASTM standard C1012, in which the specimens were soaked in a 5 % $MgSO_4$ solution for 12 months and their performance compared. The findings showed that while for the first 60 days the two systems developed the same resistance, with time, resistance declined more significantly in portland than in the alkali-activated slag concrete. Many authors [14,92,93] have concluded that alkali-activated slag mortar resistance rises after soaking in 1-2 % $MgSO_4$ for one year, whereas when the $MgSO_4$ concentration is raised to 5 %, mechanical strength increases in the first 3 months but declines after 4 or 6 months.

Puertas et al. [36] reported that slag mortars activated with waterglass were more stable and resistant to sulfates and salt spray than those activated with NaOH, due to gypsum and ettringite formation in the latter.

Calcium-low (fly ash) systems also exhibit good sulfate resistance, particularly when attacked by Na_2SO_4 solutions. Palomo et al. [94] exposed alkali-activated metakaolin pastes to a 4.4 % Na_2SO_4 solution for 270 days, observing fluctuations in early age mechanical strength and a steady rise thereafter. Moreover, infrared spectroscopy revealed no significant change in the post-test structure. Fernández-Jiménez et al. [95] reported similar behaviour when samples of alkali-activated fly ash mortar were tested for sulfate resistance. Other authors have also explored the effect of attacks with different sulfates (Na_2SO_4, MgSO4 end even mixes of the two) on the mechanical and microstructural properties of aluminosilicates with a low calcium content [35,96].

Similarly, acid attack is an issue of growing interest due to the damage that phenomena such as acid rain wreak on concrete structures around the world [97]. From the outset, alkali-activated systems have been defined as acid solution-resistant [98]. This high performance is largely attributable to the lower calcium content in these systems than in portland cement [98].

Bakharev et al. [84] proved that waterglass-activated slag concretes exhibited higher acid resistance than portland cement. That was due to the lower Ca content in the C-A-S-H gel forming in the former, which afforded them greater stability in acid solutions [99].

Fernández-Jiménez et al. [34,98] studied the behaviour of alkali-activated fly ash mortar specimens when exposed to 0.1 N HCl. Mechanical strength declined by 23 % to 25 % in these specimens, compared to 47 % in mortars prepared with OPC. These same authors also observed that the fly ash specimens appeared to be essentially intact after soaking in HCl for 90 days and exhibited no significant weight loss. Whether activated with NaOH or waterglass, the samples were observed to retain a compact N-A-S-H gel matrix in post-acid attack microscopic examination. Nonetheless, chemical characterisation showed that both the gel and the zeolites in the samples exposed to the attack contained less aluminium than the controls. Other authors [37,94] have reported very similar results.

More recently, Vargas et al. [99] showed that alkali-activated slag and fly ash pastes are much more resistant to $NH_4NO_3 \cdot 6H_2O$ acid attack than OPC. The main reaction products (C-A-S-H and N-A-S-H gels) of the alkali-activated materials decarbonated and leached much more slowly and less aggressively into this medium than the C-S-H gel in the portland cement system.

3.3.2. Resistance to chloride ion penetration

Torres-Carrasco et al. [88] and Douglas et al. [100] used the procedure described in ASTM standard C1202 to measure the charge passing through different sodium silicate-activated slag concretes, finding 28 day values of 1300 coulombs

(C) to 2600 C and 91 day charges of 650 C to 1850 C. According to the standard, values under 2000 C denote 'low' and under 1000 C 'very low' chloride penetration. These indices were indicative of the higher anti-corrosion performance of these materials than found in portland cement. ASTM standard C1202 is based on the chemistry of the pore solution, for which reason the chloride ion transport findings may sometimes be good and sometimes poor. In light thereof, the aforementioned RILEM technical committee on alkali-activated materials is presently drafting standards to introduce methods for their study and assessment more in keeping with their chemistry. One of its aims is to develop a standard for determining chloride penetration in these new binders.Studies by Shi [101] and Bernal et al. [102] showed no major fluctuations in chloride penetration with curing time in most alkali-activated slag systems.

3.3.3. Resistance to reinforcement corrosion

A number of studies have been conducted on reinforcement corrosion in alkali-activated slag mortars and concretes. Kukko and Mannonen [103] observed that their blast furnace slag-based materials protected the embedded reinforcing steel: after soaking the materials for one year in simulated seawater, they detected no visible signs of the formation of corrosion products in the samples. Deja et al. [104] and Malolepszy et al. [105] explored steel corrosion in alkali-activated slag mortars cured in water and in a 5 % $MgSO_4$ solution, plotting polarisation curves and measuring corrosion current and the loss of mass in the reinforcement. The addition of $MgSO_4$ passivated the reinforcement bars slightly, whilst the fresh water had barely any impact. According to their data, steel corroded at a faster rate in the alkali-activated slag than in portland cement mortars, although the current declined over time in both systems.

Holloway and Sykes [106] conducted a detailed electrochemical analysis of steel bars in sodium silicate-activated slag mortars, using malic acid as a retarding admixture and NaCl in the water to accelerate corrosion. In their study, the inclusion of higher concentrations of NaCl appeared to reduce the initial corrosion current, a finding they were unable to explain chemically.

These and other results that cannot be straightforwardly explained by standard theory denote the existence of a clear need for scientific and analytical research to determine the mechanisms involved in steel corrosion control in alkali-activated slag systems. Based on the chemistry of pore solutions and electrochemical tests, Halloway and Sykes [106] suggested that the sulfur present in the slag was the agent involved in the electrochemical complexities of their samples,

affecting both corrosion kinetics and corrosion current measurement [107].

Bastidas et al. [108] and Fernández-Jiménez et al. [109] studied steel bar corrosion in sodium silicate- or sodium carbonate-activated fly ash mortars with and without portland cement, to which chlorides were added ($CaCl_2$ = 2 wt% of the paste). The samples were stored at ambient temperature and the test consisted in exposing the samples first to 95 % relative humidity for 90 days, then to 30 % RH for 180 days, followed by 95 % RH through the end of the 760-day test. Under these conditions, the fly ash mortars successfully maintained the passive layer over the steel despite the high humidity.

3.3.4. Resistance to carbonation

Although the mechanism governing carbonation in alkali-activated materials is not yet fully understood, its chemistry has been shown to consist in essentially two steps: 1) pore solution carbonation, which induces a decline in the pH and possibly the precipitation of sodium-high carbonates; and 2) decalcification of the calcium-high phases and carbonation of the secondary reaction products present in the system [110,111]. Compared to portland cement-based products, these materials normally perform poorly when tested in accelerated carbonation conditions. Nonetheless, carbonation rates as low as 1 mm per year [17] have been observed in materials exposed for many years. That is an indication that the accelerated test methods applied to alkaline materials do not accurately replicate what actually occurs under natural carbonation conditions and defines a need for a new methodology to study these materials. Research in this connection is presently being conducted and coordinated by RILEM Technical Committee TC 247-DTA ('Durability tests in alkali-activated materials').

The carbonation mechanism in alkali-activated materials is highly dependent upon the type of material used (slag or ash) [102], as well as on the nature and composition of the activator [112]. The compositional and structural differences in the C-A-S-H gels formed, which depend on the type of alkaline activator used, affect carbonation [113]. In these alkaline systems CO_2 interacts directly with the C-A-S-H gel, inducing its carbonation [112]. The higher C/S ratio in the C-A-S-H gel, along with the shorter silicate chain observed in the slag pastes activated with NaOH, might favour the formation and precipitation of a larger amount of carbonates to fill the pores than in the products of sodium silicate-activated slag products. And that would affect CO_2 diffusion through the material. More recent studies have shown that the MgO content in slag has a bearing on the extent of carbonation and the mechanism involved in alkali-activated slag pastes, whereby an increase in the MgO content in the slag induces

a significant decline in carbonation[114]. Pursuant to these studies, the presence of hydrotalcite as a secondary product has a beneficial effect on CO_2 fixation, lowering decarbonation in C-A-S-H gels.

Carbonation has been less extensively studied in fly ash than in blast furnace slag, although a few papers are worthy of note [111,115]. Criado et al. [115] identified sodium bicarbonate formation in samples cured under atmospheric conditions, which was associated with carbonation of the alkalis present in the pores. Their findings were later corroborated by Bernal et al. [111], who observed early age sample carbonation, an indication that carbonation induces a CO_2 concentration gradient in these systems.

3.3.5. Resistance to freeze-thaw cycles

Studies covering a wide spectrum of alkali-activated materials have shown their good performance in freeze-thaw cycles and higher resistance to frost than portland cement-based materials [17,18,88,116]. Kukko and Mannonen [103] and Bin and Pu[117] also observed high frost resistance in alkali-activated slag and explained this finding on the grounds of its low total porosity and small pore radius. In the Kukko and Mannonen tests, after 100 (+20 °C/-20 °C) freeze-thaw cycles, alkaline concrete exhibited higher bending strength than the control [118], although other authors [119] showed that exposure of these materials to 700 freeze-thaw cycles lowered their strength.

Douglas et al. [100] found a similar decline in bending strength (residual strength ≈60 %) after 500 freeze-thaw cycles in most of the mixes tested. These authors observed no change in the dynamic modulus of elasticity, however. The fact that bending strength declined by 40 % while the modulus of elasticity remained constant is indicative of the need to explore the relationship between these parameters in alkali-activated concretes more thoroughly. Gifford and Gilliot [87] found that freeze-thaw resistance in sodium silicate-activated slag concretes depended primarily on their air content and distribution of air bubbles, attributing the low performance of some of their specimens to those variables. They nonetheless concluded after testing OPC concretes with similar characteristics that freeze-thaw resistance in the alkali-activated concretes was 'at least as good' as in OPC concretes.

Alkali-activated fly ash concretes exhibit acceptable freeze-thaw resistance, although performance is lower than in alkali-activated slag concretes. Their mechanical strength has been reported to remain 70 % intact after 150 freeze-thaw cycles [120]. Husbands et al. [121] also found high freeze-thaw resistance (as tested to ASTM C666 and C672) in hybrid alkali-activated concretes.

3.3.6. Resistance to high temperatures

Alkali-activated slag concretes maintain their structural performance at up to 500 °C - 700 °C, whereas their portland cement counterparts fail to perform at temperatures lower than 500 °C. The use of refractory minerals or blast furnace slag to partially replace aggregate can improve the high temperature behaviour of alkali-activated slag concretes. Adding 6 % of fibreglass in conjunction with ferrochrome-bearing slag, for instance, raises the temperatures resisted by such concretes to 800 °C - 1000 °C [122].

Some authors [123] have reported that alkali-activated slag mortars exhibit residual mechanical strength higher than observed in portland cement mortars at temperatures of up to 500 °C. Those same authors concluded that at 700 °C residual mechanical strength in NaOH-activated slag mortars was similar to the values found for portland cement, and slightly higher than observed when the activator was a sodium silicate hydrate. Lastly, they observed that at 1000 °C alkali-activated slag mortars had higher residual strength than portland cement mortars [124].

A number of studies [41,86,125] have also been conducted on the behaviour of alkali-activated fly ash at high temperatures. Fernández-Jiménez and Palomo [98] obtained results whereby bending strength in fly ash pastes remained constant after heating to 400 °C, although at higher temperatures the residual strength declined to one-third of the initial value. Nonetheless, that performance was far better than observed in conventional portland cement under the same test conditions. Compressive strength, in turn, was found to remain practically constant and even to rise slightly when the material was exposed to temperatures of 800 °C to 1000 °C.

4. Future challenges: new precursors and alternative activators

The foregoing clearly illustrates an obvious future challenge: the need for a more thorough understanding of durability-related factors in alkaline cement and concrete systems.

Another lies in the pursuit of new precursors and alkaline activators as replacements for those presently used.

The declining availability of traditional precursors (vitreous slag and fly ash) in some countries poses problems for the future manufacture of these materials. New, technologically viable precursors must be found, preferably among industrial waste and by-products, to produce new construction materials.

The sodium silicate-based alkaline activators that have proven to deliver the highest mechanical strength and resistance, in turn, have a high

economic and environmental cost. Here also, eco-friendlier and technologically feasible alternatives are needed.

Some of these alternative precursors and activators are described below.

4.1. Alternative precursors

The possible use of other aluminosilicate materials as a solution to possible metakaolin or fly ash shortages is an area of particular interest. Once their suitability for alkaline activation is determined, studies could even be conducted on their use as compositional correctors or supplements for fly ash, metakaolin or slag.

Common clays and feldspars are a possible and scanty researched source of these compounds. The work conducted to date shows that common clays could be used as starting materials in alkaline activation. Buchwald et al. [126] conducted several studies on the susceptibility of smectite- and smectite/illite-type clays to alkaline activation. They concluded that after proper thermal activation these materials dissolve partially in a basic medium (6-M NaOH), yielding a material that hardens with moderate heating (60 °C). Xu and van Deventer [127], in turn, examined the possible use of 16 natural aluminosilicate minerals with different structures and compositions (illite, sillimanite, andalusite and others) as potential sources of silicon and aluminium in alkaline activation. They observed that all dissolved to a greater or lesser degree in a basic medium (more effectively in NaOH than KOH as a rule). After curing at 35 °C for 72 hours, they developed mechanical strength ranging from approximately 2.5 MPa to 19 MPa, depending on factors such as the composition and structure of the mineral, its solubility in basic media and the alkaline cation in the activator.

Compositionally speaking, glass is comparable to crystalline materials with one exception: due to the abrupt cooling to which the molten material is subjected, it has a disorderly structure which might, a priori, be compatible with its use in alkaline cement production. Studies have initially focused on using this material as a partial clinker replacement in portland cement concretes [128,129] or as a starting material for alkaline cements [130].

Cyr et al. [130,131] proposed reusing glass rejects, consisting mostly of silicon and calcium, as the sole starting material to prepare alkaline mortars. They assessed the effect of synthesis parameters such as curing time and temperature and activating solution pH on the development of mechanical strength in mortars made from glass. They found that under optimal experimental conditions ([MOH] = 5M (M = Na$^+$, K$^+$), T = 40 °C), these mortars exhibited mechanical strength values comparable to those observed in fly ash mortars.

Other studies have tested precursors of differing composition and origin, including construction and demolition waste (C&DW) [132], spent fluid cracking catalysts (FCC waste) [133-135], cullet glass and red mud [136],

4.2. Alternative activators

A number of avenues are presently being explored to reuse different types of waste as potential replacements for commercial sodium silicates, the production of which carries a high economic and environmental cost.

Research into the use of vitreous urban and industrial waste for aluminosilicate activation is being pioneered by a group headed by Prof. Francisca Puertas at the Eduardo Torroja Institute for Construction Science [88, 137-140]. Based primarily on its chemical constituents (SiO$_2$, Na$_2$O, Al$_2$O$_3$ and CaO), it is regarded as a possible source of alternatives able to partially or wholly replace traditional compounds such as commercial sodium silicate. This would also enhance the efficiency of glass recycling, for waste unfit for use in new glass packaging and could be valorised, minimising the likelihood of its deposit in landfills.

Environmental and economic advantage may also be drawn from other alternative activators such as silica fume chemically combined with NaOH [18]. Rice husk ash [141, 142] and nanosilica [143] have likewise been assessed as possible sources of silica in these alternative activators.

5. Final comments

The development of alternatives to Portland cement to lower polluting gas emissions and generate substantial energy savings constitutes a priority line of research and one of enormous interest worldwide. Despite the progress made and ongoing research on these new alternative materials, much has still to be done to obtain a full understanding of their behaviour. Whilst that will involve overcoming additional problems that hinder their full use, geopolymers have already proven to be suitable for many of today's high technology applications. Further study is required, however, on their promising chemistry and physical properties to develop materials with higher mechanical strength and greater durability.

In a nutshell, these new geopolymers have a brilliant future. Rather than as materials aiming to compete with portland cement, the construction material par excellence for so many decades, they should be regarded as alternative approaches with benefits worth considering.

REFERENCES

1. T.M. Mahlia, Emissions from electricity generation in Malaysia, Renew. Energy, 2002, **27**, 293.
2. X.F. Zhang, S.Y. Zhang, Z.Y. Hu, G. Yu, C.H. Pei, R.N. Sa, Identification of connection units with high GHG emissions for low-carbon product structure design, Journal of Cleaner Production, 2012, **27**, 118.
3. C. Chen, G. Habert, Y. Bouzidi, A. Jullien, Environmental impact of cement production: detail of the different processes and cement plant variability evaluation, Journal of Cleaner Production, 2010, **18**, 478.
4. A. Hasanbeigi, C. Menke, L. Price, The CO_2 abatement cost curve for the Thailand cement industry, Journal of Cleaner Production, 2010, **18**, 1509.
5. K.H. Yang, Y.-B. Jung, M.-S. Cho, S.-H. Tae, Effect of supplementary cementitious materials on reduction of CO_2 emissions from concrete, Journal of Cleaner Production, 2015, **103**, 774.
6. S. Anand, P. Vrat, R.P. Dahiya, Application of a system dynamics approach for assessment and mitigation of CO_2 emissions from the cement industry, Journal of Environmental Management. 2006, **79**, 383.
7. J. Deja, A. Uliasz-Bochenczyk, E. Mokrzycki, CO_2 emissions from Polish cement industry, International Journal of Greenhouse Gas Control, 2010, **4**, 583.
8. A. Bosoaga, O. Masek, J.E. Oakey, CO_2 capture technologies for cement industry, Energy Procedia Journal, 2009, **1**, 133.
9. W.W.B.C. F. Development, The Cement Sustainability Initiative, 2010.
10. World Business Council for Sustainable Development, Cement Technology Roadmap. Carbon emissions reductions up to 2050, 2009.
11. T. Boden, G. Marland, B. Andres, Global CO_2 emissions from fossil-fuel burning, cement manufacture and gas flaring: Carbon dioxide information analysis center, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A, 2011.
12. E. Benhelal, G. Zahedi, E. Shamsaei, A. Bahadori, Global strategies and potentials to curb CO_2 emissions in cement industry, Journal of Cleaner Production, 2013, **51**, 142.
13. P.C. Hewlett, ed., Lea´s Chemistry of Cement and Concrete 4th Edition, Elsevier Science & Technology Books, 2004.
14. P.V. Krivenko, Alkaline cements, in: 1st Int. Conf. about Alkaline Cem. Concr., Kiev, Ukraine, 1994, p. 12.
15. F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt, Handbook of Alkali-activated cements, mortars and concretes, Woodhead Publishing series in civil and structural engineering, 2015.
16. J.L. Provis, J.S.J. van Deventer, Alkali-Activated Materials. State of the Art Report, RILEM TC 224-AAM, 2014.
17. C. Shi, P. Krivenko, D. Roy, Alkali-Activated Cements and Concretes, Taylor and Francis, London and New York, 2006.
18. J. Davidovits, Geopolymer chemistry and applications, Institud Géopolymère, San Quintin, France, 2008.
19. J.S.J. Deventer, J.L. Provis, P. Duxson, D.G. Brice, Chemical Research and Climate Change as Drivers in the Commercial Adoption of Alkali Activated Materials, Waste and Biomass Valorization, 2010, **1**, 145.
20. A. Tawfik, F.A. El-raoof, H. Katsuki, K.J.D. Mackenzie, S. Komarneni, K-Based Geopolymer from metakaolin : roles of K / Al ratio and water or steam Curing at different temperatures, Materiales de Construcción, 2016, **66**, e081.
21. J. Davidovits, Geopolymers - Inorganic polymeric new materials, Journal of Thermal Analysis and Calorimetry, 1991, **37**, 1633.
22. J. Davidovits, Mineral polymers and methods of making them, 1982, 386.
23. C. Ruiz-Santaquiteria, PhD Thesis, Materias primas alternativas para el desarrollo de nuevos cementos: activación alcalina de vidrios silicoaluminosos, Universidad Autónoma de Madrid, Madrid, 2013.
24. P. Duxson, A. Fernández-Jiménez, J.L. Provis, G.C. Lukey, A. Palomo, J.S.J. Deventer, Geopolymer technology: the current state of the art, Journal of Materials Science, 2006, **42**, 2917.
25. G. Habert, J.B. d'Espinose de Lacaillerie, N. Roussel, An environmental evaluation of geopolymer based concrete production: reviewing current research trends, Journal of Cleaner Production, 2011, **19**, 1229.
26. R.J. Flatt, N. Roussel, C.R. Cheeseman, Concrete: An eco material that needs to be improved, Journal of the European Ceramic Society, 2012, **32**, 2787.
27. A. Fernández-Jiménez, A. Palomo, Characterisation of fly ashes. Potential reactivity as alkaline cements, Fuel, 2003, **82**, 259.
28. A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes: A cement for the future, Cement and Concrete Research, 1999, **29**, 1323.
29. C. Shi, A. Jiménez-Fernández, A. Palomo, New cements for the 21st century: The pursuit of an alternative to Portland cement, Cement and Concrete Research, 2011, **41**, 750.
30. F. Puertas, Cementos de escorias activadas alcalinamente: Situación actual y perspectivas de futuro, Materiales de Construcción, 1995, **45**, 53.
31. A. Fernández-Jiménez, J.G. Palomo, F. Puertas, Alkali-activated slag mortars mechanical strength behaviour, Cement and Concrete Composites, 1999, **29**, 1313.
32. F. Puertas, S. Martínez-Ramírez, S. Alonso, T. Vázquez, Alkali-activated fly ash / slag cement strength behaviour and hydration products, Cement and Concrete Research, 2000, **30**, 1625.
33. E. Rodríguez, S. Bernal, R.M. De Gutiérrez, F. Puertas, Alternative concrete based on alkali-activated slag, Materiales de Construcción, 2008, **58**, 53.
34. A. Fernández-Jiménez, I. García-Lodeiro, A. Palomo, Durability of alkali-activated fly ash cementitious materials, Journal of Materials Science, 2006, **42**, 3055.
35. T. Bakharev, Durability of geopolymers materials in sodium and magnesium sulfate solutions, Cement and Concrete Research, 2005, **35**, 1233.
36. F. Puertas, R. De Gutiérrez, J.M. Delvasto S, A Fernández-Jiménez, Morteros de cementos alcalinos. Resistencia química al ataque por sulfatos y al agua de mar, Materiales de Construcción 2002, **52**, 55.
37. T. Bakharev, Resistance of geopolymer materials to acid attack, Cement and Concrete Research, 2005, **35**, 658.
38. I. García-Lodeiro, A. Palomo, A. Fernández-Jiménez, Alkali–aggregate reaction in activated fly ash systems, Cement and Concrete Research, 2007, **37**, 175.
39. F. Puertas, M. Palacios, T. Vázquez, Alkali-aggregate behaviour of alkali-activated slag mortars : Effect of aggregate type, Cement and Concrete Composites, 2009, **31**, 277.
40. D.L.Y. Kong, J.G. Sanjayan, K. Sagoe-Crentsil, Comparative performance of geopolymers made with metakaolin and fly ash after exposure to elevated temperatures, Cement and Concrete Research, 2007, **37**, 1583.
41. A. Fernández-Jiménez, A. Palomo, J.Y. Pastor, A. Martín, New cementitious materials based on alkali-activated fly ash: Performance at high temperatures, Journal of American Ceramic Society, 2008, **91**, 3308.
42. A. Fernández-Jiménez, J.Y. Pastor, A. Martín, A. Palomo, High-temperature resistance in alkali-activated cement, Journal of American Ceramic Society, 2010, **93**, 3411.
43. J. Deja, Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-activated slag binders, Cement and Concrete Research, 2002, **32**, 1971.
44. C. Shi, A. Fernández-Jiménez, Stabilization/solidification of hazardous and radioactive wastes with alkali-activated cements, Journal of Hazardous Materials, 2006, **137**, 1656.
45. S. Donatello, A. Fernández-Jiménez, A. Palomo, An assessment of Mercury immobilisation in alkali activated fly ash (AAFA) cements, Journal of Hazardous Materials, 2012, **213–214**, 207.

46. J.S.J. Van Deventer, J.L. Provis, P. Duxson, Technical and commercial progress in the adoption of geopolymer cement, Minerals Engineering, 2012, **29**, 89.

47. I.G. Richardson, The nature of C-S-H in hardened cements, Cement and Concrete Research, 1999, **29**, 1131.

48. M.C.G. Juenger, F. Winnefeld, J.L. Provis, J.H. Ideker, Advances in alternative cementitious binders, Cement and Concrete Research, 2011, **41**, 1232.

49. S. Wang, Review of recent research on alkali-activated concrete in China, Magazine of Concrete Research, 1991, **154**, 29.

50. P. Krivenko, Alkaline cements: from research to application, in: G.C. Lukey (Ed.), Geopolymer 2002, Melbourne, Australia, 2002.

51. C. Li, H. Sun, L. Li, A review: the comparison between alkali-activated slag (Si+Ca) and metakaolin (Si+Al) cements, Cement and Concrete Research, 2010, **40**, 1341.

52. C. Shi, J. Quian, High performance cementing materials from industrial slags - a review, Resources, Conservation and Recycling, 2000, **29**, 195.

53. B. Talling, P.V. Krivenko, Blast furnace slag - the ultimate binder, in: S. Chandra (Ed.), Waste Mater. Used Concr. Manuf., Park Ridge, NJ, 1997: p. 235–289.

54. S.D. Wang, X.C. Pu, K.L. Scrivener, P.L. Pratt, Alkali-activated slag cement and concrete: a review of properties and problems, Advances in Cement Research, 1995, **7**, 93.

55. N. Yang, Physical chemistry basis for the formation of alkali activated materials, Journal of the Chinese Ceramic Society, 1996, **24**, 209.

56. E. Robayo, R.M. de Gutierrez, M. Gordillo, Natural pozzolan-and granulated blast furnace slag-based binary geopolymers, Materiales de Construcción, 2016, **66**, e077.

57. F. Puertas, A. Fernández-Jiménez, Alkali-Activated slag cements: kinetic studies, Cement and Concrete Composites, 1997, **27**, 359.

58. A. Fernández-Jiménez, F. Puertas, A. Arteaga, Determination of kinetic equations of alkaline activation of blast furnace slag by means of calorimetric data, Journal of Thermal Analysis of Calorimetry, 1998, **52**, 945.

59. S.A. Bernal, J.L. Provis, R. Mejía de Gutiérrez, V. Rose, Evolution of binder structure in sodium silicate-activated slag-metakaolin blends, Cement and Concrete Composites, 2011, **33**, 46.

60. S. Wang, K.L. Scrivener, Hydration products of alkali activated slag cement, Cement and Concrete Research, 1995, **25**, 561.

61. A. Fernández-Jiménez, F. Puertas, Structure of calcium silicate hydrates formed in alkaline-activated slag : influence of the type of alkaline activator, Journal of America Ceramic Society, 2003, **86**, 1389.

62. F. Puertas, M. Palacios, H. Manzano, J.S. Dolado, A. Rico, J. Rodríguez, A model for the C-A-S-H gel formed in alkali-activated slag cements, Journal of European Ceramic Society, 2011, **31**, 2043.

63. R.J. Myers, S.A Bernal, R. San Nicolas, J.L. Provis, Generalized structural description of calcium-sodium aluminosilicate hydrate gels: the cross-linked substituted tobermorite model., Langmuir, 2013, **29**, 5294.

64. A.R. Brough, A. Atkinson, Sodium silicate-based , alkali-activated slag mortars Part I. Strength, hydration and microstructure, Cement and Concrete Research, 2002, **32**, 865.

65. M. Ben Haha, B. Lothenbach, G. Le Saout, F. Winnefeld, Influence of slag chemistry on the hydration of alkali-activated blast-furnace slag — Part I: Effect of MgO, Cement and Concrete Research, 2011, **41**, 955.

66. A. Fernández-Jiménez, F. Puertas, Effect of activator mix on the hydration and strength behaviour of alkali-activated slag cements, Advances in Cement Research, 2003, **15**, 129.

67. Y.J. Zhang, Y.L. Zhao, H.H. Li, D.L. Xu, Structure characterization of hydration products generated by alkaline activation of granulated blast furnace slag, Journal of Materials Science, 2008, **43**, 7141.

68. S. A. Bernal, R.M. de Gutierrez, J.L. Provis, V. Rose, Effect of silicate modulus and metakaolin incorporation on the

69. carbonation of alkali silicate-activated slags, Cement and Concrete Research, 2010, **40**, 898.

70. P. Barnes, J. Bensted, Structure and performance of cements, CRC Press. Taylor & Francis Group, 2002.

71. A. Fernández-Jiménez, PhD Thesis, Cementos de escorias activadas alcalinamente: influencia de las variables y modelización del proceso, Universidad Autónoma de Madrid, Madrid, 2000.

72. C. Shi, R.L. Day, Some factors affecting early hydration of alkali-slag cements, Cement and Concrete Research, 1996, **26**, 439.

73. Y. Runzhang, O. Shi-Zi, G. Qiong-Ying, Study on structure an latent hydraulic activity of slag and its activation mechanism, Journal of Wuhan University of Technology, 1987, **3**, 297.

74. M. Ben Haha, G. Le Saout, F. Winnefeld, B. Lothenbach, Influence of activator type on hydration kinetics, hydrate assemblage and microstructural development of alkali activated blast-furnace slags, Cement and Concrete Research, 2011, **41**, 301.

75. S. Wang, K.L. Scrivener, P.L. Pratt, Factors affecting the strength of alkali-activated slag, Cement and Concrete Research, 1994, **24**, 1033.

76. C. Duran Atiş, C. Bilim, Ö. Çelik, O. Karahan, Influence of activator on the strength and drying shrinkage of alkali-activated slag mortar, Construction and Building Materials, 2009, **23**, 548.

77. J. Escalante-García, A.F. Fuentes, A. Gorokhovsky, P.E. Fraire-Luna, G. Mendoza-Suarez, Hydration products and reactivity of blast-furnace slag activated by various alkalis, Journal of American Ceramic Society, 2003, **86**, 2148.

78. S.A. Bernal, R. San Nicolas, J.L. Provis, R. Mejía de Gutiérrez, J.S.J. van Deventer, Natural carbonation of aged alkali-activated slag concretes, Materials and Structures, 2013, **47**, 693.

79. V.D. Glukhovsky, Ancient, modern and future concretes, in: First International Conference on Alkaline Cements and Concrete, Kiev, Ukraine, 1994: p. 1–8.

80. A. Palomo, A. Fernández-Jiménez, G. Kovalchuk, Some key factors affecting the alkali activation of fly ash, in: 2nd Int. Symp. Non-Traditional Cement and Concrete, Czech Republic, 2005.

81. P. Duxson, S.W. Mallicoat, G.C. Lukey, W.M. Kriven, J.S.J. van Deventer, The effect of alkali and Si/Al ratio on the development of mechanical properties of metakaolin based geopolymers, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2007, **292**, 8.

82. I. García-Lodeiro, A. Palomo, A. Fernández-Jiménez, An overview of the chemistry of alkali-activated cement-based binders, in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing series in civil and structural engineering, 2014.

83. M. Criado, A. Fernández-Jiménez, A. Palomo, I. Sobrados, J. Sanz, Effect of the SiO_2/Na_2O ratio on the alkali activation of fly ash. Part II: ^{29}Si MAS-NMR Survey, Microporous and Mesoporous Materials, 2008, **109,** 525.

84. M. Criado, The corrosion behaviour of reinforced steel embedded in alkali-activated mortar, in: F. Pacheco-Torgal, J.A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing series in civil and structural engineering, 2014.

85. T. Bakharev, J. Sanjayan, Y.-B. Cheng, Resistance of alkali-activated slag concrete to acid attack, Cement and Concrete Research, 2003, **33**, 1607.

86. N. De Belie, M. Debruyckere, D. Van Nieuwenburg, B. De Blaere, Attack of concrete floors in pig house by feed acids: influence of fly ash addition and cementbound surface layers, Journal of Agricultural Engineering Research, 1997, **68**, 101.

87. A. Terzic, Z. Radojevic, L. Milicic, L. Pavlovic, J. Stojanovic, High-temperature concrete binders based on fly ash, Romanian Journal of Materials, 2013, **43**, 269.

87. P.M. Gifford, J.E. Gillott, Freeze-thaw durability of activated blast furnace slag cement concrete, ACI Materials Journal, 1996, **93**, 242.

88. M. Torres-Carrasco, M. Tognonvi, A. Tagnit-Hamou, F. Puertas, Durability of alkali-activated slag concretes prepared using waste glass as alternative activator, ACI Materilas Journal, 2015, **112**, 791.

89. E. Najafi, A. Allahverdi, J.L. Provis, Efflorescence control in geopolymer binders based on natural pozzolan, Cement and Concrete Composites, 2012, **34**, 25.

90. F. Škvára, L. Kopecký, L. Myšková, V.Í.T. Šmilauer, L. Alberovská, L. Vinšová, Aluminosilicate polymers - Influence of elevated temperatures, efflorescence, Ceramics-Silikáty, 2009, **53**, 276.

91. T. Bakharev, J.G. Sanjayan, Y.-B. Cheng, Sulfate attack on alkali-activated slag concrete, Cement and Concrete Research, 2002, **32**, 211.

92. V.D. Glukhovsky, V. Pakhomow, Slag alkaline cements and concretes, Budivelinik Publish, Kiev, Ukraine, 1978.

93. V. Glukhovsky, G. Rostovskaja, G. Rumyna, High strength slag-alkaline cements, in: 7th Int. Congr. Chem. Cem, Paris, 1980: p. 164–168.

94. A. Palomo, M.T. Blanco-Varela, M.L. Granizo, F. Puertas, T. Vazquez, M.W. Grutzeck, Chemical stability of cementitious materials based on metakaolin, Cement and Concrete Research, 1999, **29**, 997.

95. A. Fernández-Jiménez, I. García-Lodeiro, A. Palomo, Durable characteristics of alkali activated fly ashes, Journal of Materials Science, 2007, **42**, 3055.

96. F. Skvara, T. Jilek, L. Kopecky, Geopolymer materials based on fly ash, Ceramics-Silikáty, 2005, **49**, 195.

97. M. Alexander, A. Bertron, N. De Belie, Performance of Cement-Based Materials in aggressive Aqueous environments, State-of-the-Art Report, RILEM TC 211 - PAE, Series: RILEM State of the Art Reports, Springer, New York, USA, 2013.

98. A. Fernández-Jiménez, A. Palomo, Propiedades y aplicaciones de los cementos alcalinos, Revista Ingeniería de la Construcción, 2009, **24**, 213.

99. C. Varga, M.M. Alonso, R. Mejía de Gutierrez, J. Mejía, F. Puertas, Decalcification of alkali-activated slag pastes. Effect of the chemical composition of the slag, Materials and Structures, 2014, **48**, 541.

100. E. Douglas, A. Bilodeau, V.. Malhotra, Properties and durability of alkali-activated slag concrete, ACI Materials Journal, 1992, **89**, 509.

101. C. Shi, Strength, pore structure and permeability of alkali-activated slag mortars, Cement and Concrete Research, 1996, **26**, 1789.

102. S. A. Bernal, R. Mejía de Gutiérrez, J.L. Provis, Engineering and durability properties of concretes based on alkali-activated granulated blast furnace slag/metakaolin blends, Construction and Building Materials, 2012, **33**, 99.

103. H. Kukko, R. Mannonen, Chemical and mechanical properties of alkali-activated blast furnace slag (F-concrete), Nordic Concrete Federation, 1983, 1.

104. J. Deja, J. Malolepszy, G. Jaskiewicz, Influence of chloride corrosion on durability of reinforcement in the concrete, in: V.M. Malhotra (Ed.), 2nd Int. Conf. Durab. Concr., American Concrete Insitute, Montreal, Canada, 1991: p. 511–521.

105. J. Malolepszy, J. Deja, W. Brylicki, Industrial application of slag alkaline concretes, in: Proc. First International Conference on Alkaline Cement and Concrete, VIPOL Stock Company, Kiev, Ukraine, 1994: p. 989–1001.

106. M. Holloway, J.M. Sykes, Studies of the corrosion of mild steel in alkali-activated slag cement mortars with sodium chloride admixtures by a galvanostatic pulse method, Corrosion Science Journal, 2005, **47**, 3097.

107. J.S. Alcaide, E.G. Alcocel, F. Puertas, R.L.P. Garcés, Carbon fibre-reinforced, alkali-activated slag mortars, Materiales de Construcción, 2007, **57**, 33.

108. D.M. Bastidas, A. Fernández-Jiménez, A. Palomo, J. A. González, A study on the passive state stability of steel embedded in activated fly ash mortars, Corrosion Science, 2008, **50**, 1058.

109. A. Fernández-Jiménez, J.M. Miranda, J.A. González, A. Palomo, Steel passive state stability in activated fly ash mortars, Materiales de Construcción, 2010, **60**, 51.

110. S.A. Bernal, J. Provis, D. Brice, A. Kilcullen, P. Duxson, J.S.J. van Deventer, Accelerated carbonation testing of alkali-activated binders significantly underestimates service life: The role of pore solution chemistry, Cement and Concrete Research, 2012, **42**, 1317.

111. S.A. Bernal, J. Provis, B. Walkley, R. San Nicolas, J. Gehman, D. Brice, A. Kilcullen, P. Duxson, J.S.J. Van Deventer, Gel nanostructure in alkali-activated binders based on slag and fl y ash, and effects of accelerated carbonation, Cement and Concrete Research, 2013, **53**, 127.

112. M. Palacios, F. Puertas, Effect of Carbonation on Alkali-Activated Slag Paste, Journal of American Ceramic Society, 2006, **89**, 3211.

113. F. Puertas, M. Palacios, T. Vázquez, Carbonation process of alkali-activated slag mortars, Journal of Materials Science, 2006, **41**, 3071.

114. S.A. Bernal, R. San Nicolas, R.J. Myers, R. Mejía de Gutiérrez, F. Puertas, J.S.J. van Deventer, J.L. Provis, MgO content of slag controls phase evolution and structural changes induced by accelerated carbonation in alkali-activated binders, Cement and Concrete Research, 2014, **57**, 33.

115. M. Criado, A. Palomo, A. Fernández-Jiménez, Alkali activation of fly ashes. Part 1: Effect of curing conditions on the carbonation of the reaction products, Fuel, 2005, **84**, 2048.

116. G. Rostovskaja, The service properties of the slag alkaline concretes, in: Proceedings of the International Conference on Alkali Activated Materials, Prague, Czech Republic, 2007: p. 593–610.

117. X. Bien, X. Pu, Study on durability of solid alkaline AAS cement, in: P.V. Krivenko (Ed.), Proceedings of the 2nd International Conference on Alkaline Cement and Concrete, Kiev, Ukraine, 1999: p. 64–71.

118. F. Puertas, T. Amat, A. Fernández-Jiménez, T. Vázquez, Mechanical and durable behaviour of alkaline cement mortars reinforced with polypropylene fibres, Cement and Concrete Research, 2003, **33**, 2031.

119. T. Häkkinen, Durability of alkali-activated slag concrete, Nordic Concrete Research, 1987, **6**, 81.

120. F. Skavara, T. Jilek, L. Kopecky, Geopolymer materials based on fly ash, Ceramics-Silikáty, 2005, **49** (3), 195.

121. T.B. Husbands, P.G. Malone, L.D. Wakeley, Performance of Concretes proportioned with Pyrament Blended cement, U.S. Army corps of engineers construction productivity advancement research program, 1994.

122. B. Tailing, J. Brandstetr, Present state and future of alkali-activated slag concretes, in: Proc. 3th CANMET/ACI Int. Conf. Fly Ash, Silica Fume, Slag Nat. Pozzolans Concr., Trondheim, Norway, 1989: p. 1519–1546.

123. R. Mejía de Gutiérrez, J. Maldonado, S. Delvasto, F. Puertas, A. Fernandez-Jimenez, Durability of mortars made with alcali activated slag, in: Proc. 11th Int. Congr. Chem. Cem., Durban, South Africa, 2003: p. 1005–1012.

124. M. Palacios, Empleo de aditivos orgánicos en la mejora de las propiedades de cementos y morteros de escoria activada alcalinamente, Universidad Autónoma de Madrid, 2006.

125. A. Cornejo, C. Leiva, L.F. Vilches, Properties of fly ash and metakaolín based geopolymer panels under fire resistance tests, Materiales de Construcción, 2015, **65**, e059.

126. A. Buchwald, M. Hohmann, K. Posern, E. Brendler, The suitability of thermally activated illite/smectite clay as raw material for geopolymer binders, Applied Clay Science, 2009, **46**, 300. .

127. H. Xu, J.S.J. Van Deventer, The geopolymerisation of alumino-silicate minerals, International Journal of Mineral Processing, 2000, **59**, 247.

128. M. Moesgaard, S.L. Poulsen, D. Herfort, M. Steenberg, L.F. Kirkegaard, J. Skibsted, Y. Yue, Hydration of blended portland cements containing calcium-aluminosilicate glass powder and limestone, Journal of American Ceramic Society, 2012, **95**, 403.

129. M. Moesgaard, D. Herfort, M. Steenberg, L.F. Kirkegaard, Y. Yue, Physical performances of blended cements containing calcium aluminosilicate glass powder and limestone, Cement and Concrete Research, 2011, **41**, 359.

130. M. Cyr, R. Idir, T. Poinot, Properties of inorganic polymer (geopolymer) mortars made of glass cullet, Journal of Materials Science, 2011, **47**, 2782.

131. R. Idir, M. Cyr, A. Tagnit-Hamou, Pozzolanic properties of fine and coarse color-mixed glass cullet, Cement and Concrete Composites, 2011, **33**, 19.

132. L. Reig, M.V. Borrachero, J.M. Monzó, H. Savastano, M.M. Tashima, J. Payá, Use of ceramic sanitary waste as an alternative for the development of new sustainable binders, in: 15th Int. Conf. Non - Conv. Mater. Technol. NOCMAT, Brazil, 2016: p. 172–180.

133. E.A. Caicedo Casso, R. Mejía de Gutiérrez, M. Gordillo Suárez, J. Torres Agredo, Reutilización de un residuo de la industria petrolera (FCC) en la producción de elementos constructivos, Ingeniería y Universidad, 2015, **19** (1), 135.

134. L. Soriano, J. Payá, J. Monzó, M.V. Borrachero, M.M. Tashima, High strength mortars using ordinary Portland cement–fly ash–fluid catalytic cracking catalyst residue ternary system (OPC/FA/FCC), Construction and Building Materials, 2016, **106**, 228.

135. M.M. Tashima, J.L. Akasaki, J.L.P. Melges, L. Soriano, J. Monzó, J. Payá, M.V. Borrachero, Alkali activated materials based on fluid catalytic cracking catalyst residue (FCC): Influence of SiO$_2$/Na$_2$O and H$_2$O/FCC ratio on mechanical strength and microstructure, Fuel, 2013, **108**, 833.

136. T.H.A. Al-Saadi, A. Badanoiu, S. Stoleriu, G. Voicu, Effect of alkaline activator on the main properties of geopolymers based on cullet glass and red mud, Romanian Journal of Materials, 2015, **45**, 138.

137. F. Puertas, J.J. Torres, M. Torres-Carrasco, C. Varga, Procedimiento para la fabricación de cementos alcalinos a partir de residuos vítreos urbanos e industriales, PCT/ES2012/0704408, 2012.

138. M. Torres-Carrasco, J.G. Palomo, F. Puertas, Sodium silicate solutions from dissolution of glass wastes: Statistical analysis, Materiales de Construcción, 2014, **64** (314), e014.

139. F. Puertas, M. Torres-Carrasco, Use of glass waste as an activator in the preparation of alkali-activated slag. Mechanical strength and paste characterisation, Cement and Concrete Research, 2014, **57**, 95.

140. M. Torres-Carrasco, F. Puertas, Waste glass in the geopolymer preparation. Mechanical and microstructural characterisation, Journal of Cleaner Production, 2015, **90**, 397.

141. S.A. Bernal, E.D. Rodríguez, R. Mejia de Gutiérrez, J.L. Provis, S. Delvasto, Activation of metakaolin/slag blends using alkaline solutions based on chemically modified silica fume and rice husk ash, Waste and Biomass Valorization, 2011, **3**, 99.

142. J.M. Mejía, R. Mejía de Gutiérrez, F. Puertas, Rice husk ash as a source of silica in alkali-activated fly ash and granulated blast furnace slag systems, Materiales de Construcción, 2013, **63**, 361.

143. E.D. Rodríguez, S. A. Bernal, J.L. Provis, J. Paya, J.M. Monzo, M.V. Borrachero, Effect of nanosilica-based activators on the performance of an alkali-activated fly ash binder, Cement and Concrete Composites, 2013, **35**, 1.

****

MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS

Process optimisation, de-bottlenecking, production maximisation and troubleshooting, 24 - 25 April 2017, London, UK

Global CemProcess is the new conference and exhibition for the cement industry that looks at process optimisation, de-bottlenecking, production maximisation and troubleshooting. With over 2500 cement plants around the world, many of them in sold-out or in hyper-competitive markets, the drive for each additional tonne of production and for process efficiency is ever-more important.

Contact: http://www.globalcement.com/conferences/global-cemprocess/introduction

****