



## A review on alkaline activation: new analytical perspectives

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**ABSTRACT:** For many years now the idea of including alkalis in a Portland cement matrix has been regarded as a daft or inexcusably erroneous proposition: despite its absurdity, that opinion has been widely accepted as a basic premise by the scientific and technical community working in the area of the chemistry of cement. In 1957 Glukhovskiy proposed a working hypothesis in which he established a close relationship between alkalis and cementitious materials. That hypothesis has become consolidated and has served as a basis for developing a new type of binders, initially called “alkaline cements”. The present paper reviews the most significant theoretical interpretations of the role played by alkalis in the formation of the “stony” structure of cement. It ends with a broad overview of the versatility of this type of materials for industrial applications and a discussion of the possibility of building on the existing legislation to meet the need for the future regulation of alkaline cement and concrete manufacture.

**KEYWORDS:** Alkali activation; Aluminosilicates; Cements; C-S-H gel; N-A-S-H gel, Geopolymers; Hybrid binder

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**RESUMEN:** *Activación alcalina: Revisión y nuevas perspectivas de análisis.* Hace algunos años, la sola idea de la presencia de álcalis en una matriz de cemento Portland se consideraba casi como una aberración, o como un error imperdonable; convirtiéndose en un postulado básico (absurdo) ampliamente aceptado por la comunidad científica y técnica vinculada a la química de los cementos. En 1957 Glukhovskiy propuso una hipótesis en la que se establecía una estrecha relación entre los álcalis y los materiales cementantes. Hoy día nadie duda de que dicha hipótesis ha servido de base para el desarrollo de una nueva clase de materiales cementantes: “cementos alcalinos”. En el presente trabajo se hace una revisión sobre los aspectos teóricos más relevantes del papel de los álcalis en la formación de estos conglomerantes. También se da una visión genérica de su versatilidad, desarrollo industrial y estado de la normativa actual para regular en el futuro la fabricación de cementos y hormigones alcalinos.

**PALABRAS CLAVE:** Activación alcalina; Aluminosilicatos; Cementos; Gel C-S-H; Gel N-A-S-H; Geopolímero; Cemento híbrido

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### 1. INTRODUCTION

A very long time ago, alkaline metal compounds were (nearly demonised and) excluded from the mineral components in ordinary portland cement,

essentially because of their high solubility: a perfectly reasonable conclusion, in scientific-technical terms.

A sizeable volume of research conducted to determine the reasons for the excellent durability of

many ancient cements (which remain in good condition and form part of our historic heritage) has shown that the premise contending that all alkaline salts are highly soluble is not entirely accurate, however. Further to the data in the literature (1–7), the excellent durability of many known ancient structures may be attributed essentially to the mineralogy of their cements, and specifically to their large store of alkaline metal phases (alkaline aluminosilicate hydrates similar in composition to natural zeolites) that co-exist with calcium silicate hydrate phases.

As if that did not suffice, the knowledge that has been accumulating over time about the stability and composition of natural mineral formations leads to similar conclusions: the exclusion, today, of alkaline metals in “artificial” cement phases is the result of inherited prejudice that cannot be technically justified.

And yet, despite the lack of scientific evidence that would back the premises advising against the presence of alkalis in cement binders, “non-alkaline” was largely synonymous with the highest quality portland cement throughout the better part of the twentieth century.

The understanding of the chemistry of portland cement in the first half of the century was patchy at best, for want at the time of the powerful and sophisticated tools with which today’s laboratories are fitted and which are needed to unveil the mysteries of a dynamic, time-variable and consequently tremendously complex chemistry. Moreover, barely a handful of researchers engaged in studying the chemistry of cement. All that may have justified the persistence of the “non-alkaline” rule in portland cement in the post-world war years when everything had to be rebuilt and when the massive, planet-wide industrialisation of construction generated a need for universal quality criteria and product standardisation.

Today the ongoing application of the “non-alkaline” rule in binders is much more difficult to understand and justify. In fact, the more that is known about the fundamentals that govern portland cement hydration, the clearer it becomes that the material requires alkalis to survive into the immediate future. Analogously, the stable compositional harmony between alkaline and alkaline-earth metals attained in ancient cements has enabled them to survive over time intact (except where deteriorated by human savagery) as part of emblematic structures.

That the cement industry is in the midst of a major identity crisis today is unquestionable, even though the actors involved (entrepreneurs, architects and engineers, and even part of the scientific community) are reluctant to explicitly acknowledge its severity and consequently to recognise the need to address it without delay.

On the one hand, developing country growth, which is inconceivable without the short- and medium-term construction of large and modern infrastructures, clearly heralds a steep climb in the demand for cement over the next 40–50 years (doubling or perhaps trebling current output). But on the other, present portland cement technology, inherited from the twentieth century (with its energy- and non-renewable natural resource-intensity, intolerable volume of CO<sub>2</sub> emissions and questionable durability, among others), is clearly incompatible with rationally “sustainable” development.

In short, the twenty-first century cement industry is facing a conflict and if that conflict is acknowledged to lie at the root of its identity crisis, there is no time to lose. The authors of the present paper believe that a universal sustainable development strategy calls for immediate action on the part of construction in general and the cement industry in particular, which should seek support and vitality in a redefinition of the role of alkalis in the cements of the future.

The authors feel that cement science should firmly and boldly aim toward that horizon, intensifying its efforts to undertake a technological transition that is long overdue. Alternative cements are not an illusion, but a reality. Alkaline cements made their first appearance over 50 years ago (8–9).

When the subject of alkaline cements comes up, professionals (cement or concrete plant engineers, scientists not specialising in alkaline activation, architects, developers and so on) often ask: “If alkaline activation has been around for so long and is known to deliver such good results, why hasn’t it been implemented world-wide?”

That reflective (or tricky) question has no linear answer: rather, it needs to be addressed from several perspectives because in the past a number of factors, many still current, have curbed the universal development of alkaline activation technology. One obvious reason predominates over all the rest, however: the international cement majors have not been nor are they presently keen on contributing to the short- or medium-term disappearance of portland cement or its replacement by alternative binders as a construction material. Cement, after all, is a very lucrative business and the agents that monopolise it fear that a change in its production fundamentals will detract from the handsome profits that portland cement generates world-wide.

The companies that control the cement business obviously seek some manner of rationale that will enable them to continue to dominate the construction binder market for as long as possible. The main arguments wielded by portland cement’s champions, which successfully ensured the product’s supremacy during the twentieth (and so far in the twenty-first) century by hindering the technological and commercial development of alternative cements (such

as alkaline cements, the main subject of the present paper), are listed below.

#### a) The scientific background

Those who reject immediate change in construction binder technology contend that a new product cannot be launched on the market without an in-depth scientific-technical review. That would seem obvious.

And alkaline cements have passed that test with honours, even though the scientific and technical community continues to work in the field and even if it devotes the next 100 or 200 years to enhancing humanity's understanding of these materials and to developing new technologies to identify more and better applications. A careful study of the scientific databases shows that the number of papers published in the field has grown exponentially in the last 20 years (see Figure 1), also some books have been published in the last years (10-13).

The scientific case history of these materials is complex and difficult to comprehend. First of all, a single physical-chemical concept has given rise to a diverse terminology: alkaline cements, geocements, geopolymers, inorganic polymers and so on. The fact that one and the same family of materials has many different names is not merely anecdotal. It is actually an anomaly in need of correction because it has degenerated into a ritual of confusion. That situation is naturally seized upon, in their own interest, by those who would rather not see technological developments (outside portland cement) progress as rapidly as possible.

Furthermore, the scientific and technical background available on alkaline cements today is much greater than the knowledge that was in place on

portland cement when it was adopted as a basic construction material. This article describes some of the major advances made by scientists from around the world and the vast technological potential and versatility of these materials.

#### b) The durability debate

It is at the very least surprising that durability, which is so uncertain in portland cement, has been used as an excuse to thwart the birth and development of new alternative binders. The refrain “and how will the new material behave over time?” or “how durable is it?” has often been used as a lethal weapon to fend off promising new ideas.

Spanish speakers have a saying that goes something like: “We all brag about what we wish we were but aren't”. Many readers may not know that around 20–25% of the portland cement manufactured yearly on this planet is used to repair structures in service, portland cement structures that have deteriorated prematurely. In the best of cases, such structures are designed to last for 100 years, which compares very poorly to the splendid works bequeathed by past civilisations, and especially poorly given the (material and sustainability) costs involved.

Moreover, the durability problems inherent in portland cement concrete have been known for many years. That means that after a full century of research, scientists have been unable to find the key to and solve those problems. That says very little in our favour, or is it perhaps an indication that they are unsolvable?

And one last reflection on durability. Today long-term (years) experiments are no longer needed to determine the performance of a material over time

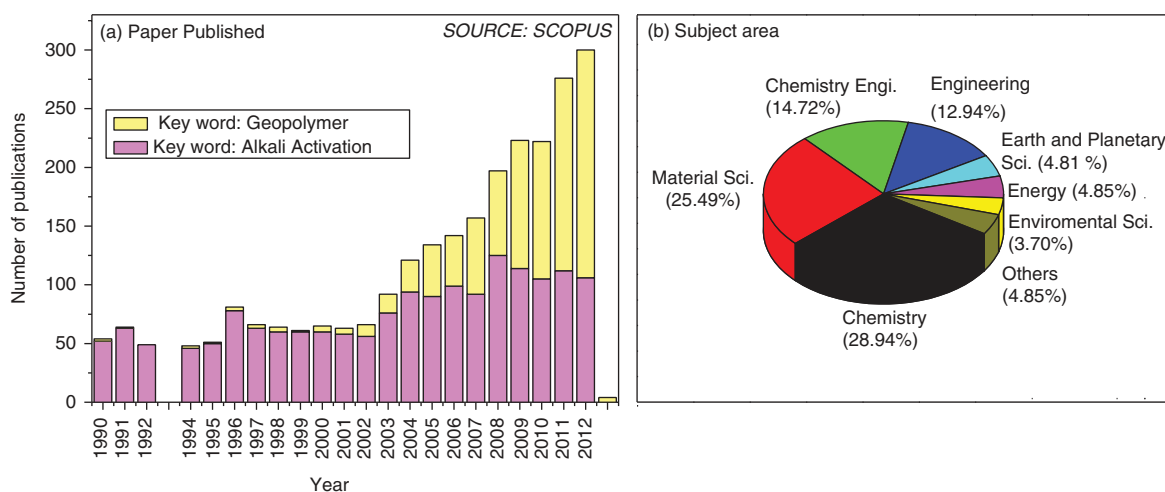


FIGURE 1. (a) Papers published on alkaline cements (=geopolymers) in the last 20 years; Source: Scopus, (b) 9 Subject Areas; more than 162 Journals analyses; Keyword: Alkali Activation: 1796 papers; Keyword: Geopolymer : 767 papers.

and ascertain its response to the action of aggressive agents. In other words, it no longer takes 100 years to know how material stability will be affected by innovative ideas. Thermodynamic models (within reach of any internet user) can be used to make highly accurate predictions about the stability or instability (durability) of the mineral phases present in a cementitious product. These same models cast serious doubts on the stability of some of the phases comprising portland cement.

## 2. ALKALIS IN NATURE

Disregarding for a moment the environmental problems associated with portland cement manufacture (which are sufficiently important to justify the existence of other cements), scientists have much to learn from nature and the planet's mineral cover (consolidated over thousands, millions of years) in their centuries-old attempts to artificially reproduce those spontaneous processes in the laboratory.

The geological data on the conditions under which sedimentary and metamorphic rocks formed and the data available on the composition of their constituent minerals provide grounds (sound theoretical explanations) for espousing the possibility of producing construction-usable concrete from alkaline metals together with the traditional calcium compounds.

Some of the processes involved in sedimentary rock formation are known to take place at temperatures and pressures similar to those required to produce certain hydraulic binders. Sedimentary zeolites such as analcime [ $\text{NaAlSi}_2\text{O}_6 \cdot x\text{H}_2\text{O}$ ], phillipsite [ $(\text{K}_2, \text{Ca})\text{Al}_2\text{SiO}_{12} \cdot 4.5 \text{H}_2\text{O}$ ], mordenite [ $(\text{Ca}, \text{Na}_2, \text{K}_2)\text{Al}_2\text{Si}_9\text{O}_{22} \cdot 6\text{H}_2\text{O}$ ], natrolite [ $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ] and scolecite [ $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ ], among others, are found in residual soils as a result of low temperature hydrothermal reactions (14–16).

Analcime, specifically, is frequently found at the bottom of certain temperate marine basins (temperatures of under 30 °C). Its formation is often the result of the interaction between volcanic ash deposited on the seabed (after volcanic eruptions such as in 2012 on El Hierro, one of the Canary Islands) and the alkaline metals dissolved in the seawater. The formation of this zeolite in particular, and others, depends only on the chemical composition of the solutions in contact with the ash (concentration of the elements in the seawater) and the intensity of the hydrothermal conditions (water temperature). In calcium-rich waters the zeolite varieties most prone to precipitate contain calcium, but if the alkali concentration in the medium rises, the alkaline-earth cations are partially or wholly replaced by sodium or potassium, leading to the formation of alkaline metals, whose co-existence with alkaline-earth metal zeolites is perfectly viable.

An in-depth analysis of the data available on natural sedimentation (14–16) reveals that rock composition can be explained in terms of its decomposition in response to the action of alkaline solutions. Aluminosilicate hydrates such as muscovite, sericite, the zeolites and others are products of the chemical decomposition of naturally abundant rocks with an aluminosilicate (alkaline and alkaline-earth) composition, such as plagioclases and (potassium or sodium) feldspars. The most characteristic type of decomposition in plagioclases is sericitisation (transformation of plagioclases into muscovite), which is actually no more than the conversion of anorthite-containing anhydrous aluminosilicates into alkaline hydrates.

In the interaction between water and  $\text{R}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot n\text{H}_2\text{O}$ -type feldspars, the two chemical reactions that may take place can be represented as follows:



or



where  $\text{R} = \text{Na}, \text{K}, \text{Li}, \text{Rb}, \text{Cs}$ .

In essence, these reactions constitute alkaline aluminosilicate hydrolysis whose result is a system of mica-like hydrates or zeolites such as analcime. Briefly, this process is highly reminiscent of mineral hydration in portland clinker. The mechanisms governing such feldspar hydrolysis might even be suspected to involve reaction product hardening, as in cementitious systems (17–18).

Alkaline and alkaline-earth elements can be classified in descending order of diffusivity at the feldspar-water interface as follows: calcium, sodium, magnesium and potassium. Potassium feldspars tend to decompose more slowly than calcium or sodium feldspars, with albite as the most stable mineral. Plagioclase behaviour differs, however: mineral resistance to dissolution is closely associated with the amount of anorthite present. Calcium plagioclases decompose at the fastest rate.

Alkaline aluminosilicate hydrates such as muscovite and paragonite clearly resist decay more effectively than calcium aluminosilicates. These minerals also afford the soundest evidence of the excellent durability of sodium- and potassium-containing products that precipitate via “alkaline activation” mechanisms.

Moreover, the tendency in portland cement hydration products to be less basic than the starting anhydrous mineral phases further supports the analogy between the processes taking place in natural rock and the artificial processes in which alkaline and alkaline-earth elements are used to generate alkaline cements.

As a rule these processes, which are associated with changes in medium alkalinity, can be divided into the following stages:

- \* alkaline and alkaline-earth metal hydration
- \* partial replacement of the alkaline and alkaline-earth metals.

The presence of protons or hydroxylions induces the precipitation of highly insoluble  $R_2O \cdot (1-3) Al_2O_3 \cdot (2-6) \cdot nH_2O$ -type aluminosilicates, along with likewise insoluble  $RO \cdot SiO_2 \cdot nH_2O$  alkaline-earth silicates and soluble phases conforming to the formulas  $R(OH)_2$ ;  $ROH$ ; or  $R_2O \cdot nH_2O$ , all in amorphous or submicrocrystalline states.

Under the low-temperature (and relatively low-pressure) hydrothermal metamorphism taking place on the Earth's crust, rock transformation is associated with feldspar mineral phase hydration and the formation of water-resistant (insoluble) and non-water-resistant (soluble) alkaline hydration products. In essence, these processes clearly parallel the mechanisms involved in the reaction product accumulation stage of portland cement hydration.

The (non-alkaline or low alkaline content) aqueous phase is alkalinised in a way that essentially resembles a) clay conversion into zeolites or micas in an autoclave; b) low-alkalinity silicate hydrate formation from a mix of lime and silica; or c) tricalcium silicate formation from  $\beta$ -C<sub>2</sub>S and lime. In all these cases natural metamorphosis generates changes in the hydration products as a result of the loss of alkaline substances induced by the circulation of warm aqueous solutions.

The end result is alkali, zeolite and hydromica elimination or fixation and mica crystallisation and, under metamorphic thermal conditions, recrystallisation into albite, orthoclase, feldspathoids and similar.

Another prominent characteristic of rock metamorphism is the high pressures required (much higher than present in normal portland cement production), which render laboratory simulation extremely difficult. Nonetheless, research conducted in Kiev (19-21) showed that processes similar to those taking place in metamorphic rocks could be simulated in large volumes and under the curing conditions (temperature and humidity) used in traditional portland cement concrete production. This was achieved by combining laboratory reagent alkaline (silicate or otherwise) metals and metastable aluminosilicates in amounts sufficient to synthesise alkaline aluminosilicate hydrates.

The conclusion that can be drawn from the foregoing is that silicate condensation and polymerisation (along with any number of transformations in

the mineral phases present), processes thoroughly studied under laboratory conditions, also take place, stage by stage, on the Earth's crust. The participation of alkaline and alkaline-earth oxides in these processes is much the same as observed in alkaline cement hydration and hardening.

These data serve as an initial guide for synthesising products analogous to natural sodium-potassium-calcium minerals containing chemically combined water via the alkaline or alkaline-earth hydration of a variety of natural substances or industrial by-products (such as slag, ash, intrusive and effusive rock, clay minerals or silica). Minerals similar to the ones found on the Earth's crust precipitate during the interaction of these substances with alkaline metals.

A flowchart for sedimentary rock formation based on rock weathering products was analysed in prior research (20-23) as a basis for modelling artificial minerals. That study showed that in an aqueous medium, alkaline hydroxides and alkaline metal salts prompt an alkaline reaction with the clay minerals (Figure 2) or aluminosilicate glass (Figure 3) present, inducing the formation of new water-resistant, alkaline and alkaline-earth hydration products (zeolite- and mica-like minerals).

### 3. ALKALINE ACTIVATION AS A PROCEDURE FOR SYNTHESISING CEMENTITIOUS MATERIALS

The earliest attempts to use alkalis in cement date back to 1930, when H. Kuhl (24) published research on the setting of slag mixed with dry potash solutions. L. Chassevent (25) and R. Feret (26) subsequently defined the need to study slag as a cement component. In 1940, A.O. Purdon (8) published the results of the first large-scale laboratory study on cements made with slag and live lime in the absence of portland clinker.

Later, in 1957, Victor Glukhovsky was the first to research the possibility of preparing low-calcium or even calcium-free cementitious materials, which he initially called "soil cements", using clays and alkaline metal solutions (9). Depending on the composition of the starting materials, Glukhovsky classified these products under two main systems:  $Me_2O$ - $Me_2O_3$ - $SiO_2$ - $H_2O$  and  $Me_2O$ - $MeO$ - $Me_2O_3$ - $SiO_2$ - $H_2O$ .

These early approaches were followed by any number of formulations using a wide spectrum of materials, including blast furnace slag, clay, aluminosilicate rocks and ash.

A timeline of highlights in alkaline cement research is summarised in Table 1.

In 1981 Joseph Davidovits (27), a French researcher, published results obtained with blends of metakaolinite, limestone and dolomite, whose products he called geopolymers (on the grounds of

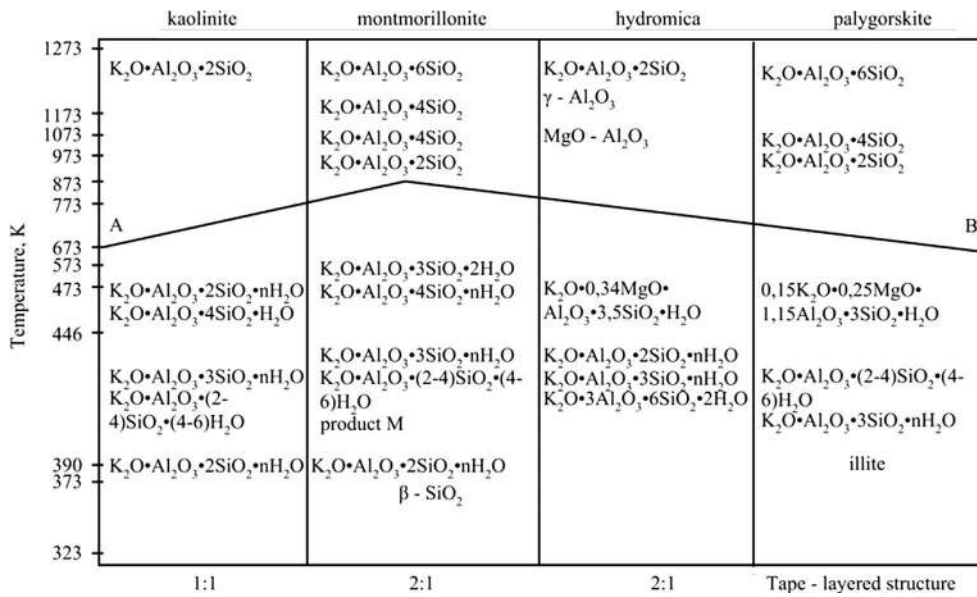


FIGURE 2. Conditions for clay- and potassium carbonate-based zeolite formation (21–22).

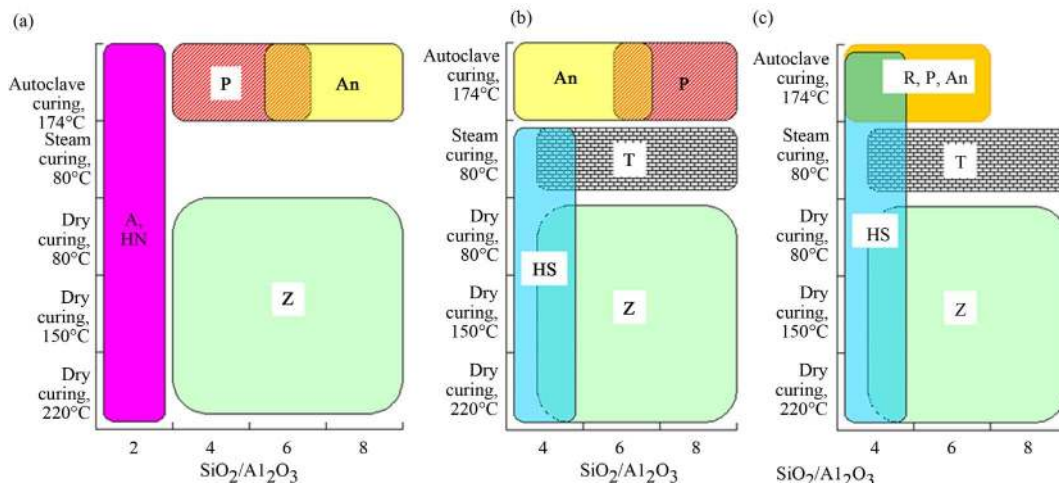


FIGURE 3. Geocement composition (source of aluminosilicate): (a) Metakaolin, (b) fly ash 1, (c) – fly ash 2 vs. curing conditions and hydration products. An – analcime; A – zeolite Na-A; P – zeolite P; R – zeolite R; HN – nepheline hydrate; HS – hydroxysodalite; Z – trona, T – sodium carbonate hydrate (12,23).

their polymeric structure). That term has since been widely accepted for the group of materials associated with the  $[Me_2O-Me_2O_3-SiO_2-H_2O]$  system defined earlier by Glukhovskiy.

In 1986 Pavel Krivenko published the results of research on the principles governing the physical and mechanical properties of concretes prepared by alkali-activating slag (17). That same author, in conjunction with professors D. Roy and C. Shi, published the first book on alkaline activation in 2006.

Another breakthrough came in 1999 when A. Palomo published the first article addressing the

possibility of producing technologically competitive cements by alkali-activating fly ash from coal-fired steam power plants (28).

### 3.1. Alkali-activated cements

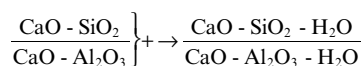
The simulation of the conversion of anhydrous aluminosilicates into aluminosilicate hydrates furthered the development of cementitious systems (29). These studies showed that the differences between the chemical composition and crystalline structure of hydrated products and anhydrous

TABLE 1. Alkali Activated Cements timeline

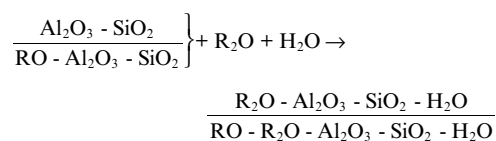
Year	Name	Country	Study/impact
1930	Kühl	Germany	Slag setting in the presence of dry potash (24)
1937	Chassevent	unknown	Slag reactivity measurement using a dry potash and soda solution (25)
1940	Purdon	Belgium	Clinker-free cements consisting of slag and caustic soda or slag and caustic alkalis synthesised with a base and an alkaline salt (8)
1957	Glukhovskiy	USSR	Binder synthesis using hydrous and anhydrous aluminosilicates (vitreous rocks, clays, steel mill slag) and alkalis; proposal for a $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$ cementitious system; coining of the term “soil cement” (9)
1981	Davidovits	France	Alkalis mixed with a blend of burnt kaolinite, limestone and dolomite, and trademarks such as Geopolymer, Pyrament, Geopolycem, Geopolymite (27)
1986	Krivenko	USSR	Principles governing system $\text{Me}_2\text{O}-\text{MeO}-\text{Me}_2\text{O}_3-\text{SiO}_2-\text{Al}_2\text{O}_3$ properties; proposal for the generic name “alkaline cements” and the specific name “geocement” (17)
1999	Palomo	Spain	Production of hardened cementitious materials from alkali-activated type F fly ashes (28)
2006	Shi & Krivenko & Roy	Ukraine - USA	First book on alkali-activated cements (11)
2014	Provis J., & van Deventer J.S.J	UK & Australia	Alkali activated Materials State of the art Report. RILEM TC 224-AAM (13)

materials depended on the curing and service conditions of the concretes manufactured with the respective binders.

The result has been the pursuit, for some time now, of ways to switch from ordinary and high-alumina portland cement (OPC and CAC) formulations:



to an ALTERNATIVE approach (alkali-activated cement or AAC):



where  $\text{R}=\text{Na}, \text{K}, \text{Li}, \text{Rb}, \text{Cs}$  or  $\text{Ca}$ .

Reality is much too complex, however, to propose radical, short-term change in the manufacturing models in place, i.e., abrupt replacement of the TRADITIONAL by a new ALTERNATIVE approach.

That notwithstanding, a wide variety of alkali-activated cements has been developed in the last twenty years (30), all in keeping with criteria of technological, environmental, economic and of course geographic rationality.

In this context of necessary change and based on the nature of their cementitious components

( $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$  system), alkaline cements may be grouped under three main categories:

1. moderately calcium-rich cements
2. low-calcium cements
3. hybrid cements.

Activation procedures differ in each category.

**Procedure 1:** activation of materials with moderately high *calcium* and *silicon* contents [ $(\text{Na}, \text{K})_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system]. An example of this model is the activation of *blast furnace slag* ( $\text{SiO}_2+\text{CaO}>70\%$ ) under relatively moderate alkaline conditions (11, 31–35). In this case the main reaction product is a *C-S-H* (calcium silicate hydrate) gel, similar to the gel obtained during portland cement hydration, which takes up a small percentage of Al in its structure (C-A-S-H gel).

**Procedure 2:** activation of materials comprising primarily aluminium and silicon ( $(\text{Na}, \text{K})_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  system). This second alkali activation procedure involves materials with low CaO contents such as metakaolin or type F fly ash (from coal-fired steam power plants). In this case more aggressive working conditions are required to kick-start the reactions (highly alkaline media and curing temperatures of 60–200 °C). The main reaction product formed in this case is a three-dimensional inorganic alkaline polymer, a N-A-S-H (geopolymer) gel that can be regarded as a *zeolite precursor* (10, 12, 13, 27, 28, 36, 37).

**Procedure 3:** today, a mixed alkaline activation procedure, a combination of the preceding two, can also be described. The product in this case is a new type of binder known as a hybrid alkaline cement, formed as the result of the alkaline activation of materials with CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> contents >20% (38–46).

These hybrid materials can be divided into two groups. **Group A** includes materials having a low portland cement clinker content and a high proportion (over 70%) of mineral additions. Examples are cement+slag, cement+fly ash, cement+slag+fly ash (38–42). **Group B** comprises blends containing no portland cement: blast furnace slag+fly ash, phosphorous slag+blast furnace slag+fly ash and similar (43–46).

The reaction products precipitating as a result of hybrid cement hydration are very complex, comprising a mix of cementitious gels, including C-A-S-H (containing sodium) and (N,C)-A-S-H (high calcium content N-A-S-H gels) gels (38–42). The following is a description of the most significant features of the aforementioned procedures and the activation reactions governing each.

### 3.1.1. Fundamentals of alkaline activation in calcium-rich systems: [(Na,K)<sub>2</sub>O-CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O]

The material most prominently used to prepare calcium-rich alkaline cements and concretes is steel mill, and more specifically blast furnace slag.

Blast furnace slag is a vitreous product formed as the result of the combination of acid oxides [SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> from the combination of acid clay gangue present in iron ore and sulfur ash in coke] and basic oxides [CaO and MgO present in the limestone or dolomite used as fluxes] smelted at high temperatures (1600 °C) and then abruptly cooled to temperatures of around 800 °C (11, 34).

The main slag components are CaO (35–40%), SiO<sub>2</sub> (25–35%), MgO (5–10%) and Al<sub>2</sub>O<sub>3</sub> (5–15%) and the minority constituents include S, Fe<sub>2</sub>O<sub>3</sub>, MnO and K<sub>2</sub>O (with percentages of under 1%). In other words, slag contains both network-forming anions (SiO<sub>4</sub>)<sup>4-</sup>, (AlO<sub>4</sub>)<sup>5-</sup> and (MgO<sub>4</sub>)<sup>6-</sup> and network-modifying cations, Ca<sup>2+</sup>, Al<sup>3+</sup> and Mg<sup>2+</sup>.

On average, slag contains a 90–95% vitreous phase (a depolymerised calcium silicate) and a mix, usually as a solid solution, of minority crystalline phases: gehlenite (2CaO·Al<sub>2</sub>O<sub>3</sub>·SiO<sub>2</sub>) and akermanite (2CaO·MgO·2SiO<sub>2</sub>), melilite family crystals that form tetragonal lattices (11, 34).

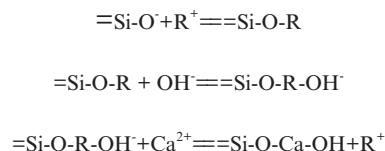
A number of research studies have shown that slag reactivity in alkaline activation processes depends largely on its component phases and vitreous structure (47–48). No direct relationship between reactivity and vitreous phase content has been proven, however. Hence, while some authors (49) deem that

the vitreous phase content should be over 90% for slag activation to be highly effective, others (50) conclude that slag with a low vitreous content (30 to 65%) may be suitable for these purposes. In any event, slag reactivity is largely described by a parameter known as degree of polymerisation (DP, see Eq. [1]) (10, 51).

$$DP = \frac{n(\text{CaO}) - 2n(\text{MgO}) - n(\text{Al}_2\text{O}_3) - n(\text{SO}_3)}{n(\text{SiO}_2) - 2n(\text{MgO}) - 0.5n(\text{Al}_2\text{O}_3)} \quad [1]$$

Its value normally ranges from 1.3–1.5: the higher the value, the greater the degree of polymerisation and consequently the higher slag reactivity (51).

Glukhovskiy and Krivenko (22, 52) proposed a model that would explain the alkaline activation of SiO<sub>2</sub>- and CaO-rich materials such as blast furnace slag by means of the series of reactions summarised below:



In that sequence the alkaline cation (R<sup>+</sup>) acts as a mere catalyser in the initial phases of hydration, via cationic exchange with the Ca<sup>2+</sup> ions. These same authors believed that as the reactions advance, the alkaline cations are taken up into the structure.

Fernández-Jiménez et al. (34, 53) reported that the nature of the anion in the solution also plays an instrumental role in alkaline activation, especially in the early stages of hydration and in particular with regard to paste setting. Their model for the reaction mechanisms (based on a model proposed by Glasser in 1990 (54)) is depicted in Figure 4.

In alkaline cements developed from materials with a high calcium content such as blast furnace slag, activation generates reaction products that resemble the products precipitating during portland cement hydration. The main reaction product formed is a C-A-S-H gel whose composition (lower Ca/Si ratio: 1–1.2) and structure vary

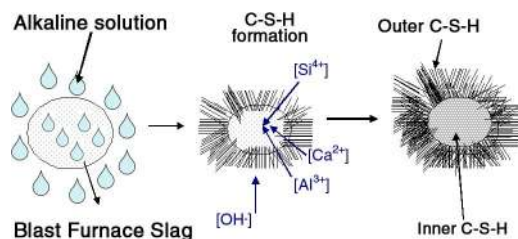


FIGURE 4. Reaction mechanism in an alkali-activated slag particle.



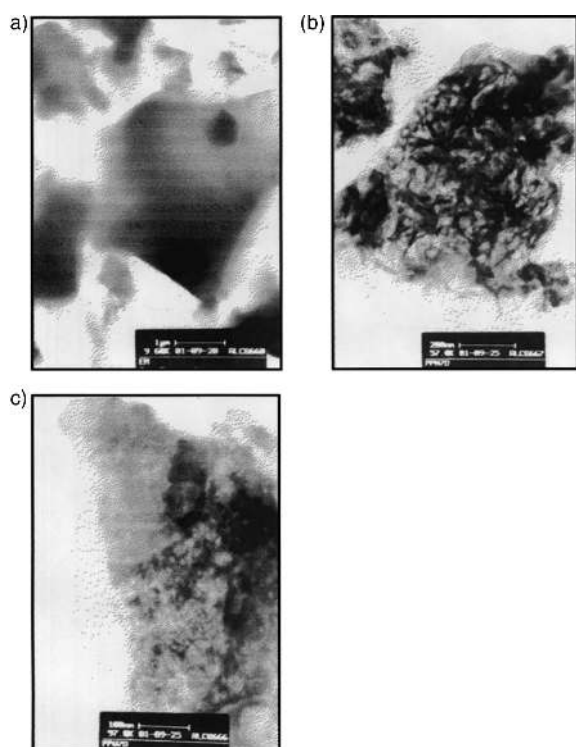


FIGURE 5. TEM micrographs of (a) anhydrous slag (Ca/Si=1.21, Ca/Al=2.63, Si/Al=2.13); (b) slag hydrated with NaOH for 7 days (Ca/Si=0.93, Ca/Al=1.35, Si/Al=1.45); (c) slag hydrated with waterglass for 7 days (Ca/Si=0.64, Ca/Al=1.49, Si/Al=2.32) (53).

from the typical C-S-H formed from OPC. A number of secondary products may form, including hydrotalcite, calcite and bases such as AFm, depending on activator type and concentration, slag structure and composition, and the curing conditions under which the paste hardens (11, 31–34, 55–58).

The microstructure of the gels formed during slag activation has been explored by several authors (53, 55, 59–65).

Fernández Jiménez et al. (53) used transmission electron microscopy (TEM) to confirm that the main reaction product is a leaf-like semi-crystalline calcium silicate hydrate. Micrographs of the initial slag and its alkaline activation products after hydration with NaOH and waterglass are reproduced in Figure 5.

The nanostructure of cementitious gels cannot be readily characterised due to their amorphous nature. Nonetheless, the information reported in recent years as a result of the application of a number of characterisation techniques, most prominently nuclear magnetic resonance (NMR), has proven to be very helpful for developing models to ascertain the structure of the various gels formed.

Taylor based his well-known model for the C-S-H formed during OPC hydration on the structure of defective tobermorite, also known as dreierkette-type chains (29, 64, 65). Perfect tobermorite consists of two linear chains of silica tetrahedra arranged on either side of a central sheet of CaO. The linear chain consists of a repetitive series of three tetrahedra, two of which are connected to the centre sheet of CaO with two oxygen bridges while the third, known as the bridging tetrahedron, is not. In this nanostructural context, tobermorite consists of infinite linear chains of silica tetrahedra ( $Q^2$  units), whereas in C-S-H gel many of the bridging tetrahedra are missing, giving rise to finite, two-, three- or five-link chains (the mean chain length is defined by the formula  $(3n-1)$  tetrahedra).

Schilling et al. (66), based on  $^{29}\text{Si}$  and  $^{27}\text{Al}$  MAS NMR studies, proposed that Al is taken up in the C-S-H gels generated in alkali-activated slag pastes, in which aluminium tetrahedra replace silicon tetrahedra in bridging positions to give rise to  $Q^1$ ,  $Q^2$  and  $Q^2(1\text{Al})$  units. The aluminium uptake was shown to depend on the concentration of alkalis and to be greater at high temperature and humidity. Richardson et al. (65, 67, 68) also explored Al uptake in C-(A)-S-H gels in tetrahedral bridging positions and proposed a series of equations to calculate mean silicon chain length and the Si/Al ratio in the gel formed from NMR data.

This model was subsequently ratified by Fernández-Jiménez et al. (34, 53). They showed that the presence of Al gives rise to gels with longer linear chains as well as to the possible existence of sporadic inter-chain, Si-O-Al bonds and consequently two-dimensional ( $Q^3(n\text{Al})$  unit, cross-linked) structures. Under those conditions, the C-S-H gels would become C-A-S-H gels (see Figure 6). These same authors established that the type of activator has a direct effect on the degree of silicate species condensation in the gel structure; when the activator used was waterglass, highly condensed structures formed. Consequently, a substantial number of  $Q^2(1\text{Al})$  and  $Q^3(n\text{Al})$  units were observed, along with  $Q^1(0\text{Al})$  and  $Q^2(0\text{Al})$  units, favouring the formation of two-dimensional, cross-linked structures. When NaOH was the activator, however, the C-(A)-S-H gel generated had a significant number of  $Q^2(1\text{Al})$  units, but no  $Q^3$  units (34, 53).

Many papers can now be found in the literature that confirm the presence of  $Q^3(n\text{Al})$  units in the C-A-S-H gels forming during slag alkaline activation (53, 63, 69, 70). One prominent article, authored by Puertas et al. (69), reported that in C-A-S-H gels forming in slag activated with a NaOH solution, the existence of tetrahedral Al in bridging positions in the silicate chains goes hand-in-hand with a considerable increase in the number of  $Q^2(1\text{Al})$  units, as well as with a small amount of  $Q^3(n\text{Al})$  units. When waterglass was used as an activator, the C-A-S-H

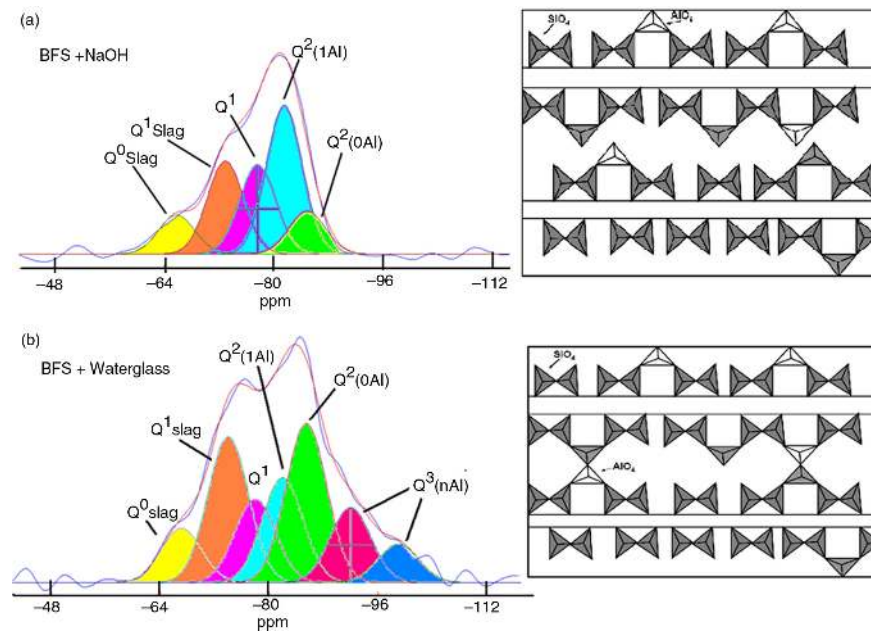


FIGURE 6. Structural model for an Al-containing C-S-H gel: (a) linear chains C-(A)-S-H gel (66–68); (b) linear chains with occasional cross-linking, forming planes C-A-S-H gel (34, 53).

gels forming had a higher aluminium content in tetrahedral bridging positions, favouring chain cross-linking and raising the percentage of  $Q^3(nAl)$  units significantly and with it the formation of layered structures in certain regions.

This gel was also observed to contain a small amount of alkalis (normally Na), that neutralised the charge imbalance created when a Si is replaced by an Al tetrahedron. Actually, then, these are calcium-sodium aluminosilicate hydrate [C-(N)-A-S-H] gels (70–73) proposed a model to describe this gel as a mix of cross-linked and non-cross-linked tobermorite-based structures (the cross-linked substituted tobermorite model, CSTM).

### 3.1.2. Fundamentals of alkaline activation in low-calcium systems: $[(Na,K)_2O-Al_2O_3-SiO_2-H_2O]$

Fly ash and metakaolin are the low-calcium materials most commonly used in alkaline cement and concrete, although metakaolin (74–79) is used very sparingly in the cement industry due to its high cost.

Fly ash is an industrial by-product generated in coal-fired steam power plants, where the coal is ground to a very fine powder before being used as a fuel. Its combustion gives rise to coarse ash (known as bottom ash) and other much finer particles, known as fly ash that are carried by smoke and trapped in electro filters to prevent their release into the air. Fly ash particles are characteristically

spherical, and may be hollow or contain other smaller particles. They consist primarily of a glassy phase and a few minority crystalline phases such as quartz (5–13%), mullite (8–14%) and magnetite (3–10%) (80).

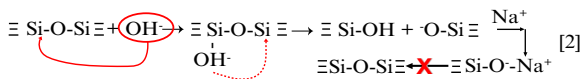
Fly ash composition may nonetheless vary depending on the type of coal used and the incineration process in place at the power plant. After an exhaustive study of a large number of types of ash, Fernández-Jiménez and Palomo (80–81) concluded that for type F fly ash to be apt for use in the manufacture of alkaline cements, it must meet the following requirements:

- a unburnt percentage <5%
- b  $[Fe_2O_3] \leq 10\%$ ;
- c  $[CaO] \leq 10\%$ ;
- d reactive  $SiO_2 > 40\%$
- e 80–90% particles <45  $\mu m$
- f vitreous phase content >50%
- g a  $[SiO_2]_{reactive} / [Al_2O_3]_{reactive}$  ratio >1.5

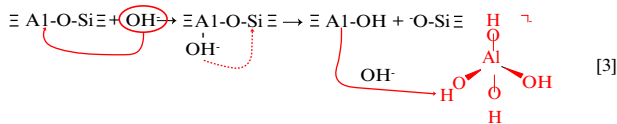
The alkaline activation of  $SiO_2$ - and  $Al_2O_3$ -rich, low CaO materials is a pursuit that has arisen in response to a fairly recent environmental need. The knowledge accumulated in connection with this process is therefore somewhat less developed than in slag activation. Glukhovskiy (52) proposed a general model to describe and explain the activation reactions in this type of materials, in which he identified three very distinct

stages: (a) destruction-coagulation; (b) coagulation-condensation; and (c) condensation-crystallisation.

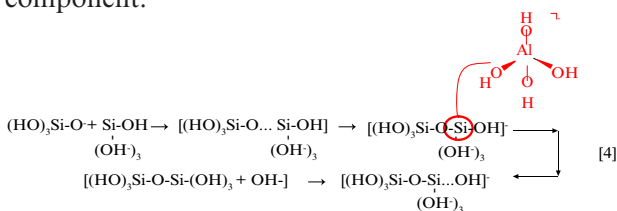
In the first (see Eq. [2]), the OH<sup>-</sup> ions in the alkaline activator start the reaction by breaking the Si-O-Si bonds. These ions redistribute their electronic density around the silicon atoms, weakening the Si-O-Si bonds and making them more liable to rupture. This attack yields silanol (-Si-OH) and silolate (-Si-O<sup>-</sup>) species. The presence of the alkaline cation neutralises the resulting negative charge. The formation of Si-O<sup>-</sup>Na<sup>+</sup> bonds hinders the reversion to siloxane (Si-O-Si).



The OH<sup>-</sup> groups also affect the Si-O-Al bonds (see Eq. [3]).



In the second stage, coagulation-condensation, the accumulation of ionic species favours the contact between the disaggregated products and polycondensation begins. The silica monomers inter-react to form dimers, which in turn react with other monomers to build polymers (see Eq. [4]). This stage is catalysed by the OH<sup>-</sup> ions. The clusters formed as a result of the polymerisation of the silicic acid begin to grow in all directions, generating colloids. The aluminates also participate in polymerisation, isomorphically replacing the silicon tetrahedra. While the alkaline metal catalyses the reaction in the first stage, in the second it acts as a structural component.



Lastly, in the third stage, condensation-crystallisation, the presence of particles in the initial solid phase furthers reaction product precipitation. The composition of these products depends on the mineralogy and chemical composition of the prime materials, the alkaline activator used and the curing conditions.

The mechanism governing the alkaline activation of fly ash has been researched in depth in recent decades. Palomo and Fernández-Jiménez proposed a model to describe the process based on zeolite synthesis (37). Under this model, the process consists of

two stages: (a) nucleation, with the dissolution of the aluminates present in the ash and the formation, via polymerisation, of complex ionic species (stage highly dependent upon thermodynamic and kinetic parameters and which would cover the first two stages proposed by Glukhovskiy); and (b) growth, when the nuclei reach a critical size and the crystal begins to grow. This stage is very slow due to experimental conditions. The final result of the alkaline activation of fly ash is an amorphous matrix with cementitious properties whose main component is none other than N-A-S-H gel (also called a “zeolite precursor”).

More recently, the same authors (82) proposed a more detailed structural model to explain N-A-S-H gel formation (see Figure 7), which would include a series of stages that can be summarised as follows. When the source of aluminosilicate comes into contact with the alkaline solution it dissolves into several species, primarily silica and alumina monomers. These monomers interact to form dimers, which in turn react with other monomers to form trimers, tetramers and so on. When the solution reaches saturation, an Al-rich, metastable N-A-S-H gel precipitates (called Gel 1) as an intermediate reaction product (81). Its formation can be explained by the high Al<sup>3+</sup> ion content in the alkaline medium in the early stages of the reaction (from the first few minutes through the first few hours), 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 in the original source of aluminosilicate dissolve, raising the silicon concentration in the reaction medium and its proportion in the N-A-S-H gel (Gel 2).

This structural reorganisation determines the final composition of the polymer as well as pore microstructure and distribution in the material, which are instrumental in the development of many physical properties of the resulting cement.

The secondary reaction products in this type of systems are zeolites such as hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite (28, 36, 80–83).

Studies conducted by a number of authors (84–94) showed that both the curing temperature and type of activator impact reaction kinetics, with the degree of reaction rising with curing temperature. In addition, the nature of the products generated (N-A-S-H gel-like and zeolite precipitates) in of aluminosilicate activation varies with curing time and temperature. Long curing times give rise to the formation of silica-rich products, favouring the development of mechanical strength in the material.

Many papers has been published in recent years on the nature of the alkaline activators used to study fly ash reactivity (94–95). Criado et al. (87, 96) studied the effect of waterglass with different degrees of polymerisation (SiO<sub>2</sub>/Na<sub>2</sub>O ratios of 0.17, 0.60

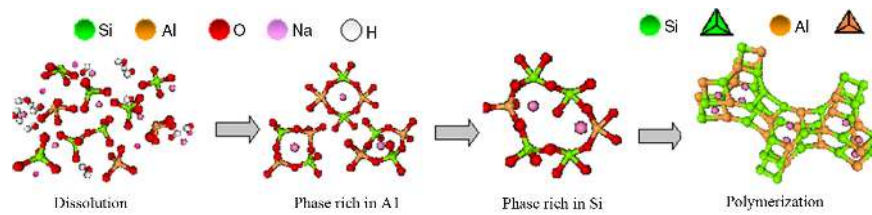


FIGURE 7. Model proposed for N-A-S-H gel formation (36, 65, 82).

and 1.90) on the intermediate reaction products generated in the alkaline activation of fly ash. They observed that this product played an instrumental role in the kinetics, structure and composition of the initial gel formed. The same authors (87) proposed that the presence of highly polymerised silica may affect N-A-S-H gel formation kinetics, retarding ash reaction and zeolite crystallisation. Over time, the system was consistently observed to evolve toward the most thermodynamically stable product.

The degree of fly ash reaction and the microstructure and chemical composition of the precipitates depend on factors such as the particle size in the anhydrous material, the composition of the starting ash, and the nature and concentration of the alkaline activator used. The mechanisms that govern activation in general are independent of the aforementioned variables, however.

Anhydrous ash characteristically consists of a series of spherical particles of different sizes (with diameters normally ranging from to 10 to 200  $\mu\text{m}$  (Figure 8(a)). Some of these spheres are hollow, while others house smaller spheres inside. The SEM micrograph of a post-alkaline activation matrix (8-M NaOH, 85  $^{\circ}\text{C}$ , 20 h) reproduced in Figure 8(b) shows a massive and uniform N-A-S-H gel. Secondary reaction products (zeolites) are also

visible, with a morphology that depends on the type of zeolite formed (see Figures 8(c) and 8(d)).

In the nineteen eighties, Davidovits (10, 92) pioneered the use of NMR techniques to explore the nanostructure of the N-A-S-H and K-A-S-H gels generated in metakaolin alkaline activation. A full understanding of the structure of these gels was not possible until many years later, however, due to the low spectral resolution available at the time. Today's equipment is fortunately much more powerful and sophisticated, delivering much higher resolution spectra.

The structure of the gels forming in the alkaline activation of low-calcium aluminosilicate materials differs substantially from the structure of the gels formed in the activation of calcium-rich cements. These (N-A-S-H) gels are characterised by a three-dimensional (3D) structure in which the Si is found in a variety of environments, with a predominance of ( $\text{Q}^4$ ) and ( $n\text{Al}$ ) ( $n=0, 1, 2, 3$  or 4) units (see Figure 9).

The  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  cations are tetrahedrally coordinated and joined by oxygen bonds. The negative charge on the  $\text{AlO}_4^-$  group is neutralised by the presence of alkaline cations (typically  $\text{Na}^+$  and  $\text{K}^+$ ). Nonetheless, gel structure may vary significantly depending on the degree of reaction, curing temperature and particularly the presence of soluble silica in the activator.

Duxson et al. (93) analysed the nanostructure of N-A-S-H gel generated during metakaolin alkaline

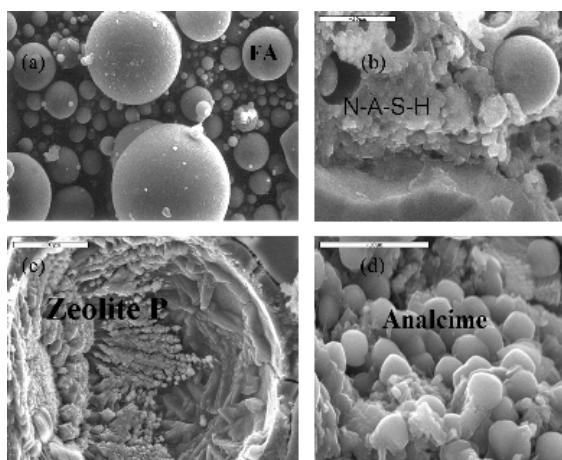


FIGURE 8. SEM micrographs: (a) original fly ash; (b) N-A-S-H gel; (c) zeolite P; (d) analcime.

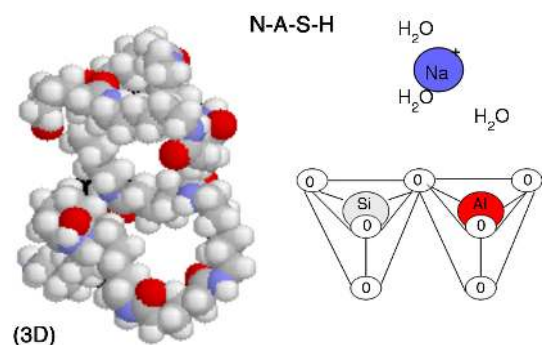


FIGURE 9. Plan view projection of the three-dimensional structure of a N-A-S-H gel.

activation (using  $^{29}\text{Si}$  MAS NMR spectra) with NaOH and waterglass solutions, the latter with different degrees of polymerisation ( $\text{SiO}_2/\text{Na}_2\text{O}$  of 0.5, 1.0, 1.5 and 2.0). These authors observed the presence of a single, wide, asymmetric signal in all cases, whose  $\delta$  position (centre of gravity between  $-82$  and  $-92$  ppm) and width depended on the activator used. The analysis of these factors furnished information on the Si/Al ratio of the geopolymer formed and the replacement ratio of aluminium in the gel structure. The substitution of silicon for aluminium in the structural network translated into a chemical shift in the signal toward less negative values. The gels with higher Si/Al ratios exhibited greater substitution and a narrower distribution of  $\text{Q}^4(\text{nAl})$  connectivity types (tetrahedral Si surrounded by 4-OAl bonds and (4-n)-OSi bonds).

The nanostructure of N-A-S-H gels generated in the alkaline activation of fly ash has also been widely studied (12, 37, 51, 81, 87). *Fernandez-Jimenez et al.* (81) studied the variations in gel nanostructure ( $^{29}\text{Si}$  MAS NMR) during the early stages of fly ash activation with 8-M NaOH at  $85^\circ\text{C}$  (see Figure 10). The  $^{29}\text{Si}$  MAS NMR spectrum for the anhydrous ash differed substantially from the post-activation spectra. The most prominent changes occurred during the early reaction stages (from 2 to 8 hours). The most intense signal, located at around  $-86$  ppm, was associated with the formation of an aluminium-rich N-A-S-H gel with a predominance of  $\text{Q}^4(4\text{Al})$  environments. The signals detected at higher shift values (around  $-80$ ,  $-77$  and  $-72$  ppm), whose intensity declined as the reaction progressed, were attributed to the presence of less condensed units (monomers and dimers). Assigning signals located at chemical shifts of under  $-88$  ppm is complex because they overlap with the signals generated by the unreacted ash.

As the reaction progressed (24 h and 7 d) the spectra changed substantially. Five signals were clearly visible at around  $-110$ ,  $-104$ ,  $-98$ ,  $-93$  and  $-88$  ppm, respectively attributed to the presence of silicon tetrahedra surround by zero  $\text{Q}^4(0\text{Al})$ , one  $\text{Q}^4(1\text{Al})$ , two  $\text{Q}^4(2\text{Al})$  or four  $\text{Q}^4(4\text{Al})$  aluminium tetrahedra, indicative of a N-A-S-H gel with a higher silicon content (Gel 2).

Studies conducted by a number of authors (37, 73, 85–87) showed that both curing temperature and the nature of the activator play a significant role in reaction kinetics. While the role of the alkalis in the alkaline aluminosilicate hydrate structure is assumed to be to neutralise the excess negative charge generated by the replacement of silica tetrahedra with  $\text{AlO}_4$  species during gel formation, scant information is available on this question.

Duxson et al. (95), analysing the  $^{23}\text{Na}$  spectra generated in gels formed in the alkaline activation of metakaolin, concluded from the two signals observed at around  $-4$  and  $0$  ppm that sodium can neutralise the excess negative charge in two ways. The  $-4$  ppm signal was attributed to sodium associated with aluminium in the gel structure (offsetting the excess negative charge). The signal at  $0$  ppm, which only appeared in spectra for alkaline aluminosilicate gels with Si/Al ratios of under 1.4, was associated with the sodium present in the pore solution, which neutralises the negative charge in the  $\text{Al}(\text{OH})_4^-$  groups.

Criado et al. (87, 96) also studied the position of sodium in the N-A-S-H gel formed during fly ash alkaline activation. In dehydrated zeolites the sodium ions were coordinated directly with oxygen anions, translating into signals located at very negative chemical shifts (around  $-20$  ppm). Garcia-Lodeiro et al. (97), also studying the  $^{23}\text{Na}$  MAS NMR spectra generated by synthetic N-A-S-H

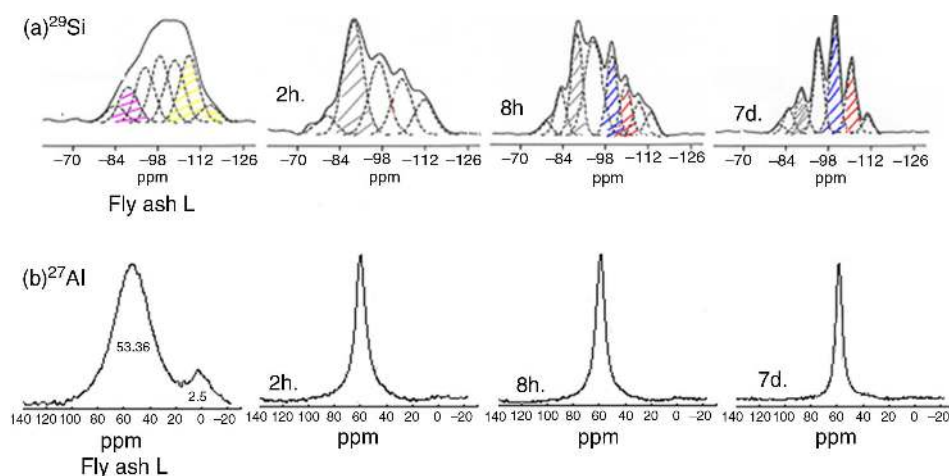


FIGURE 10 (a) 8-M  $^{29}\text{Si}$  MAS NMR spectra and (b)  $^{27}\text{Al}$  MAS NMR spectra for anhydrous fly ash; and ash alkali-activated with 8-M NaOH at  $85^\circ\text{C}$  for 2 hours; 5 hours; 8 hours; 20 hours and 7 days (81).

gels, confirmed the presence of a sole signal located at around -10 ppm, likewise attributed to partially hydrated sodium ( $\text{Na}(\text{H}_2\text{O})_x^+$ ).

### 3.1.3. Fundamentals of alkaline activation in hybrid systems: $[(\text{Na},\text{K})_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}] - [(\text{Na},\text{K})_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}]$

The hybrid cementitious systems most frequently studied include, most prominently:

- portland cement – fly ash blends
- portland cement – fly ash – blast furnace slag blends

In the systems containing portland clinker (clinker + fly ash, clinker + slag + fly ash), C-S-H gel normally prevails as the main reaction product in slightly alkaline media (i.e., 2-M NaOH), whereas N-A-S-H gel prevails in highly basic environments (10-M NaOH) (38).

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 significant technological implications for future cementitious systems in which both products might be expected to precipitate (38–40).

### 3.2. Co-precipitation of cementitious gels: C-S-H + N-A-S-H

Hybrid alkaline cements are complex cementitious blends with initial  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents of over 20% (98–101); their reaction products are intricate mixes of different gels (the type of product formed depends largely on the reaction conditions).

The reaction products forming during the alkaline activation of cement and ash blends is an area of keen scientific and technological interest and the compatibility between the main cementitious gels, N-A-S-H and C-S-H, precipitating in the two systems is the object of considerable research today (98, 102–104).

Prior studies have shown that the co-precipitation of these two gels in hybrid cements is possible (38–46), although recent research has revealed that the two products do not develop singly as two separate gels, but that they interact, undergoing structural and compositional change in the process (104).

Those studies were conducted with synthetic gels to determine the effect of each constituent on the other. The conclusion drawn was that high pH values and the presence of aluminium in the aqueous phase had a significant effect on C-S-H gel structure and composition (102–103). The presence of calcium in the solution, in turn, modified the N-A-S-H type gels, in which sodium was partially replaced by

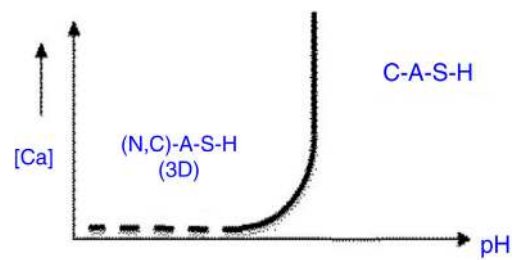


FIGURE 11. Model proposed to define N-A-S-H gel stability in terms of pH and calcium content (104).

calcium to form (N,C)-A-S-H-type gels (97). Recent studies conducted by Garcia-Lodeiro et al. on synthetic samples to analyse C-S-H / N-A-S-H compatibility in greater depth showed that the stability of the N-A-S-H structure in the presence of calcium depends heavily on the pH in the medium (104). In the presence of sufficient calcium and pH values of over 12, C-A-S-H gel is favoured over N-A-S-H gel formation (see Figure 11). The experiments yielding these findings were conducted in equilibrium conditions, however, which are not normally in place during binder hydration, particularly in the early stages of the reaction.

In 2002, Yip et al. (39) studied the co-existence of the two gels, C-S-H and geopolymer, in the alkaline activation of blends of slag and metakaolin. Using scanning electron microscope (SEM) techniques, these authors proved that the co-precipitation of the two gels was possible, albeit highly conditioned by system alkalinity. The two gels only co-precipitated at low pH values. In the presence of high (7.5 M) NaOH concentrations, the geopolymer predominated and took up small amounts of calcium. The two phases were only observed to co-exist where a sufficient source of reactive calcium was present.

Some years later (2007), Palomo et al. (40) studied both the mechanical behaviour and the reaction products generated in hybrid systems containing minority (30%) proportions of portland cement clinker and high (70%) fly ash contents. The cementitious material was mixed with deionised water (L1) and two alkaline solutions ((L2) (NaOH) and (L3) (NaOH+ waterglass)). The pastes were prepared at ambient temperature and cured in a laboratory chamber for 28 days. Mechanical strength and the reaction products generated were analysed in the 2- and 28-day materials.

Mechanical strength in the cementitious systems differed greatly with the type of hydration liquid used. The pastes prepared with water and NaOH exhibited similar 28-day strength values, at around 24–28 MPa, although in the early ages the water-hydrated system performed better than the alkali-activated paste. At 37 MPa, the 28-day strength in the system prepared with the blend of NaOH and sodium silicate exceeded the requirements laid down

in European standard EN 197-1:2000 for 32.5-type cement.

These results confirmed that portland cement hydration is affected by alkaline content ( $\text{OH}^-$  concentration) and the presence of soluble silica. In addition, fly ash activation at ambient temperature was accelerated by the presence of portland cement clinker. This beneficial effect can be explained by the heat released during cement hydration, the energy from which would favour the chemical reactions that induce ash dissolution, setting and hardening.

The micro- and nanostructural characterisation of the pastes generated in the aforementioned systems showed that a complex mix of amorphous gels (C-A-S-H+(N,C)-A-S-H) precipitates in activated systems (see Figure 12).

The interpretation of the  $^{29}\text{Si}$  NMR signals (see Figure 12 (b) (40)) provided insight into the microstructural evolution of the cementitious matrices studied and therefore into the nature of the gels making up the skeleton that affords these materials their strength. Particular importance was attached to the component responsible for the signal at  $-86$  ppm in spectra C and D (See Fig. 12(b)), which may be associated with either C-S-H gel ( $\text{Q}^2$  units) or N-A-S-H gel ( $\text{Q}^4(4\text{Al})$  units). The presence of anhydrous silicates in both spectra (signal at  $-72$  ppm) supported the premise that C-S-H gel was not the only binder forming in systems C and D. The gel did, however, form part of both binders, since some of the clinker disappeared (was hydrated) in these

systems: note the difference in the signal at  $-72$  ppm between spectra B and C on the one hand and spectrum A on the other. The presence of low intensity signals at  $-90$ ,  $-95$  and  $-102$  ppm in spectra C and D was also significant, since in prior studies (37, 40, 81, 87, 88) these signals were associated with N-A-S-H gel and attributed to  $\text{Q}^4$  units with 3, 2 or 1 aluminium atoms.

These results are wholly consistent with the data reported by Krivenko et al. (105, 106) on blast furnace slag and van Deventer et al. (107), who conducted in-depth reactivity studies of systems containing metakaolin and blast furnace slag.

### 3.3. Activation models

The research conducted on hybrid cements appears to clearly show that the type and characteristics of the gel/s formed are significantly impacted by the working pH and the calcium concentration in the system; a high calcium content and pH level favour C-A-S-H over N-A-S-H gel formation. Nonetheless, little is known about the kinetics of the reactions taking place during the alkaline activation of this type of hybrid systems, particularly in the early stages.

García-Lodeiro et al., based on their own experience in the analysis of the compatibility of the two synthetic gels (97, 102–104) and real cementitious blends (70% FA+30% OPC activated with NaOH+ waterglass) (42) and on data drawn from the literature on hybrid systems (38–40, 65,

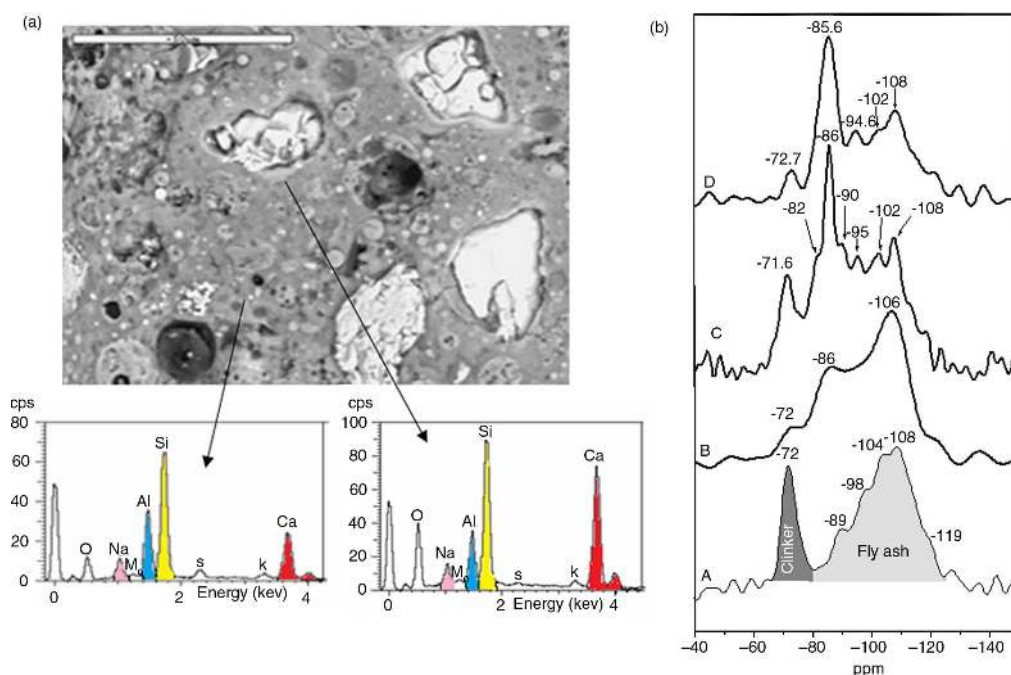


FIGURE 12. (a) 28-day SEM micrograph of the cementitious matrix in the system hydrated with solution L3 (NaOH+Wg); (b)  $^{29}\text{Si}$  MAS NMR spectra: A: initial anhydrous blend (70% FA+30% CK); B: 28-day water-hydrated blend; C: 28-day NaOH-hydrated blend; D: 28-day NaOH+Wg-hydrated blend (40).

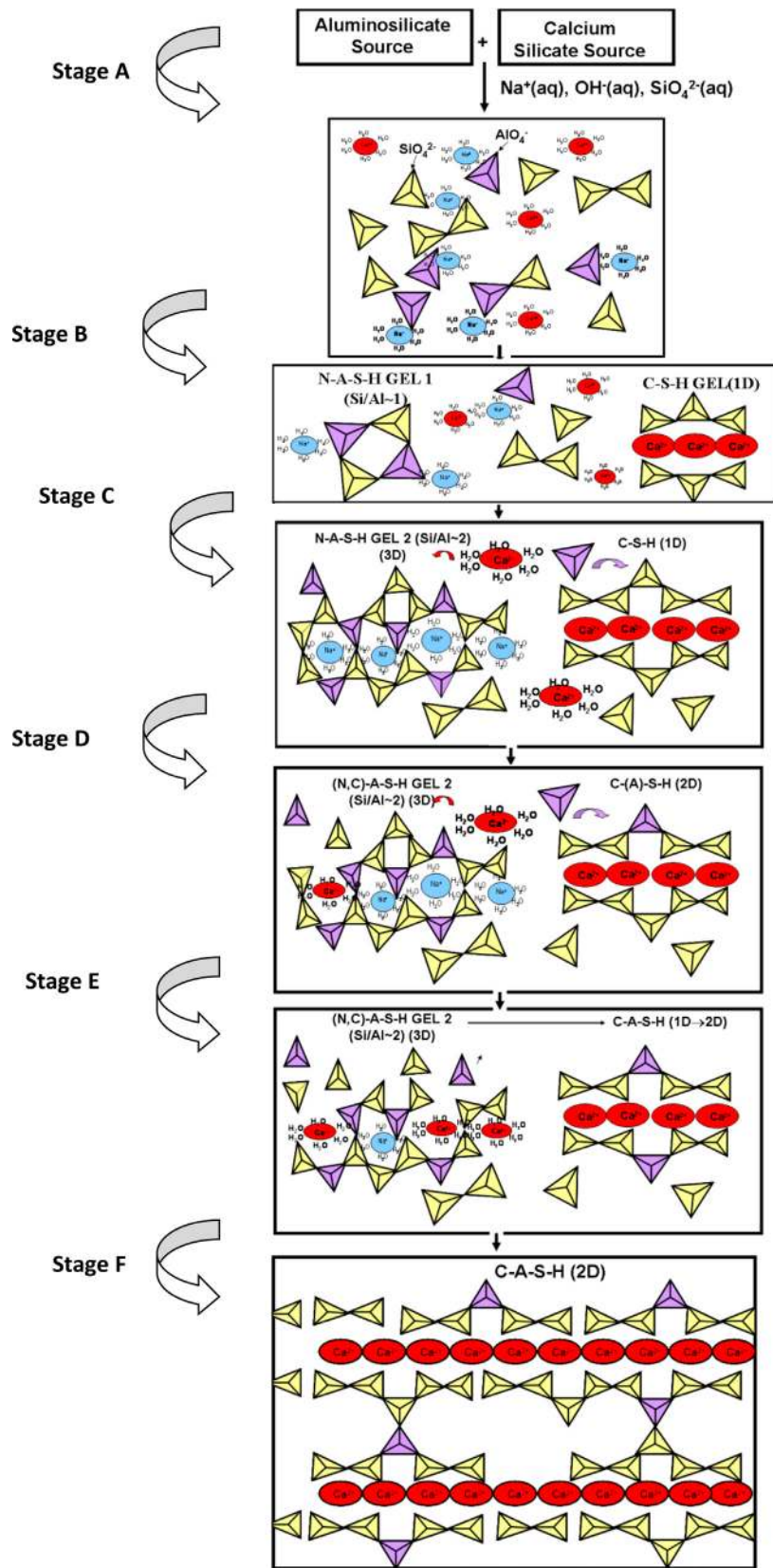


FIGURE 13. Alkaline activation model for cement blends with high silica and alumina and low calcium contents (70 % FA+30% OPC, Activator: NaOH+Wg) (42).



98–101, 107), also proposed a conceptual model describing the activation stages of high-silica and alumina and fairly low-calcium cementitious blends from the outset (first few hours) up to a full year (see Figure 13) (42).

The process begins with the dissolution of the sources of calcium and aluminosilicates in the alkaline solution via rupture of the T-O-T bonds (T: Si or Al) in the ash and the Ca-O and Si-O bonds in the cement, leading to a wide variety of dissolved species (*Stage A*). When the solution reaches saturation, N-A-S-H, an aluminosilicate gel, precipitates (*Stage B*). This gel initially adopts a compositionally metastable form with a high aluminium content (81). Analogously, the  $\text{Ca}^{2+}$  and silicon species resulting from the dissolution of portland cement react to form a C-S-H type gel. As the reaction progresses, more Si-O groups dissolve from both the original aluminosilicate (fly ash) and from the calcium silicate in the cement, raising the silicon concentration in the reaction medium and with it the silicon uptake in both gels. Hence, the N-A-S-H gel would change from a type 1 gel (*Gel 1*, Si/Al ratio  $\approx 1$ ) to a type 2 gel (*Gel 2*, Si/Al ratio  $\approx 2$ ) (81). In the C-S-H gel, in turn, Si uptake would enhance gel polymerisation (from chains comprising three silica tetrahedra to chains with five or more links, i.e., gels with a higher percentage of  $\text{Q}^2$  than of  $\text{Q}^1$  units) (*Stage C*). Stages B and C may take place at a relatively quick pace in these hybrid systems, and lead directly to the following stage, described below.

As the reactions progress, the Ca and Al ions present in the aqueous solution begin to diffuse across the cementitious matrix formed. A small number of Ca ions (not participating in the C-S-H gel) interact with the N-A-S-H gel to form a (N,C)-A-S-H gel. Given the similar ionic radius and electronegative potential between sodium and calcium ions, calcium replaces the sodium ions via ion exchange reminiscent of the mechanisms observed in clay and zeolites, maintaining the three-dimensional structure of the (N,C)-A-S-H-type gel (97). Similarly, the C-S-H gel forming from the silicates in cement takes aluminium into its composition (preferably) in bridge positions (65–69), yielding C-(A)-S-H or C-A-S-H gels as the aluminium content rises. The presence of tetrahedral aluminium in the bridge position may favour chain cross-linking, generating two-dimensional structures. This is the situation prevailing in 28-day hybrid cements (*Stage D*).

Where a sufficient store of calcium is available, it continues to diffuse into the pores in the matrix and interact with the (N,C)-A-S-H gel. The polarising effect of the  $\text{Ca}^{2+}$  (to form Si-O-Ca bonds) distorts the Si-O-Al bonds, inducing stress and ultimately rupture. As the N-A-S-H gel releases aluminium, less polymerised structures such as C-A-S-H gels form. At the same time, the C-A-S-H gel that formed in preceding stages is able to take up more

silicon and aluminium ions in bridge positions (68). The 1-year hybrid cements studied here would be in this stage of the reaction (*Stage E*).

Lastly, in the hypothetical stage in which hydration finalises (which may take years), the system would evolve, given sufficient time and the necessary experimental conditions (suitable calcium concentration and pH (104)), toward the most thermodynamically stable gel, a C-A-S-H-type gel.

In any event, sight should not be lost of the fact that although close to, the system studied was not in equilibrium. After one year of hydration, unreacted ash and cement particles co-existed in the cementitious matrix with secondary phases such as AFm or  $\text{Al}(\text{OH})_3$  type gels, along with a (N,C)-A-S-H / C-A-S-H gel mix which, over time, would evolve toward a single C-A-S-H gel.

#### 4. THE INDUSTRY AND ALKALINE CEMENTS. BRIEF CONSIDERATIONS ON CODES AND STANDARDS

The earliest known small-scale tests and large-scale industrial trials with alkaline cements date back to the nineteen sixties (applications in areas such as hydroelectric engineering, roads, civil engineering and mining). These initial experiences (105–112) confirmed the high performance of the concrete made with such cements, which proved to be particularly effective in specific sectors (see Table 2).

Over 50 years have lapsed since alkaline cements first made their way into the lives of construction material scientists and professionals. The efficiency and potential of these cements have been amply proven by the exhaustive research conducted in the interim in countries such as Russia, Ukraine, Poland, Finland, Japan, China, United States, Canada, India, Australia, Spain, United Kingdom and many others (108–115).

Over the years, any number of companies have been engaging in the manufacture, commercialisation and use of alkaline (primarily blast furnace slag) cement-based concrete structural members in a wide range of construction applications. Their experience has shown that when in service these concretes generally out-perform portland cement concretes in terms of many key properties. These materials are exceptionally effective under very severe service conditions. Moreover, unlike traditional cements, they have poly-functional properties and can be successfully used where high strength is needed in combination with quick hardening or corrosion or fire resistance (106, 109).

Many years of practical experience have been acquired by the pioneering Kiev school, while others (the Spanish (114) and Australian (116) schools in particular) have also gained a good deal of hands-on experience. More recent contributions have likewise

TABLE 2. Cement properties

Cement type	Early-age strength	<sup>1</sup> Durability	<sup>2</sup> Chemical resistance
Portland cement	++	++	+
Blended cement	+	+++	++
High alumina cement	+++	+	+++
High sulfate cement	+	++	+++
Sulfoaluminate cement	+++	++	+++
<b>Alkali-activated cement</b>	<b>+++</b>	<b>+++</b>	<b>+++</b>

<sup>1</sup>Durability = Degradation via mass transport and physical processes as freeze-thaw, wet/dry cycling, chloride penetration, steel corrosion in alkali-activated cement, carbonation, etc.

<sup>2</sup>Chemical resistance = basic chemical matrix degradation processes, as chemical attack by aggressive solution (seawater, sodium sulphate solution, acid solution, etc.), alkali-aggregate reactions, etc.

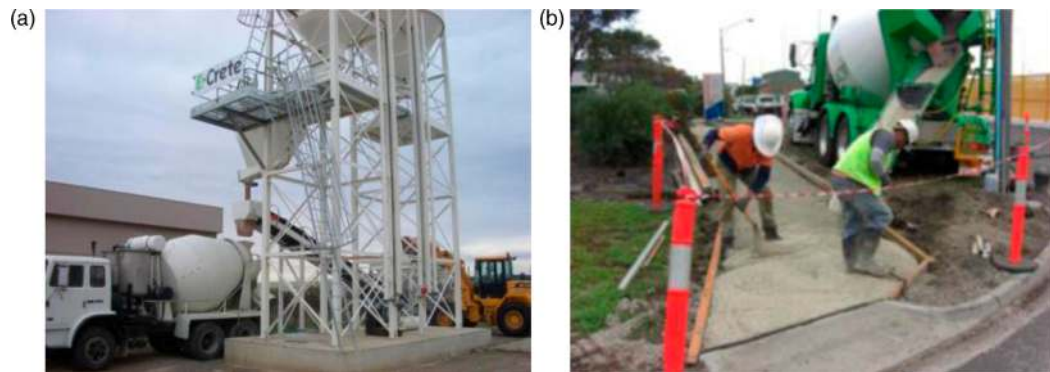


FIGURE 14. (a) Photograph of a concrete plant made from E-Crete™ (116); (b) E-crete FOOTPATHS at Brady St in Port Melbourne, Australia (117).

been forthcoming from academic institutions scattered around the world and private companies such as Zeobond and Cerasec, which have clearly placed their stakes on alkaline activation-based innovation. The joint findings of all these actors have led to the development of a series of technologies that capitalise on the enormous operating versatility of alkaline cements and concretes. The technologies in place today are briefly described below.

- In concrete technology (see Figure 14), prime materials (the aluminosilicate-bearing material, the alkaline activator and the rheology-modifying admixtures) are poured into a mixer, dry or in solution, and the components are simply mixed as they would be in conventional concrete technology.
- In cement technology (see Figure 15), all the prime materials (the aluminosilicate component, the alkaline activator and the rheology-modifying admixture) are ground jointly. The end product is packaged in bags for subsequent use in much the same way as conventional portland cement. The diagram in the figure below illustrates alkaline cement technology in simple

terms. With the technological improvements available today, plant equipment can be successfully adapted to this cement manufacturing process.

- With precasting technology (see Figure 16), precast elements can be made from alkaline concretes or alkaline cements made as described above. The most significant characteristic of precasting technology may be that it accommodates thermal curing of the material. That, in turn, is highly beneficial, for it enhances the manufacturing pace, shortening the time to placement on the worksite with no adverse effect on precast element durability.
- Other technologies have yet to be developed. Activities such as (structural and non-structural) clay-based materials manufacture, soil stabilisation, and toxic and hazardous waste immobilisation will certainly adapt alkaline activation to their standard working protocols in the near future.

The information in Table 3 reveals the enormous potential of alkaline activation as a source of products with a wide spectrum of applications.

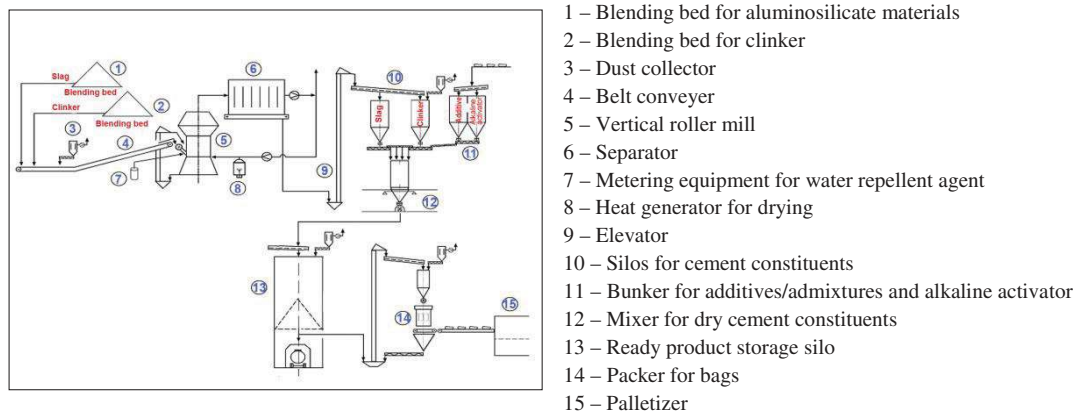


FIGURE 15. Hybrid cement plant.



FIGURE 16. (a) Photograph of a precasting plant; Production of (b) type 14 wall blocks (c) type 6 pavers.

By way of conclusion, some thoughts may be in order about how the quality of the products offered consumers by innovative companies can be regulated.

Today, before it can be brought to market, a newly developed product must be able to meet the standards required by national and international authorities. Alkaline cements could be commercialised in the former USSR thanks to the comprehensive codes and standards then in place. The Russian and Ukrainian (countries that formed part of the USSR during the better part of the twentieth century) industries are today benefitting from that legacy, which adopts the form of a substantial number of national standards on the industrialisation and commercialisation of this type of cements (117–119). In other words, the USSR authorities officially approved alkaline cements for the construction of all manner of structures, on a par with OPC (115, 11–13) (see Figure 17)

The latest standard on alkaline cements, and more specifically on the regulation of the various types of such cements, was approved in Ukraine in 2009. Like European standard EN-196, Ukrainian standard DSTU B V.2.7-181:2009 (120) classifies commercial cements based on their 2-, 7- and 28-day compressive strength. In the latter standard, alkaline cements are classified into the typologies given in Table 4 on the grounds of their 28-day composition and strength. The (compressive) strength

classes considered are: 300, 400, 400R, 500, 500R, 600, 600R, 700, 800, 900 and 1000. The standard applies to concrete manufacture for ordinary use.

In Ukraine, a whole body of standards (any number of documents) regulate the large-scale use of alkaline cements in construction. The symbolic significance of that *acquis* is of great value, for any other country in the world can follow in Ukraine’s footsteps.

Ukraine’s pioneering activity in the development of specific legislation on alkaline cements and concretes need not, however, be the sole inspiration for “legislators” drafting future standards. A highly promising alternative is to be found in US Standard ASTM C 1157 (121). This performance specification covers hydraulic cements for both general and special applications. There are no restrictions on the composition of the cement or its constituents.

This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of standard users to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. ASTM C 1157 covers hydraulic cements for both general and special applications:

- \* General Use (GU)
- \* High Early-Strength (HE)
- \* Moderate Sulfate Resistance (MS)
- \* High Sulfate Resistance (HS)

TABLE 3. Examples of potential uses of alkaline cements

		Corrosion-resistant concretes for marine engineering applications Immobilisation of liquid radioactive waste in alkali-activated cement.					
2010	Inorganic adhesives and glues, protective coatings for corrosive and high temperature environments						
1990			Acid-resistant concrete articles and structures		High-rise building with precast and cast-in-situ concrete		Compounds for radioactive waste immobilisation Precision tool housing
1985			Cast-in-situ concrete floors and landings		Concrete blocks for buildings, garages, storage houses, etc.		Dies, moulds
1980			Heat resistant concrete articles and structures		Floor slabs, foundation wall blocks, foundation blocks, piles	Oil well mortars and grouts	Linings of MD-pumps for aluminium melts
1975		Strengthened soils for road bases					
1970	Tubing of anti-slide systems	Cast-in-situ concrete pavements and precast reinforced concretes pavers	Cast-in-situ and precast concrete pasture sites, fertiliser storage space, silo pits	Foundation blocks, floor slabs, columns, beams, foundation wall blocs, elements of cleaning-up systems		Reinforced pit props, sleepers	
1960	Cast-in-situ and precast prestressed concrete sea break-waters, irrigation systems components	Pavement slabs, kerbs, landing field slabs					
	<b>Hydraulic Civil engineering</b>	<b>Roads</b>	<b>Agricultural</b>	<b>Industrial</b>	<b>Residential</b>	<b>Mining</b>	<b>Non-civil engineering</b>

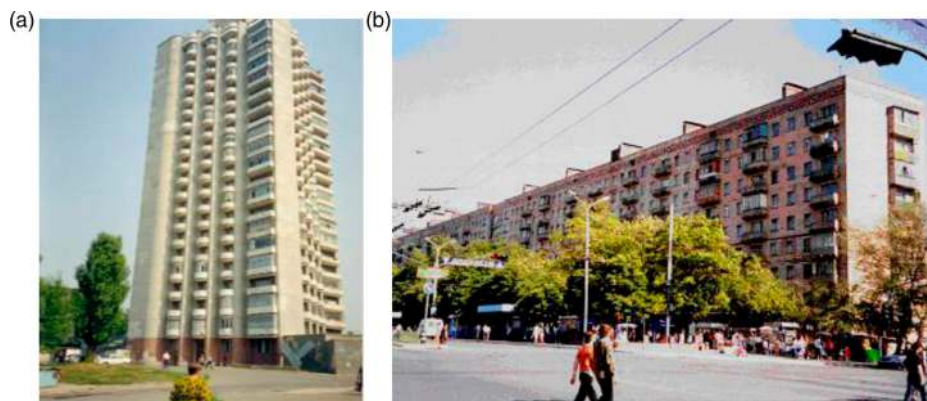


FIGURE 17. (a) The first residential building made of alkali-activated cement concrete without any OPC. (20-storey residential building, Lipetsk, Russian Federation, 1987–1989); (b) One of two 9-storey residential buildings, Mariupol, Ukraine, 1960 (11, 13, 115).

TABLE 4. Alkali-activated cement classification according to Ukrainian national standard DSTU B V.2.7-181:2009 (120)

Alkaline cement type	Designation	Content, % by mass					Alkali metal compounds (sodium or potassium)
		Aluminosilicate component					
		Granulated blast-furnace slag	OPC clinker	Fly ash	Basalt		
ACEM I	Slag alkaline cement	ACEM I	90–100	0–10	–	–	1.5–12
	Slag alkaline cement with additive of fly ash	ACEM I–3	55–90	0–10	10–35	–	1.5–12
ACEM II	Alkaline portland cement	ACEM II	–	100	–	–	1.5–12
ACEM III	Alkaline pozzolan cement	ACEM III–3	20–64		36–80	–	1.5–12
		ACEM III-B	←—————→		–	36–80	1.5–12
ACEM IV	Alkaline slag portland cement	ACEM IV	36–89	11–64	–	–	1.5–12
ACEM V	Alkaline composite cement	ACEM V	30–50	5–10	40–65	–	1.5–12

\* Moderate Heat of Hydration (MH)

\* Low Heat of hydration (LH)

With a view to the large-scale adaptation of alkaline cement technology the world over, in 2007 a RILEM technical committee (TC 224 – AAM) began to compile and summarise experiences (13) in connection with prime materials, cements, concretes, structures, output, test procedures, durability, envisaged use and so on. The ultimate aim is to develop basic recommendations for specifications designed to bring these cements to a market where they can compete on a level playing field with portland cements.

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