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New cements for the 21st century: The pursuit of an alternative to Portland cement

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ABSTRACT

Preparation of this article entailed authors analyzing the contents of quite a number of papers, although the main objective *was never to review the state of the art* of new cements. Rather authors intend to discuss why they believe alkaline activated cement can be positioned at the epicentre of a new and necessary transition from today's Portland cement to the new cements of the future. A brief history of alkaline cements serves as an introduction to the technology itself. The interest roused around calcium sulfoaluminate-based cements is also reviewed, albeit summarily. The greater part of the article focuses, however, on alkaline cements which are classified into five categories. The fundamental chemical and structural characteristics of aluminosilicate-based alkaline cements are also described, and the key advances made in the understanding of synthetic gels are discussed. The paper ultimately finds *hybrid cements* to be technologically viable materials for contemporary construction.

Contents

1. Introduction

In certain closed ecosystems herds of herbivorous species graze on pastures unchecked. Under these conditions, the herd size gradually increases to a point at which it can no longer be sustained because of

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scarcity of food. The ensuing death rates drive the herd to near extinction. When only a few feeding individuals are left, the plant cover revives. The renewed abundance of pasture leads to a second round of herd growth and a new cycle. What remains to be seen is whether the human race can do more than emulate the behaviour of these irrational animals, and how long it would take the planet to recover from the sophisticated pillage perpetrated by humanity. Is it reasonable to wait and find out?

Despite the failure of the Copenhagen summit (December 2009), it is tempting to think that the twenty-first century still has time to prove its sensitivity to environmental issues. Certain political initiatives would appear to point in that direction. Most of the pressure brought to bear to enhance environmental protection, however, is due to global awareness among the public at large of the severity of the problems that will have to be faced in a not-so-distant future as a result of unsustainable development: i.e., poorly managed technologically speaking and highly skewed geographically speaking.

In this context, water management and air pollution (in terms of CO_2 concentration) are surely the areas where the need for action is most pressing, given the enormity of the consequences. Indeed, one item around which a certain consensus was reached at the Copenhagen climate summit held in late 2009 was the existence of key dates: the members of the international community agreed that the years 2020 and 2050 should be regarded to be points of reference on the climate change horizon and therefore milestones in the very difficult task of changing habits and lifestyles.

At the dawn of the industrial revolution in the mid-eighteenth century, the concentration of CO_2 in the air came to around 280 ppm. By the outbreak of World War II 200 years later, CO_2 levels had risen to 310 ppm, i.e., at a rate of 0.15 ppm per year (see Fig. 1). But between 1960 and 2000, CO_2 concentration soared from 315 ppm to 365 ppm in just 40 years (1.25 ppm/year) [1].

Globally, cement companies are producing nearly two billion tonnes/year of their product and emitting nearly two billion tonnes of CO_2 (or around 6 to 7% of the planet's total CO_2 emissions) in the process. At this pace, by 2025 the cement industry will be emitting CO_2 at a rate of 3.5 billion tonnes/year, more or less equal to the total emissions in Europe today (including the transport and energy industries) [2].

2. Portland cement: the debate around a historic material

In light of the foregoing facts, there would appear to be little doubt that alternative binders, less aggressive to the environment, must (at least partially) replace Portland cement. At the same time, however, serene reflection on the reasons why Portland cement has remained such a successful building material since its advent *in the nineteenth century* may prove to be helpful for the design of future strategies. Portland cement constitutes one of the most important technological advances in the history of humanity (thanks to this material the twentieth century saw the consolidation and acceleration of the reconstruction and even the redefinition of many of the world's major cities), but more than that, scientific studies of cement have contributed significantly to progress in materials science as a whole. *In short, in its long lifetime Portland cement has surmounted many (local and global) crises with sizeable economic, social and environmental consequences, a fact that should not be overlooked by those who predict the immediate demise of traditional cement.*

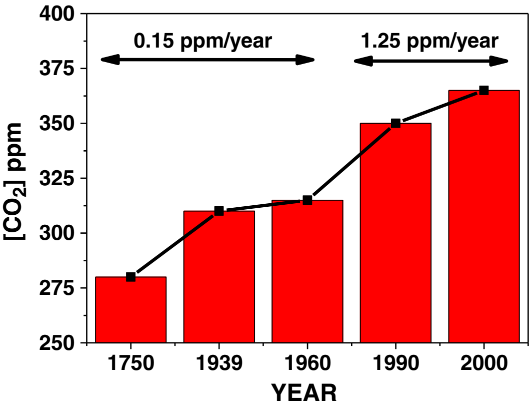

Fig. 1. Global CO_2 emissions.

To contribute to sustainable development, the cement industry (in general) has assumed two important challenges in recent years. The first is to reduce particle and gas emissions. The second involves assuming the Kyoto Protocol commitments, striving to reduce greenhouse gas emissions by establishing measures in the processing stage and implementing clean development mechanisms.

At the same time, throughout the twentieth century, the number of scientific papers on cements and derived materials (mortars, concretes, and other cementitious materials) has not only risen steadily, but it has done so at a brisk pace. And more importantly, the quality of publications (measured in terms of the number of citations) has undergone exponential growth.

It is no coincidence that this rise in the number and quality of articles has concurred with a period of exceptional cement industry strength. This would appear to imply that a radical change in the future of binders for construction is only possible if all the actors involved in this broad area of work (scientific community, industry, and users) are fully committed to the endeavour.

At the same time, however, research is tantamount to transgression. In other words, conducting research means accepting that there is no such thing as absolute truth. Consequently, the admission that other cements are possible is a logical outcome of this simple approach to scientific activity.

The international scientific community began to address the environmental problems associated with Portland cement manufacture some time ago; consequently, scientists have been working on a design for new binders for many years now. In this context, the 13th International Congress on the Chemistry of Cement may provide a forum from which scientists and cement manufacturers can drive the “change to a new sustainable model” through scientific discussion of the technical and economic imperatives. The authors of this paper firmly believe that the course has been clearly charted and that all that remains to be done is define a formula to ensure a smooth transition from the manufacture of Portland cement to the definition of the cement of the future, whatever that cement may be.

3. Calcium sulfoaluminate cements

Calcium sulfoaluminate (CSA) cements were developed by the China Building Materials Academy in the 1970s, with the intention of manufacturing self-stressed concrete pipes to capitalise on the expansive properties of this material. These cements were produced by adding gypsum to CSA clinkers, which consist mainly of $C_4A_3\hat{S}$ (ye'elimite), belite and ferrite. Normally, 15 to 25 wt.% of gypsum is ground with the clinker to attain optimum setting time, strength development and volume stability [3]. The temperatures for the production of CSA clinkers range from 1200 to 1300 °C, i.e., about 200 °C lower than needed to manufacture Portland cement clinkers. The amount of limestone required to produce CSA cements is considerably smaller than needed for Portland cement. The specific CaO requirement (referred to unit mass of the compound) for $C_4A_3\hat{S}$ synthesis is 0.368, i.e. 50%, 56%, 59% and 80% of the unit mass needed to form C_3S, C_2S, C_3A and C_4AF, respectively [4]. Furthermore, the high porosity of CSA clinkers facilitates grinding [5]. The lower limestone content and fuel consumption reduce the CO_2 emissions to around half the values associated with Portland clinker. *SO_2 emissions are significantly higher, however.*

The resulting blend hydrates and gains strength rapidly when mixed with water as follows:

In the absence of calcium hydroxide:

$$C_4A_3\hat{S} + 2C\hat{S}H_2 + 34H \rightarrow C_3A\hat{S}_3H_{32} + 2AH \tag{1}$$

In the presence of calcium hydroxide:

$$C_4A_3\hat{S} + 8C\hat{S}H + 6CH_2 + 74H \rightarrow 3C_3A\hat{S}_3H_{32} \tag{2}$$

The ettringite produced in reaction 1) exhibits expansive behaviour that can be exploited to produce special binders such as shrinkage-resistant and self-stressing cements [6]. The ettringite generated in the presence of lime (Reaction 2), while not expansive, raises the early age strength of the cement significantly [7].

The hydrated paste matrix consists mainly of a crystalline phase, ettringite, and lesser amounts of AFm, C-S-H and gibbsite. Rapid hardening CSA cements are characterised by high impermeability and chemical resistance, low drying shrinkage and low alkalinity. Ettringite decomposition is unlikely to impact performance significantly except in very hot and dry environments. The Ca/Si ratio in the C-S-H is ≈1.5 and the gel is considerably more crystalline than the C-S-H in Portland cement. CSA cements are also far more sensitive to temperature, w/c ratios, pozzolan replacements and the like than Portland cement. At summer temperatures (over 27–29 °C), non-retarded CSA concrete with a w/c of 0.35 can set in as little as 5 min. With a suitable retarder, that time can be extended to 15 to 20 min of workability and a few more minutes before setting takes place. Superplasticisers, especially polycarboxylates, and viscosity modifiers are as effective with CSA as they are with Portland cement. In the former, the pH value is only 10.5–11, whereas ordinary Portland cement (OPC) has a pH of 13, making it 100 to 300 times more alkaline than CSA cement. Such low alkalinity naturally minimises the likelihood of the onset of the alkali aggregate reaction in CSA concrete. This is important when glass is used in the mix and the hardened material is exposed to moisture.

Limestone, bauxite and gypsum are the main raw materials involved in the manufacture of CSA cements. Replacing some of these natural materials with industrial waste and by-products such as blast furnace slag, fly ash from both traditional combustors and fluidised bed reactors, red mud, phosphogypsum and flue gas desulfurisation gypsum is a challenge of utmost social and technical significance [8–12]. The substitution of Al_2O_3-rich by-products for an expensive raw material such as bauxite is a particularly attractive objective.

In any event, *at this writing*, the authors of the present article do not believe that CSA cements have the potential to lead the transition to the cements of the future. Their view of alkaline cements, by contrast, is entirely different.

4. Alkaline cements as an alternative in the transition

The first use of alkalis as a component of cementitious materials dates back to 1930, when Kuhl studied the setting behaviour of mixtures of slag ground to a powder and a KOH solution. Since that time many studies have been conducted on the role that alkalis may play in potential cementitious systems. One early milestone was reached in 1940, when Purdon conducted the first extensive laboratory study on clinkerless cements consisting of slag and NaOH [13].

In 1967 Glukhovsky made a significant breakthrough in the understanding and development of binders from low calcium or calcium-free aluminosilicate (clay) and alkaline metal solutions [14]. He called these binders "soil cements" and the respective concretes "soil silicates". Glukhovsky classified binders into two groups, depending on the composition of the starting materials: alkaline binding systems $Me_2O–Al_2O_3–SiO_2–H_2O$ and "alkali–alkaline-earth" binding systems $Me_2O–MO–Al_2O_3–SiO_2–H_2O$ (where Me = Na, K,… and M = Ca, Mg,…).

This set off extensive research on and developments in alkali-activated cement and concrete, although both the intensity and direction of this type of research were haphazard and subject to contemporary scientific and technological needs.

Initially, most alkali activation effort focused on the materials classified by Glukhovsky in group 2 (alkali–alkaline-earth binding systems $Me_2O–MO–Al_2O_3–SiO_2–H_2O$); Scandinavian F-cements [15,16] and alkali-activated blended cements [17–21] are good examples of research in this regard.

The last ten years, however, have seen exponential growth in research related to Glukhovsky's first group of materials (alkaline binding systems: $Me_2O–Al_2O_3–SiO_2–H_2O$). And although in 1982 Davidovits produced binders by mixing alkalis with a burnt mix of kaolinite, limestone and dolomite [19] (calling the binders geopolymers while also generating a number of trademarks such as Pyrament, Geopolycem and Geopolymite), these cements have only recently began to acquire true technological significance.

At the same time the gradually growing knowledge base on alkali–activated cements and concretes has cast light not only on their benefits in terms of low energy costs and environmental impact, but also their good mechanical performance [20–24] and long durability [14–30].

Mention should also be made of a series of recent publications of particular significance in the area of alkaline cements. The most prominent include: a special issue of J. Mat. Sci (2007) [31] with a fair number of articles specifically addressing the alkali activation of aluminosilicates (Glukhovsky's first group); a book by Shi, Roy and Krivenko [32] covering many aspects of alkali-activated cement and concrete (most in connection with Glukhovsky's second group of materials); a book by Davidovits [33]; and lastly a book edited by Provis and Van Deventer [34] with articles by several authors, also focusing on Glukhovsky's first group of materials.

4.1. Classification and characteristics of alkali-activated cements

Alkali-activated cements usually consist of two components: a cementitious component and alkaline activators. Caustic alkalis or alkaline salts are normally used as alkaline activators in alkali-activated cements and concretes. A variety of industrial by-products and waste as well as a number of aluminosilicate raw materials have been used as the cementitious components in alkali-activated cements and concretes. These materials include granulated blast furnace slag, granulated phosphorus slag, steel slag, coal fly ash, volcanic glass, zeolite, metakaolin, silica fume and non-ferrous slag.

Using the composition of the cementitious component(s) as a criterion, alkali-activated cements can be classified into five categories [32,35]:

(1) alkali-activated slag-based cements
(2) alkali-activated pozzolan cements
(3) alkali-activated lime-pozzolan/slag cements
(4) alkali-activated calcium aluminate blended cements
(5) alkali-activated Portland blended cements (hybrid cements)

A brief description of the main characteristics of these five categories follows.

4.1.1. Alkali-activated slag-based cements

The following cementitious systems can be included in this category:

- alkali-activated blast furnace slag cement

- alkali-activated phosphorus slag cement
- alkali-activated blast furnace slag-fly ash
- alkali-activated blast furnace slag-steel slag
- alkali-activated blast furnace slag-MGO
- alkali-activated blast furnace slag-based multiple component cement

Alkali-activated blast furnace slag cement was, of the above, the system most widely researched in the 1980s and 90s. The major features of alkali-activated blast furnace slag cement are summarised below.

(1) The performance of alkali-activated slag cement and concrete is governed primarily by the nature of the slag and the nature and dosage of the activator(s) used. Properly designed alkali-activated slag cement and concrete exhibit much higher strength than conventional Portland cement and concrete, as well as improvements in other properties.
(2) Depending on the nature of the activator, alkali-activated slag cement paste and mortars may be more or less porous than Portland cement pastes and mortars. Porosity and strength are not related in the same way in alkali-activated slag cement as they are in Portland cement.
(3) In moist conditions, alkali-activated slag cement and concrete are less permeable to water and chlorides and more resistant to corrosive media such as acids, sulphates or chlorides than conventional OPC and concrete.
(4) Older carbonate- or carbonate/hydroxide-activated slag-concrete blends (up to 35 years) have acceptable carbonation rates [36]. Moreover, when an alkali-reactive aggregate is used, alkali-activated concrete may have expansive properties.
(5) The addition of the commercial water reducers or superplasticisers designed for Portland cements have a limited or nil effect on alkali-activated slag cement paste and mortar workability and setting times. SRA has been known to reduce shrinkage by up to 85 and 50% when alkali-activated slag mortar specimens are cured at relative humidities of 99 and 50%, respectively [37].
(6) The main reaction products formed in all cases is a C-S-H gel containing Al in its structure [38]. No free $Ca(OH)_2$ appears. Consequently, hardened alkali-activated slag paste and concrete resist fire more effectively than Portland cement paste and concrete. The Ca/Si ratio and Al content in the gel depend on the nature of the activator, the chemical composition of the cementitious components and curing conditions (time and temperature), however.

4.1.2. Alkali-activated pozzolan cements

As noted above, in the late 1950s and early 60s, Glukhovsky discovered the principles underlying the production of hydraulic binders by alkali-activating a number of aluminosilicate materials [14], which he called “soil cements”. Krivenko [39] later called these binders “geocements”, to highlight the presence of natural mineral analogues in their hydration products and the similarities in the mechanisms governing the formation of these binders and natural geological materials. Davidovits [33] called these binders geopolymers because of their polymeric structure**.** Other names have been coined by other authors: hydroceramics (Grutzeck), inorganic polymers (van Deventer) and zeocements (Palomo). Alkali-activated pozzolan cements include the following cementitious systems:

- alkali-activated fly ash cement
- alkali-activated natural pozzolan cement
- alkali-activated metakaolin cement
- alkali-activated soda lime glass cement

Over the past decade, any number of papers has been published on alkali-activated pozzolans, especially alkali-activated fly ash cements and alkali-activated metakaolin binders. *The sections below address this group of cementitious materials in some detail, for the radical difference between their chemistry and Portland cement chemistry affords innovations that merit scholarly exploration.*

4.1.3. Alkali-activated lime-pozzolan/slag cements

Lime-pozzolan mortars were among the earliest building materials. A concrete slab uncovered in southern Galilee has shown that the invention of lime and lime-pozzolan concrete dates back to the Neolithic period (7000 BC), rather than to Greek and Roman times as formerly believed [40]. These materials were widely used by Roman masons to build aqueducts, arch bridges, retaining walls and buildings [41].

It was not until the 17th century that lime–Dutch trass mixtures began to be used in England. Such mixtures were also used extensively in Holland to build harbours and dykes [42]. In Iceland, mortars made of lime and volcanic ashes were used in the construction of many early stone buildings. These mortars were found to be very strong or rock-like and durable, with survival times of 90 to 400 years [43].

The nineteenth century invention of Portland cement led to a drastic reduction in the use of lime–pozzolan cements due to the faster setting and higher early age strength afforded by the new material. Nevertheless, with their low cost and long durability, lime–pozzolan cements continue to be attractive for some applications.

The addition of alkali activators, alkali sulphates in particular, to different systems has improved setting and strength development in lime–pozzolan cements. These alkali-activated lime–pozzolan/slag cementitious systems include:

- alkali-activated lime–natural pozzolan cement
- alkali-activated lime–fly ash cement
- alkali-activated lime–metakaolin cement
- alkali-activated lime–blast furnace slag cement

The main features of alkali-activated lime–pozzolan/slag cements are summarised below.

(1) Only alkali hydroxides and alkali sulphates can normally be used as activators.
(2) The use of alkaline activators can double or triple the strength of lime–pozzolan cements, especially at early ages.
(3) Alkali-activated lime–pozzolan/slag cements may still not be strong enough for structural uses. The main reaction product is a C-A-S-H gel, although a mixture of C-S-H and N-A-S-H gel may form in highly alkaline environments (research conducted at the Eduardo Torroja Institute [44,45] has shown that C-S-H and N-A-S-H gels are compatible in alkali-activated lime–metakaolin mixtures).

4.1.4. Alkali-activated calcium aluminate blended cement

Theoretically, all aluminosilicate materials can be activated by alkalis. Nonetheless, certain requirements must be met, including: i) high solubility in basic media; and ii) high availability of Al_2O_3 and SiO_2 in the medium. As a general rule, materials with a high reactive silica content are more plentiful than materials containing reactive alumina. In light of that fact, the possibility of using calcium aluminate cement (CAC) as a source of reactive alumina in the alkali activation of aluminosilicates has been the object of recent studies [46,47]. Three combinations were explored:

- alkali-activated metakaolin/CAC
- alkali-activated pozzolan/CAC
- alkali-activated fly ash/CAC

The main features of alkali-activated CAC blended cement are summarised below.

(1) Proportions of under 30% of CAC may be used as a source of reactive Al in the alkali activation of materials with low reactive alumina but high reactive silica contents.
(2) Under these conditions CAC does not undergo normal hydration. While it appears to form a metastable intermediate compound, no cubic or hexagonal hydrates or $Al(OH)_3$ have been detected in any of the materials studied.
(3) Under synthesis conditions, the Al and Ca present in the CAC are taken up into the N-A-S-H gel formed as the primary reaction product in the alkali activation of aluminosilicates materials. Depending on blend proportions and reaction conditions, two aluminium-rich gels are obtained: the majority N-A-S-H gel and a minority C-A-S-H product.

Aluminium plays a primary role in the formation of hydrated sodium aluminosilicate gel (N-A-S-H), particularly in the early phases of the reaction, for as the link between the silicon tetrahedra it initiates the condensation reactions**.** Although no definitive studies on how to enhance or reduce aluminium availability during the synthesis of these alkaline mineral polymers have been forthcoming, strength development in the final product has been shown to depend on the presence of a certain minimum quantity of reactive aluminium in the original system [46,47]. In these alkali-activated CAC blended cements, the calcium aluminate supplies tetrahedral aluminium and enhances the reactivity of the mixes; CAC may even contribute to mechanical strength.

4.1.5. Alkali-activated Portland blended cement: hybrid cements

This group of materials may well attract greater attention in the context of the cements of the immediate future. In fact, supplementary cementitious materials such as blast furnace slag, phosphorus slag, coal fly ash and natural pozzolans are widely used in the manufacture of blended cement or as a cement replacement in concrete (generally speaking, the use of these materials tends to lengthen setting times and lower early age strength in cement and concrete). Many researchers have shown that the addition of alkaline activators could enhance the potential pozzolanicity of such supplementary materials and improve the properties of the respective cementitious systems, especially at early ages. Many cementitious systems have now been studied, including:

- alkali-activated Portland blast furnace slag cement
- alkali-activated Portland phosphorus slag cement
- alkali-activated Portland Fly ash cement
- alkali-activated Portland blast furnace slag–steel slag cement
- alkali-activated Portland blast furnace slag–fly ash cement
- alkali-activated multiple components blended cements

This group of cements, here denominated hybrid cements, is addressed in greater detail in a specific section at the end of this article.

4.2. Alkaline activation of aluminosilicates. Fundamentals

Simply stated, the alkaline activation of a silicoaluminous material can be described as a mix of a liquid (with a very high alkali concentration) and a solid (with the suitable proportions of highly reactive silicate and aluminate) [48–53]. The solid and liquid can be mixed in variable proportions (with liquid:solid ratios ranging from 0.2 to 1.0), depending on the fineness of the solid material (the finer the material, the higher the water demand). The resulting paste can set and harden like a Portland cement (see Fig. 2).

Conceptually speaking, this process can be described in terms of a polymeric model similar to the schemes proposed for the reactions leading to the formation of certain zeolites: initially, the Al and Si dissolved in the medium react to form complex poly-hydroxy-silicoaluminate complexes [50–52]**.** The end product is an alkaline aluminosilicate hydrate (a $Na_2O{\cdot}Al_2O_3{\cdot}2SiO_2{\cdot}nH_2O$ type gel [N–A–S–H gel], also known in the literature as a geopolymer) with a three-dimensional structure that, on an atomic to nanometric scale, resembles zeolitic nanoscale structures [49,54–56].. Both the Al and the Si found in this product are tetrahedrally coordinated and the alkali (Na or K) that compensates for the electric charge generated by the substitution of Al^{3+} for Si^{4+} is housed in the voids in this three-dimensional framework. Terminal hydroxy groups are also found on the gel surface, although their presence has scant impact on microstructural development. The alkali activation of aluminosilicates is completely different from the chemical process involved in Portland cement hydration, where the main reaction product is a C–S–H-type calcium silicate gel ($CaO{\cdot}SiO_2{\cdot}nH_2O$).

From the standpoint of the reaction mechanisms, Glukhovsky observed as early as 1967 [14] that the alkaline component in these cementitious systems acted as a formative element in the nanostructure, with a fairly high uptake (3–20%, wt., calculated as Me_2O, where Me is Na or K). Taking the principles of the physical–chemical mechanics of solid bodies as a starting point, that author developed a model that suitably explains the mechanisms governing the formation of the three-dimensional structure of aluminosilicate alkaline cements. Briefly, the model describes a number of destruction–condensation transformations that take place in the starting solid. The series of units with an unstable structure initially formed subsequently gives rise to another series of thixotropic coagulation structures that ultimately condense to generate the hydrated products.

According to Glukhovsky, the stages comprising the alkaline activation reaction are as described below.

4.2.1. First stage: "destruction–coagulation"

This first disaggregation process entails the severance of the Me–O, Si–O–Si, Al–O–Al and Al–O–Si bonds in the starting material. Glukhovsky suggested that this disaggregation of the solid phase may be governed by the formation of complex unstable products whose origin lies in the change in the ionic strength of the medium prompted by the addition of electron donor atoms (the alkaline metals). The result is a redistribution of the electronic density around

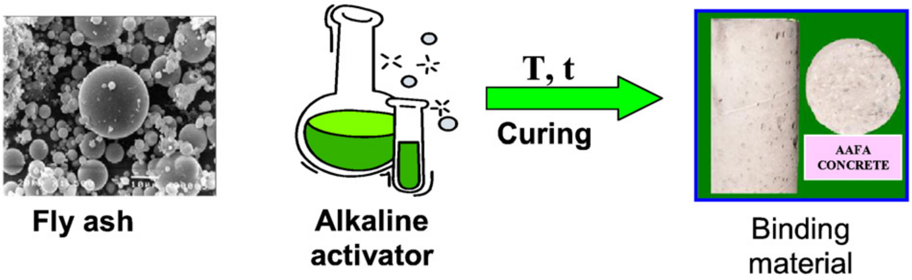

Fig. 2. Schematic description of the alkaline activation of fly ash.

the silicon atom, rendering the Si–O–Si bond more susceptible to rupture.

The presence of alkaline metal cations neutralises these anions, generating Si–O–Na$^+$ bonds, thereby hindering reaction reversibility. Moreover, the conditions created by the Si–O–Na$^+$ complexes, which are stable in alkaline media, are suitable for the transport of the reacting structural units and the development of the coagulated structure.

Since the hydroxy groups have the same effect on the Al–O–Si bond, the aluminates in the alkaline solution form complexes such as Al(OH)$_4^-$ or Al(OH)$_6^{3-}$, depending on the pH in the medium [57].

4.2.2. Second stage: "coagulation–condensation"

In this second stage, accumulation enhances contact among the disaggregated products, forming a coagulated structure where polycondensation takes place.

The polycondensation rate is determined by the state of the dissolved ions and the existence or otherwise of the conditions necessary for gel precipitation. Silicic acid condensation is therefore favoured at pH values in which the acid is slightly dissociated or in a molecular state. At pH>7, for instance, disaggregation of the Si–O–Si bond gives rise to Si(OH)$_4$-like hydroxylated complexes.

4.2.3. Third stage: "condensation–crystallisation"

The presence of particles from the initial solid phase, together with the appearance of microparticles resulting from condensation, favours product precipitation. The mineralogical composition of the initial phase, the nature of the alkaline component and the hardening conditions determine the qualitative and quantitative composition of the crystallised products.

In 2005, Fernández-Jiménez and Palomo proposed the graphic model for the microstructural development of alkaline aluminosilicate cements (based essentially on MAS-NMR and FTIR findings) depicted in Fig. 3. The model, which describes the stages in the alkaline activation of aluminosilicates in terms reminiscent of postulates on zeolite synthesis [54], is consistent with Glukhovsky's chemical description.

In the first step, the vitreous/amorphous component of the solid particles dissolves when it comes into contact with the alkaline solution (pH>10). This is the mechanism that governs the early stage solid particle dissolution, in which aluminates and silicates are released, probably as monomers (see Fig. 3, step 2). The dissolution rate depends on the pH of the medium and the possible presence of other system components.

The smaller molecules agglutinate to form larger molecules that precipitate in the form of a gel, in which some minor degree of structural order can be identified (polymer precipitation). According to NMR and FTIR data, the conditions prevailing in this stage favour the formation of an Al-rich metastable compound. The Si and Al tetrahedra initially bond together to form rings containing four secondary (usually alternating aluminium and silicon) tetrahedral units, i.e., S4-type secondary building units with a predominance of Q^4(4Al) units [52,54,55]. The cations that neutralise the electrical charge resulting from replacing a silicon with an aluminium tetrahedron are positioned in the gaps left in the structure (see Fig. 3, step 3).

The high aluminium content in this intermediate reaction product (denominated Gel 1, Si/Al ratio ≈1) may be explained by the higher concentration of Al^{3+} ions in the alkaline medium in the early hours of the process. Such higher concentration, in turn, can be attributed to the readier dissolution of aluminium than silicon, because Al–O bonds are weaker and hence more easily severed than Si–O bonds [49,51,55].

As the reaction progresses, more Si–O groups in the initial solid source dissolve, favouring the evolution of the initial Gel 1 (Al-rich phase) into a new Gel 2 (Si-rich phase, Si/Al≈2, see Fig. 3, step 4). This assertion is supported by the changes observed in the ^{29}Si NMR and FTIR spectra. The intensity of the NMR signals associated with slightly condensed structures (Q^4(4Al)) declines, while the intensity of the signals associated with the presence of closely condensed structures (Q^4(3Al) and Q^4(2Al)) grows [52,54], giving rise to D6R- and D8R-type structures [55]. Raising the Si/Al ratio considerably improves the mechanical properties of the aluminosilicate gels formed [32–52].

This three-dimensional order exists on the atomic to nanometric scale only, however. On the microstructural scale the main reaction product is an amorphous alkali aluminosilicate gel, (N–A–S–H gel), whose chemical composition varies slightly depending on the starting material, the type of alkaline activator used and the synthesis conditions.

This model was recently revised by Duxson et al. to include water in the reaction [32]. Amorphous aluminosilicates dissolve rapidly at high pH, quickly creating a supersaturated aluminosilicate solution. In concentrated solutions the result is the formation of a N–A–S–H gel, as

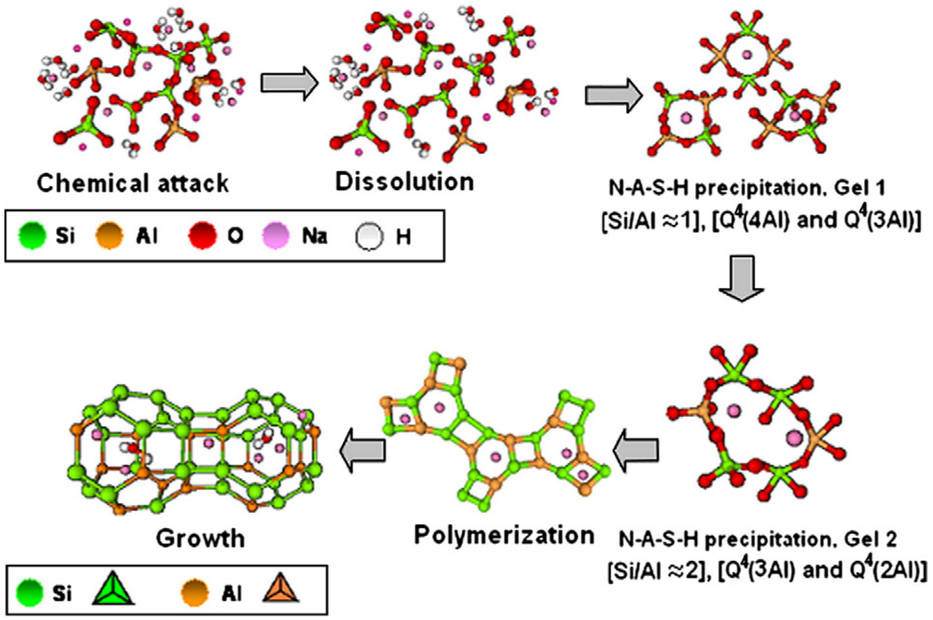

Fig. 3. Descriptive model for alkali activation of aluminosilicates.

the oligomers in the aqueous phase condense into large networks. The water nominally consumed during dissolution is released in the process. While water constitutes the reaction medium, it is found inside the gel pores. This type of gel structure is commonly referred to as biphasic, the phases being the aluminosilicate binder and water. These structural reorganisation processes determine the final composition of the N–A–S–H gel as well as the cement microstructure, two critical factors in the development of many physical properties of the resulting material.

4.3. Recent progress in the understanding of N–A–S–H gel

Iller [58,59], among others, pioneered silica and silicate colloid chemistry research. The fundamentals of silicic acid polymerisation in aqueous solutions established by that author laid the groundwork for the modern techniques used to produce highly concentrated yet stable silica gels and precipitates.

Indeed, sol–gel chemistry was a necessary preliminary in the development of mixed silica–alumina oxides with different Al/Si ratios. The properties of the oxides obtained are highly dependent upon sol–gel synthesis parameters, including the type and concentration of precursor molecules, solvent used, temperature, amount of water available for hydrolysis, and pH [60,61].

The most recent advances in the understanding of N–A–S–H gel are the result of two very different lines of research: a) application of new characterisation techniques and tools to the study of alkaline cements prepared with “industrial” prime materials; and b) study of pure gels synthesised with chemical products (laboratory reagents).

The present article discusses a number of pertinent details in the study of laboratory-synthesised gels, for this line of work, while explored much less intensely by scientists, opens up promising prospects for the development of new cementitious materials.

The working hypothesis is simple:

A glance at the ternary phase diagram for $CaO–Al_2O_3–SiO_2$ [62] suffices to realise that this system can make a substantial contribution to materials science applied to construction cement. This diagram is the sum of three binary systems: the $CaO–SiO_2$ system (with the calcium silicates present in Portland cement); the $CaO–Al_2O_3$ system (with the calcium aluminates present in aluminous cement); and the $SiO_2–Al_2O_3$ system (with the alkaline aluminosilicates present in alkaline cements). There is every indication that the uptake of a fourth element (such as alkalis) into this ternary system may lead to many innovations in the development of new cements (see Fig. 4). Hence the importance of deeply researching the quaternary phase diagram $CaO–Al_2O_3–SiO_2–Na_2O$; that is to say, pure phases and inter-phase compatibility.

Ikeda [63] and Fernandez–Jimenez et al. [64] used the sol–gel procedure to synthesise N–A–S–H and K–A–S–H gels (similar to the products of metakaolin and fly ash alkaline activation). The gels synthesised at a low pH do not polycondense, but are mere co-precipitates, for at acid pH the particles grow as a result of the combined effect of aggregation and polymerisation [63–65]. The ^{27}Al NMR-MAS spectra for the gels prepared at low pH values contain resonances for both tetrahedrally and octahedrally coordinated Al (see Fig. 5(a), spectrum A). Hence these gels may be biphasic. Octahedrally coordinated Al is associated with the formation of gibbsite and hydrated gel-like Al oxyhydroxide pseudobohemite [65]. In contrast, the gel prepared at high pH values shows predominantly tetrahedral peaks (see Fig. 5a, spectrum B). The higher the pH, the greater is the role of polymerisation in particle growth.

For pH values of over 7, polymerisation is in fact the prevailing mechanism and $[SiO_2(OH)_2]^{2-}$ the predominant chemical species during hydrolysis. The higher the pH, the higher the solubility of silicate ions; consequently, the reaction rate can be expected to rise as alkalinity increases. Under these conditions, particles grow into colloids as a result of Ostwald ripening [66], in which large particles increase in size at the expense of smaller grains [58,59] to form a sol. The colloids themselves form cross-links, generating 3-D structures. In other words, at basic pH, all the condensed species are ionised. With the mutual repulsion generated, particles grow more as a result of the addition of monomers to the more condensed species than through particle aggregation, due to the repulsive forces acting on the very small particles (nanometric species).

^{29}Si NMR-MAS data confirm the foregoing. The ^{29}Si spectra for the gel prepared at low pH and a low K_2O content (Gel A, Fig. 5(b)) are characterised by two major tetrahedral peaks; the sharper of the two is centred at around −78 ppm and the broader at about −99 ppm. In contrast, the gel prepared at high pH values with a high K_2O content (gel B) is characterised by one broad ^{29}Si peak centred at around 85 ppm. The −78 ppm peak is assigned to Q^1 units, an indication of the presence of dimers. The broad peak at -98 ppm is most likely due to a combination of resonances such as Q^3+Q^4 and a small amount of Q^2. The broad peak at −85 ppm would be generated by a combination of Q^1+Q^2 units with a small amount of Q^3. The usual position of Q^4 (around −110 ppm) is known to be strongly influenced by the uptake of $[AlO_4]$ into $[SiO_4]$, however [67]. Consequently, the broad resonances at -85 ppm probably reflect a predominance of Si(4Al) units. This is consistent with the signal detected in alkali-activated metakaolin or fly ash in the early stages of the activation reaction [51,52,68–70], associated with an Al-rich gel.

Another relevant development in connection with gels synthesised at alkaline pH is the Al_2O_3/K_2O ratio, which remains constant and near to 1 (see the chemical composition of Gel B in Fig. 5). The reason is that certain other ions must be taken up in the structure to offset the electrical imbalance generated when Al^{3+} ions replace Si^{4+} ions in the polymer. If all the aluminium added were included in the system, the structure would have to be neutralised with the uptake of an equal number of potassium ions.

More recently, Garcia-Lodeiro et al. [71] not only perfected the procedure for synthesizing N–A–S–H gel, but studied its characterisation

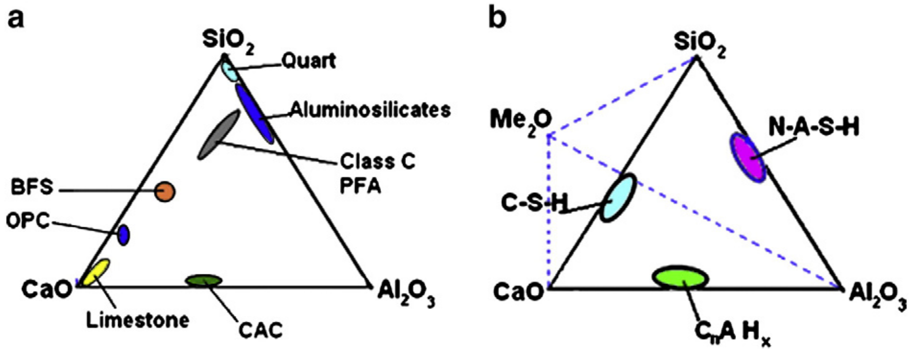

Fig. 4. (a) Anhydrous cementitious materials in the $CaO–SiO_2–Al_2O_3$ system; (b) hydration products with cementitious properties in the $Me_2O–CaO–SiO_2–Al_2O_3.H_2O$ system.

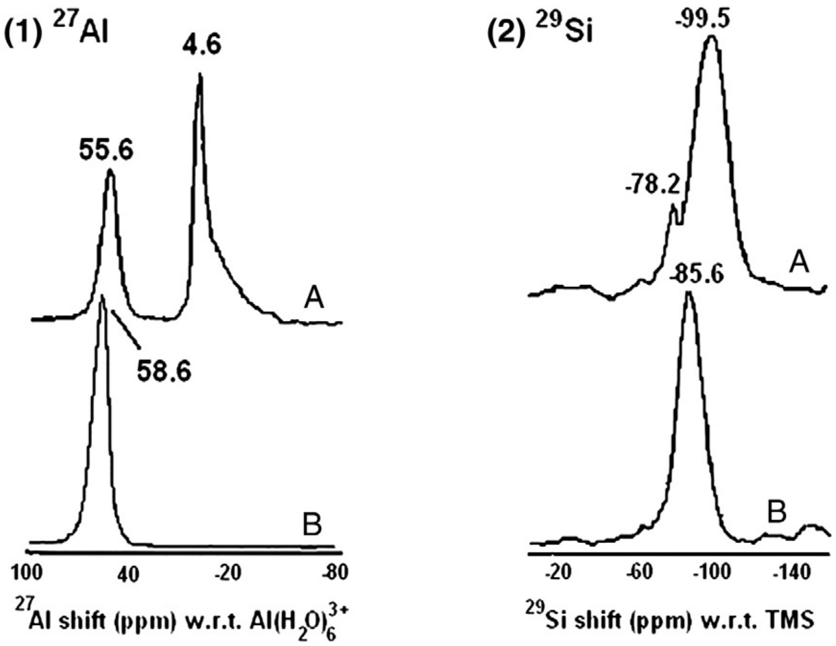

Fig. 5. Selected gel MAS-NMR spectra, (1) ^{27}Al and (2) ^{29}Si; *Gel A*, pH = 2.9, $[SiO_2] = 77.80$ (mol%); $[Al_2O_3] = 20.58$ (mol%) and $[K_2O_3] = 1.63$ (mol%); *Gel B*, pH = 12.8, $[SiO_2] = 60.26$ (mol%); $[Al_2O_3] = 19.75$ (mol%) and $[K_2O_3] = 19.99$.

in considerable depth. These authors also deployed the sol–gel procedure to synthesise N–A–S–H gels with different Si/Al ratios. Specifically, N–A–S–H gels with Si/Al ratios of 1 (*Gel 1*) and 2 (*Gel 2*) were prepared at pH values greater than or equal to 12.5. These gels were chosen to exemplify the two models of gels observed in the alkali activation of metakaolin and fly ash, as described in item 3.1, Fig. 3. The solutions were placed in an ice bath (temperature between 2 and 5 °C) and stirred constantly during synthesis in a controlled N_2 atmosphere to prevent possible carbonation.

The FTIR spectra for N–A–S–H gels obtained in this study were similar to the spectra generated by gels prepared by alkali activating fly ash and metakaolin [48,55,72,73]. The main band at 1007 cm^{-1} (see Fig. 6, which shifted to a higher frequency in *Gel 2* (G2), whose target Si/Al was higher) was attributed to the asymmetric stretching vibrations generated by T–O–T bonds (where T is Si or Al).

The rest of the bands characteristic of N–A–S–H gels were also present: the 560-cm^{-1} band attributed to tetrahedral aluminium stretching bands, and bands in the 690–440 cm^{-1} interval attributed to the bending vibrations generated by Si–O–Si/Si–O–Al bonds.

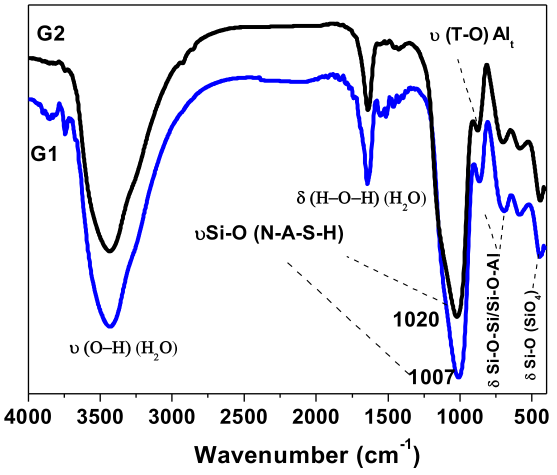

Fig. 6. FTIR spectra for *Gel 1* (G1) and *Gel 2* (G2) prepared with 0.1-M and 0.2-M sodium silicate solutions and a 0.1-M aluminium nitrate solution. A 10-M solution of NaOH was also used in gel synthesis to regulate the pH (synthesis pH was consistently greater than or equal to 12.5).

Fig. 7 shows the ^{29}Si NMR spectra for gel G1 and gel G2 with target $Si/Al \approx 1$ and 2, respectively. The silicon spectra for both gels contained a wide, asymmetric signal around −86.0 ppm for G1 and 88 ppm for G2. Such wide and poorly defined signals are consistent with cross-linked aluminosilicates, indicating a low degree of crystallinity and the probable presence of a mix of components. The shift toward more negative values in G2 was consistent with the higher silicon content in this gel [67]. Application of the Engelhardt and Lee deconvolution model [67,74] for ^{29}Si NMR interpretation revealed the presence of several components: the −72.6 ppm component in gel G1 (−76.8 ppm for G2) was associated with Q^0 units (monomers) and the remaining resonances with $Q^4(mA1)$ units ($m = 0, 1,2, 3,4$).

The sole signal on the ^{27}Al spectra (Fig. 8(a)) for the two gels, at around +57 ppm, was associated with tetrahedral aluminium [51,67]. The chemical shift in the NMR line is characteristic of Al surrounded by four SiO groups, $Al(OSi)_4^{55}$. Taken together with the ^{29}Si spectra, these NMR findings indicated that the Al atoms were homogeneously distributed in the gels, giving rise to the main Si $(OAl)_4$, $Si(OAl)_3(OSi)$ and $Si(OAl)_2(OSi)_2$ assignment [75].

The ^{23}Na spectra (Fig. 8 (b)) for both gels exhibited only one signal at around −9 ppm further to the literature [67], this signal was attributed to sodium cations that balance the charge generated by the substitution of aluminium for silicon. The position of the signal also indicated that the sodium was partially hydrated [65]. The fact that the position of this signal was the same for gels synthesised with different Si/Al ratios is consistent with the findings reported by Duxson et al., who observed that the chemical shift and shape of this resonance remained unchanged in sodium aluminosilicates synthesised with different Si/Al ratios [53].

5. Hybrid alkaline cements: prospects

At this writing, immediate global replacement of Portland cement by any of the possible alkaline cements (or any other binder) is virtually impossible. Technical issues around alkaline cements such as paste, mortar and concrete rheology or the supply of universally

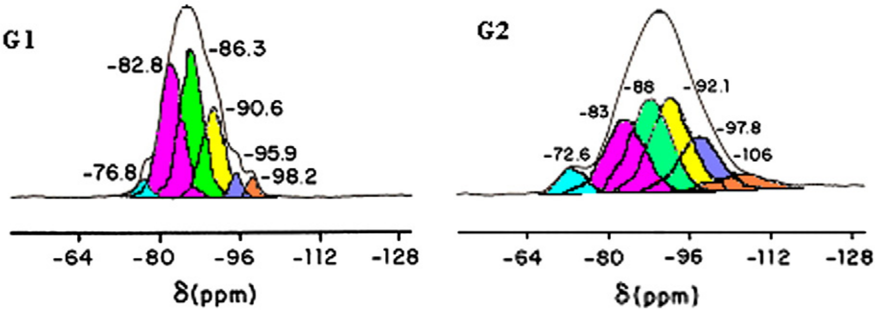

Fig. 7. ^{29}Si NMR-MAS spectra for *Gel 1* (G1, Si/Al ≈ 1) and *Gel 2* (G2, Si/Al ≈ 2).

available, standardised quality prime materials, are still outstanding viable solutions. But is total substitution truly desirable?

One of the possibilities being considered in the context of the aforementioned environmental issues is to dilute Portland cement with high volumes of SCMs. Dilution of the PC content reduces the effectiveness of SCM activation, however, unless an alkaline activator can be added. This is the solution adopted in hybrid PORTLAND CEMENT–ALKALI ACTIVATED ALUMINOSILICATE systems. Consequently, the compatibility of the two cementitious gels, C–S–H (the main reaction product of ordinary Portland cement hydration) and N–A–S–H (the main product of the alkali activation of aluminosilicate materials), may have important technological implications for future cementitious systems in which both products might be expected to precipitate [44,45,76,77].

5.1. Phase compatibility studies

Studies have been conducted on synthetic gels to explore the effects of the constituents of one gel on the other. According to the findings, high pH media and the presence of aqueous aluminate impact C–S–H composition and structure [78,79], while aqueous Ca modifies N–A–S–H gels, partially replacing sodium with calcium to form (N,C)–A–S–H gels [80]. The conditions in which such modifications take place have not been fully defined, however, and given the possible co-existence of the two gels in construction cements, a systematic study of [N -A -S -H] -[C -A -S -H] compatibility would appear to be in order.

In an initial attempt at determining the compatibility of "[N -A -S -H] -[C -A -S -H]" gels, García-Lodeiro et al. studied the possibility of co-precipitating the two cementitious gels in a sol–gel process [71,81]. The laboratory reagents used were sodium silicate (source of silicon), calcium nitrate (source of calcium) and aluminium nitrate (source of aluminium) solutions. The alkalinity of the medium was controlled with an NaOH solution. The synthesis parameters analyzed were pH and the initial Si/Al and Ca/Si ratios. The resulting synthetic gels were characterised by XRD, TEM/EDX and NMR. The findings showed that the type of products formed and their characteristics depended heavily on the pH in the synthesis medium and the initial Ca/Si and Si/Al ratios. While a medium-high lime content favoured the formation of C–A–S–H gels, the presence of a high alumina and silica content led to the formation of an (N,C)–A–S–H gel [78–82].

Fig. 9 shows the TEM results for two mixed gels, *A2* (synthesised at pH = 13.10, for theoretical (Si/Al) and (Ca/Si) values of 2.0 and 0.5, respectively) and *A3* (pH = 12.87, for theoretical Si/Al and Ca/Si values of 2.0 and 1.0). An amorphous calcium silicoaluminate (Ca/Si ~0.59, Si/Al ~ 1.32) gel was observed to form in *A2*, which had a lower calcium content. The chemical composition of this gel was reminiscent of a C-A-S-H gel with a high aluminium and silicon content.

The chemical composition graph plotted from the EDX findings for sample *A3* (Fig. 9(b)), which had a higher calcium content, shows two

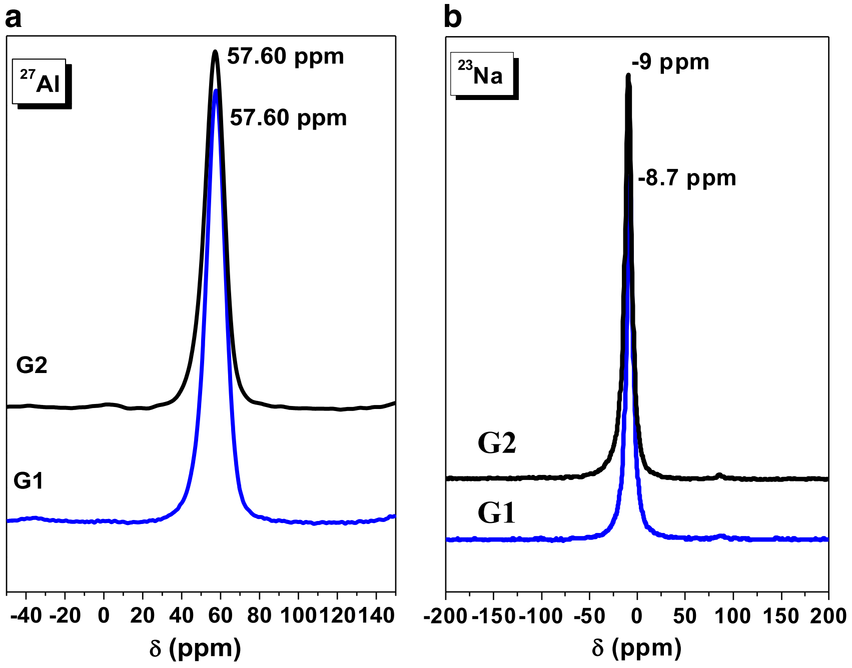

Fig. 8. (a) ^{27}Al NMR-MAS spectra for G1 and G2; (b) ^{23}Na NMR-MAS spectra for G1 and G2.

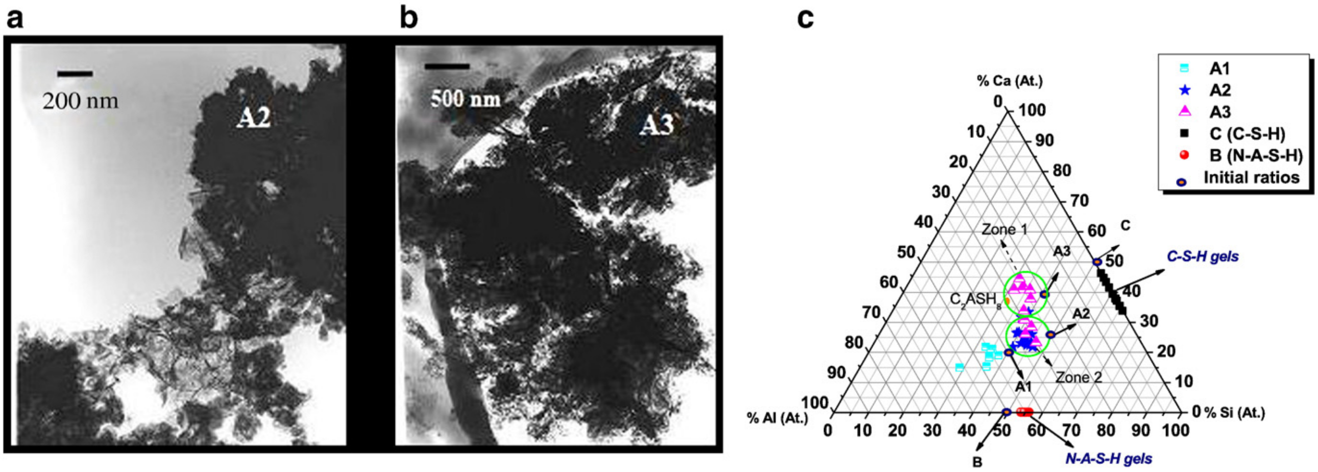

Fig. 9. TEM micrograph of mixed gels (a) A2 and (b) A3; (c) EDX analysis.

groups of points on the inner part of the diagram (see Fig. 9(c)). In the first group (*zone 1*), the chemical composition could be likened to the composition of an aluminium-containing C-S-H gel, with Ca/Si ≈ 1.02 and Si/Al ≈ 1.36. The aluminium content detected was too high to be attributed to a C-(A)-S-H type gel only, however. The inference would be that the predominant phase might have been a calcium silicoaluminate, perhaps associated with the compound (composition $Ca_2Al(AlSi)_{1.11}O_2(OH)_{12}(H_2O)_{2.25}$) detected with XRD. The second group of representative points (*zone 2*) was attributed to a gel similar in morphology to the above precipitate, but whose chemical composition, slightly richer in silicon, was thought to be associated with the formation of a C-A-S-H-type or an (N,C)-A-S-H gel.

But an important experimental parameter was omitted in this study, namely carbonation during gel precipitation (the samples had undergone substantial carbonation). Consequently, the findings reported cannot be regarded to be wholly accurate, thermodynamically speaking.

Very recently, the same group of authors [82] proposed a tentative phase diagram for the Na_2O–CaO–Al_2O_3–SiO_2 system at 25 °C, based on a series of solution/precipitation studies. At pH values relevant to cement, the predominant phase was a solid solution designated C–A–S–H with compositional ranges of $0.72 < CaO/SiO_2 < 1.94$ and $0 < Al_2O_3/SiO_2 < 0.1$. The Na_2O content in this and related CaO-rich phases was negligible. Note that in the present study, all phases were assumed to be water-saturated.

A gel denominated N–A–S–H, exhibiting a three-dimensional structure, was also observed in this system. In the presence of Ca, however, it was only found to be stable at low pH values (<12). At high values (>12), the presence of Ca favoured C–A–S–H formation to the detriment of N–A–S–H. At low pH, this phase behaved like a zeolite and an ion exchange process was observed in which the Na was replaced by Ca until the available store of the latter was completely depleted.

These authors also conducted studies [82] on the compatibility between cementitious gels by directly mixing pre-synthesised C–S–H or C–A–S–H with N–A–S–H. Having observed that the two gels inter-reacted under these conditions, they predicted gradual degradation of N–A–S–H to C–A–S–H until the C–A–S–H reached a composition reflecting its minimum CaO/SiO_2 and maximum Al_2O_3/SiO_2 ratios. In the resulting mixture, the remaining N–A–S–H and C–A–S–H gels would be in equilibrium.

5.2. Studies on real hybrid cements

While research on synthetic gels (with laboratory reagents) furnishes a good deal of basic knowledge about the nature of new cements, studies involving real systems provide insight into the actual technological potential of these materials. Alkali activation reaction kinetics in real cements has in fact been found to involve pathways (at least in fairly short periods of time) that differ from thermodynamic predictions that suggest the formation of a single gel [82].

In 2007, Palomo et al. [45] reported the results of research on hybrid cements of the type discussed here. The experiments were performed on blended cements (**S**) containing 30% Portland cement clinker and 70% fly ash. The powdery material was mixed with deionised water for "normal" hydration (L1), as well as with two alkaline activation solutions (L2 and L3) at ambient temperature. The mechanical strength developed by this highly blended cement differed significantly depending on the hydrating solution used. Characterisation studies were conducted to obtain information on the complex structural nature of the hardened matrices, which in all cases consisted of a mixture of amorphous gels (C–S–H + N–A–S–H).

These systems were tested for mechanical strength. Table 1 shows that strength development in the water-hydrated system (S1) was relatively poor and similar to the behaviour observed in materials activated with solution L2. The S3 blends activated with solution L3, however, were compliant with the strength requirements laid down in European standard EN 197–1:2000 and are comparable to the values for standard 32.5 cement.

Two conclusions can initially be drawn from these findings. On the one hand, Portland cement hydration follows different pathways depending on the OH^- concentration and the presence of soluble silica in the medium. And on the other, fly ash activation at laboratory temperatures is accelerated by the presence of Portland cement.

The positive effect of the presence of Portland cement on ash activation at laboratory temperature may be explained by the heat released during the hydration reaction; the energy from this heat would

Table 1
Mechanical strength development of hybrid cements.

Material			Paste		
Blended cement	Liquid	"Liquid/solid" ratio	Sample	Compressive strength (MPa)	
				2-day	28-day
S-70% FA	^{1}L1	0.325	S1	11.23	28.91
+	^{2}L2	0.407	S2	4.83	24.72
30% Clinker	^{3}L3	0.487	S3	12.91	36.94

^{1}L1—Deionised water; ^{2}L2—NaOH solution; ^{3}L3—sodium silicate solution (waterglass) NaOH solution with SiO_2/Na_2O—1.5. The two alkaline solutions were prepared to a density of 1.20 g/cm^3.

in turn activate the chemical reactions that originate fly ash setting and hardening in highly alkaline media.

The above strength data were related to the mineralogical and microstructural information about these systems provided by a variety of characterisation tools (FTIR spectroscopy, ^{29}Si MAS NMR, SEM and XRD) to ensure the correct interpretation of system evolution.

Given that the material hydrated with liquid L1 (water) was merely a highly blended cement (used essentially as a reference material) and that blended cement hydration has been extensively studied, there is little point in devoting time and space to a discussion of the hydration products observed in this system. By contrast, attention should be drawn to the presence of a hydroxysodalite-type zeolite in the crystalline phases of the cementitious matrix formed by the material activated with alkaline solution L2 (see Fig. 10). This may be an indication of the reaction of the fly ash in the original solid with the alkalis and the hydroxy ions in the medium to form the alkaline silicoaluminate gel (N–A–S–H gel) characteristic of the activation of this sort of materials. The presence of substantial quantities of anhydrous silicates (alite and belite from the clinker) would confirm that in the composition of the cementitious matrix under formation, the N–A–S–H-gel generated by the fly ash during activation prevailed over the C–S–H gel generated by the Portland clinker during hydration. The absence of portlandite among the crystalline phases of this material (regardless of curing time) and the appearance of moderate amounts of calcite were also significant in this regard, providing further evidence that the clinker component in the original solid did not hydrate “normally”. This naturally had an adverse effect on the amount of C–S–H precipitating in the system. The inference is that the clinker component contributes only scantly to the development of mechanical strength at the curing times considered.

The interpretation of the ^{29}Si NMR signals (see Fig. 11) provided insight into the microstructural evolution of the cementitious matrices studied and therefore into the nature of the gels making up the skeleton responsible for the strength of these materials. In this respect, key importance was attached to the component corresponding to the peak at −86 ppm in spectra **C** and **D**, which may be associated with either the C–S–H gel (Q^2 units) or the N–A–S–H gel (Q^4(4Al) units). The presence of anhydrous silicates in both spectra (signal at −72 ppm) supported the premise that C–S–H was not the only binder forming in systems S2 and S3. The gel did, however, form a part of both binders, since part of the clinker disappeared (was hydrated) in these systems: note the change in the signal at −72 ppm in spectra **B** and **C** compared to spectrum **A**. The presence of low intensity signals at −90, −95 and −102 ppm in spectra **C** and **D** was also significant, since in prior studies [52,67,83] these signals were identified as pertaining to the N–A–S–H gel and attributed to Q^4 units with 3, 2 or 1 aluminium atoms.

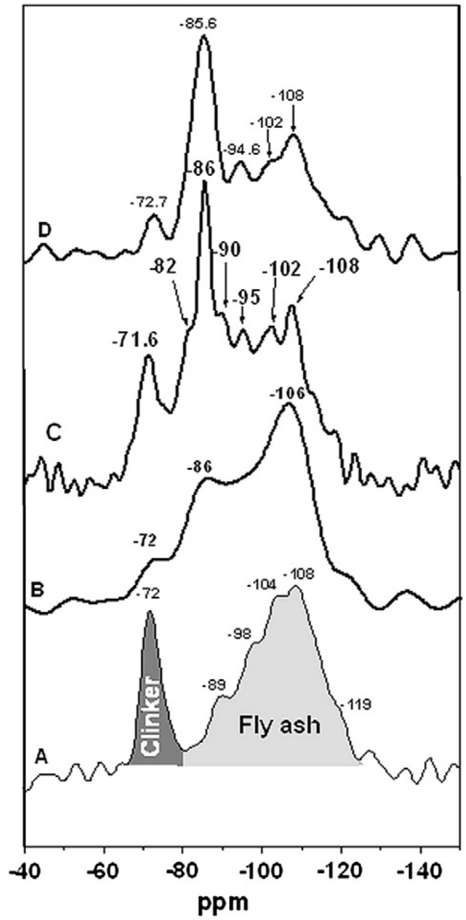

Fig. 11. ^{29}Si MAS NMR spectrum for cementitious matrices: A = dry mix of starting materials (solid “S”); B = 28-day samples hydrated with L1; C = 28-day samples hydrated with L2; D = 28-day samples hydrated with L3.

Electronic microscopy, in turn, was used to describe the morphological and structural development of these materials, as shown in the micrograph in Fig. 12 (for the cementitious matrix formed when hybrid cement was hydrated with *caustic soda + waterglass*). Two phases, one light and the other dark, can be distinguished in the figure. The difference in tone is naturally indicative of different chemical compositions. Microanalysis showed that the light phase is C–S–H + Al (C–(A)–S–H) gel and the dark phase N–A–S–H + Ca ((C, N)–A–S–H) gel.

In short, the working techniques used show that the precipitation of a mix of (C–S–H and N–A–S–H) gels is responsible for the setting

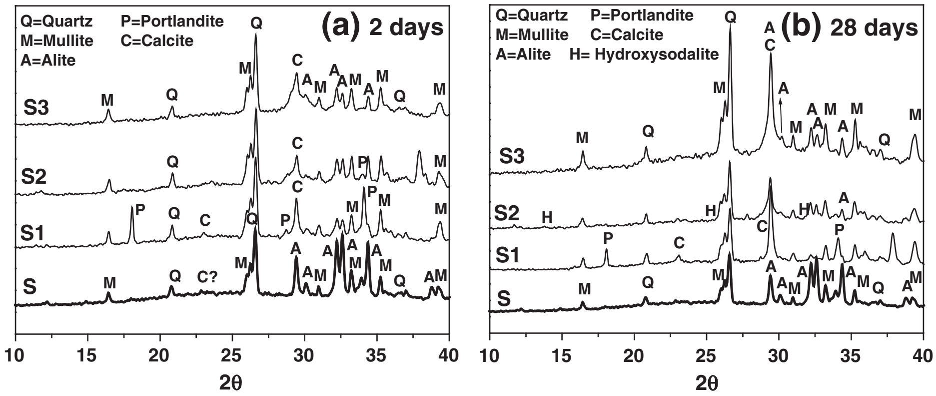

Fig. 10. X-ray diffraction patterns of the cementitious material hydrated with Liquids L1, L2 and L3; (a) two days and (b) 28 days (in both charts the diffractogram labelled “S” reflects the findings for the blended material before hydration).

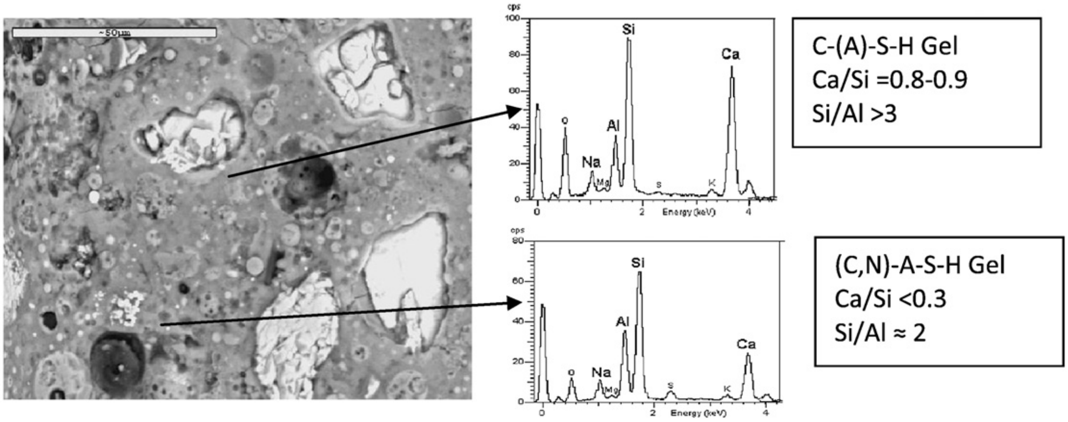

Fig. 12. Cementitious matrix S3 (70% fly ash + 30% clinker) hydrated with *caustic soda + waterglass*.

and hardening of this type of (fly ash-rich) super-blended cement when highly alkaline hydration solutions are used. These results are wholly consistent with the data reported by Krivenko et al. [84] for research on blast furnace slag and van Deventer et al. [85], who conducted in-depth studies of the reactivity of systems containing metakaolin and blast furnace slag.

6. Conclusions: Alkaline activation as a model for transition to the design of new alternative cements. Future research

The authors' intention in drafting this article was to discuss the environmental issues surrounding binders used in construction as a whole, and, especially, to provide a certain amount of elementary information on alkaline activation technology and alkaline cements. In particular, they stressed that such technology may shortly reach a stage of development in which it will serve as a link in the necessary transition from Portland cement to the cements of the future. No attempt has been made in this text to reflect different lines of opinion about specific issues of questionable importance. For these reasons, in an attempt to introduce formal innovation, the present conclusions do not contain a summary of the most significant data discussed above. Rather, they enumerate gaps in the knowledge base in areas that will be essential to progress in the technological development of alkaline binders and to the aforementioned transition from Portland and traditional to new, more sustainable cements.

One significant example of the scientific and technical gap in alkali activation procedures is the lack of a systematic and orderly study of the mechanisms governing the effect of the known alkali activators (sodium and potassium hydroxides, silicates, carbonates and sulfates) on silicoaluminous materials. The relationship between *"reaction mechanisms, the chemistry of alkaline activating solutions and end product properties"* needs to be explored, along with the decisive effect of calcium (with enormous technological implications) on such mechanisms.

While alkaline silicate solutions have likewise been widely used in alkaline activation, essential aspects of the reactive process are still poorly understood, such as the effect of the various chemical species present in the solution on reaction kinetics or the composition of the end product.

Finally, working with solid activators instead of alkaline solutions would afford an enormous technological advantage, for the former would emulate one of the most estimable properties of Portland cement: its conversion from a dehydrated solid state into an effective binder by mere mixing with water. In pursuit of such activators, some authors have proposed using cementitious formulas (with silicoaluminous materials) that contain sodium and/or potassium carbonates or even sodium and/or potassium sulfates. In any event, the literature on alkaline activation with these products is scant, and primarily geared to obtaining cementitious products. Nothing, or barely anything, has been published that would relate the interaction of silicoaluminous materials with concentrated sodium or potassium carbonate or sulfate solutions to the formation of N–A–S–H or K–A–S–H type cementitious gels. And nothing has been written to date that would indicate (in formulas with carbonates or sulfates) the structural destination of carbonate or sulfate anions if they are taken up into the three-dimensional cementitious skeleton of Si/Al binders. Another under-studied area is the formation of other phases not generally found in these cementitious systems.

Prime materials also constitute a further sizeable gap in the understanding of these cements. The institution of a universal, standardised, economical and sustainable system for processing raw materials (such as is in place for Portland cement) and activating the resulting products would be extremely beneficial.

Lastly, a word is in order on hybrid cements. Work is needed on hybrids with a low Portland clinker content and high proportion of aluminosilicates, especially on their behaviour in alkaline environments. Setting, rheology, mechanical strength development and durability in this type of hybrids must also be studied.

Acknowledgements

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