



## CIMENTURI HIBRIDE ALCALINE. PARTEA I: FUNDAMENTE<sup>▲</sup> HYBRID ALKALINE CEMENTS. PART I: FUNDAMENTALS

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*Concerns around the CO<sub>2</sub> emitted in Portland cement manufacture have driven the scientific community to seek alternative materials with the same features as Portland cement but which can be sustainably manufactured. One such category of materials includes the blended or hybrid cements.*

*These cements form when blends containing low proportions of cement and high proportions (60-70 %) of mineral additions (slag, fly ash or metakaolin) are alkali activated. This article reviews the fundamental chemistry governing these new reactive systems. It also analyses the nature of the reaction products formed and their compatibility under different reaction conditions.*

*Problemele îngrijorătoare, create de emisia de CO<sub>2</sub> în tehnologia de fabricare a cimentului portland au determinat orientarea comunității științifice către găsirea unor noi materiale, cu caracteristici asemănătoare cimentului portland, dar care pot fi fabricate fără implicații de ordin ecologic.*

*Acești lianți se pot obține prin amestecarea unor proporții mici de ciment, cu proporții mari (60-70%) de adaosuri minerale (zgură, cenușă zburătoare, sau metacaolin), cu activare alcalină. Lucrarea realizează o sinteză a fundamentelor chimice care guvernează aceste noi sisteme reactive. Se analizează, de asemenea, natura produșilor de reacție formați la întărire, în corelare cu diferite condiții de reacție.*

**Keywords:** hybrid cement, alkaline activation, N-A-S-H gel, geopolymers

### 1. Introduction

Portland cement concrete is today's construction material per excellence. It owes this pre-eminence to its mechanical strength, high value for money and generally good performance. Nonetheless, Portland cement manufacture raises certain energy and environmental issues, since it calls for temperatures of up to 1500 °C and raw materials whose quarrying mars the landscape, while emitting gases such as CO<sub>2</sub> and NO<sub>x</sub>. Moreover, concrete poses certain durability problems, such as the aggregate-alkali reaction and attendant expansion, chloride-induced corrosion in reinforcing steel [1, 2].

One of the options, widely accepted in the industry today, for reducing this impact while contributing to solve other environmental problems (finding a use for industrial by-products or wastes that must otherwise be stockpiled, a costly and pollution-prone procedure) is to include active (mineral or industrial by-product) additions at Portland cement clinker. This has given rise to different types of ordinary cements, presently listed in Spanish and European standard UNE-EN 197-1:2000, which specifies both the type and maximum amount of additions allowed.

Another more innovative option consists of

developing alternative, less expensive and less environmentally damaging cements (involving lower CO<sub>2</sub> emissions or the re-use of industrial by-products), that exhibit characteristics or performance comparable to or even better than ordinary Portland cements (OPC). One such category of materials includes a series of binders generically known as alkaline cements.

The alkali activation of fly ashes (AAFA) has shown to be an effective alternative to the traditional OPC systems. The AAFA systems have exhibited an excellent behavior, even better than the analogous hydrated OPC systems. However the chemistry involved in the reaction mechanisms (alkali activation of aluminosilicates vs hydration of calcium silicates) is quite different, as will be explain in detail below.

Today, there is a third option, a new type of binder known as a **blended or 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 around 20 %. The cementitious gels forming in this group are very complex and are in fact mixed, (C,N)-A-S-H or N-(C)-A-S-H-type gels.

This new option is an area of keen scientific and technological interest, and the compatibility between the two cementitious gels, N-A-S-H (the main reaction product in the alkali activation of

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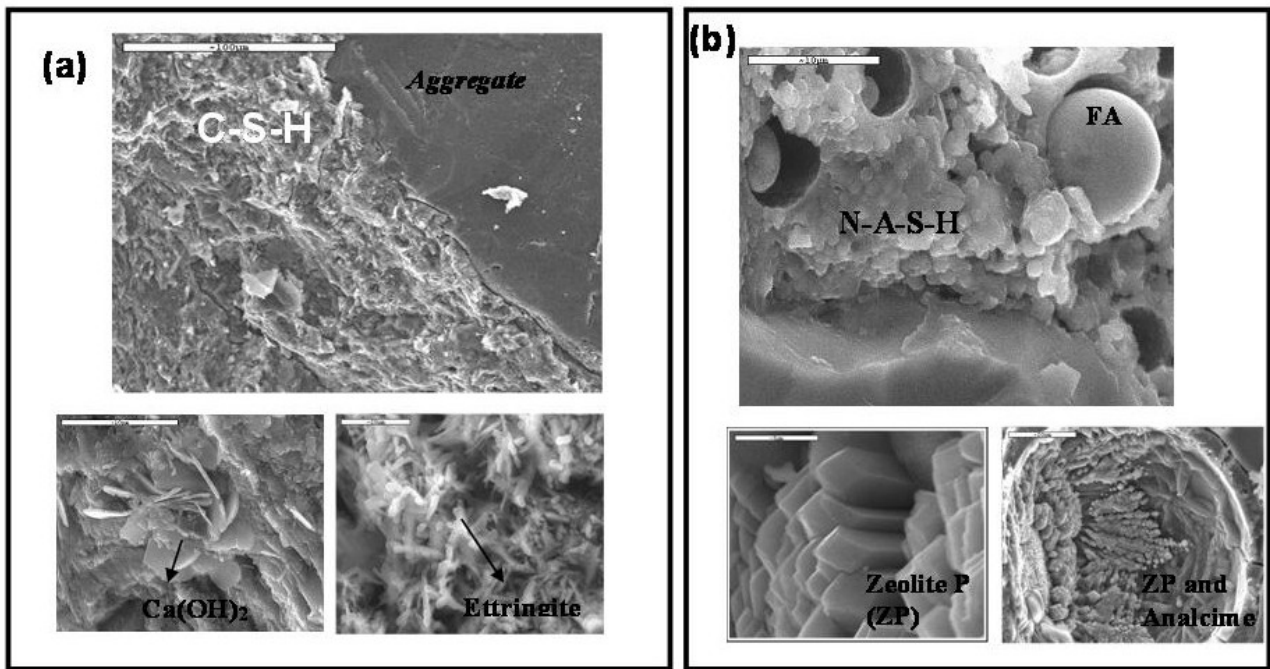


Fig. 1 - (a) SEM micrographs of a C-S-H gel and some secondary products (Ca(OH)<sub>2</sub> and ettringite) (b) SEM micrograph of a N-A-S-H gel and zeolites / (a) Micrografii SEM ale unui gel C-S-H și unor produși secundari - (Ca(OH)<sub>2</sub> și etringit); (b) micrografii SEM ale hidrocompușilor N-A-S-H gelici și compușilor zeolitici.

aluminosilicates, See Figure 1(a) and C-S-H or C-A-S-H (C-S-H containing aluminium in its compositions, See Figure 1(b)) as main reaction product in the OPC hydration, is the object of considerable research today [3]. The main details for this kind of systems will be explained below.

## 2. OPC hydration vs Alkali Activation of Aluminosilicates

It is well known that the main reaction product in Portland cement hydration, is calcium silicate hydrate, known as C-S-H gel, which is the respon-

sible for the mechanical properties of the end material. Portlandite, ettringite and calcium monosulphoaluminate, among others, form as secondary products [2] (See Figure 1(a)).

However, the alkaline activation of silica- and alumina-rich (and low calcium) materials such as fly ash and metakaolin leads to the precipitation of the main reaction product, an amorphous alkaline aluminosilicate hydrate (M<sub>n</sub>-(SiO<sub>2</sub>)-(AlO<sub>2</sub>)<sub>n</sub>·wH<sub>2</sub>O) known as N-A-S-H gel [3] (See Figure 1(b)). The secondary reaction products in this type of systems are zeolites such as hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite [3].

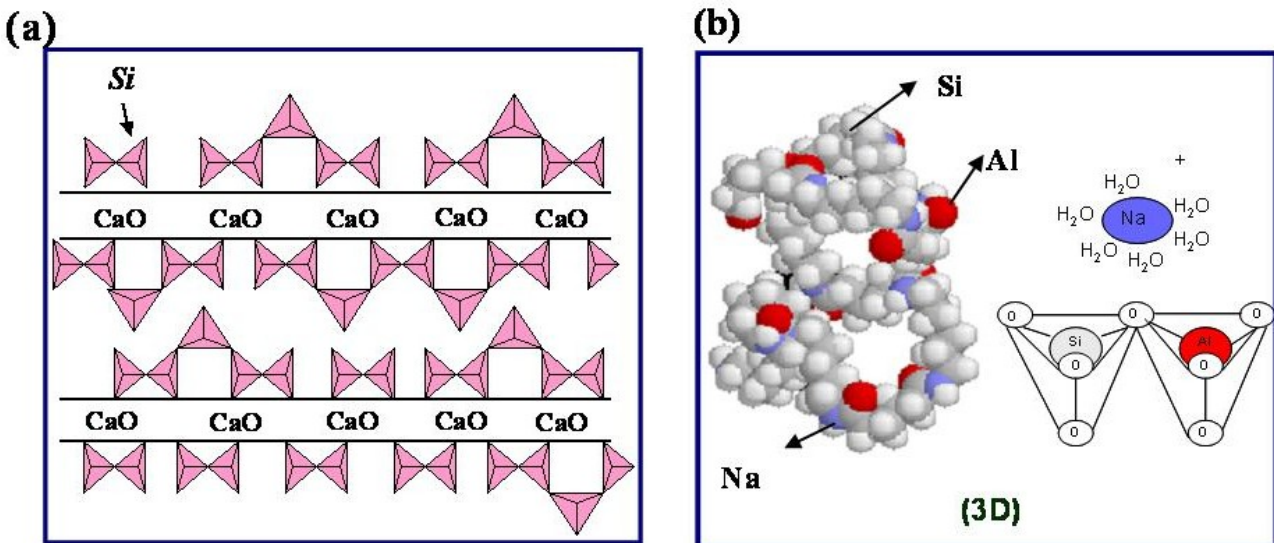


Fig. 2 - (a) C-S-H gel structure (b) N-A-S-H gel structure / (a) structura C-S-H gelici; (b) structura N-A-S-H gelici.

The two gels, C-S-H and N-A-S-H, have very different chemical composition and very different structures. Taylor based his well-known model for the C-S-H formed during OPC hydration on the structure of defective tobermorite, also known as dreirketten type chains [2] (see Figure 2(a)). Perfect tobermorite consists of two linear chains of silica tetrahedra arranged on either side of a central sheet of CaO. Every fourth silicate in the linear chain is repeated; of the three tetrahedra in each group, two are connected to the centre sheet of CaO by two oxygen bridges while the third, known as the bridging tetrahedron, is not connected to the CaO. On the nanostructural scale, then, 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-, or five-link chains (see Figure 2(a)).

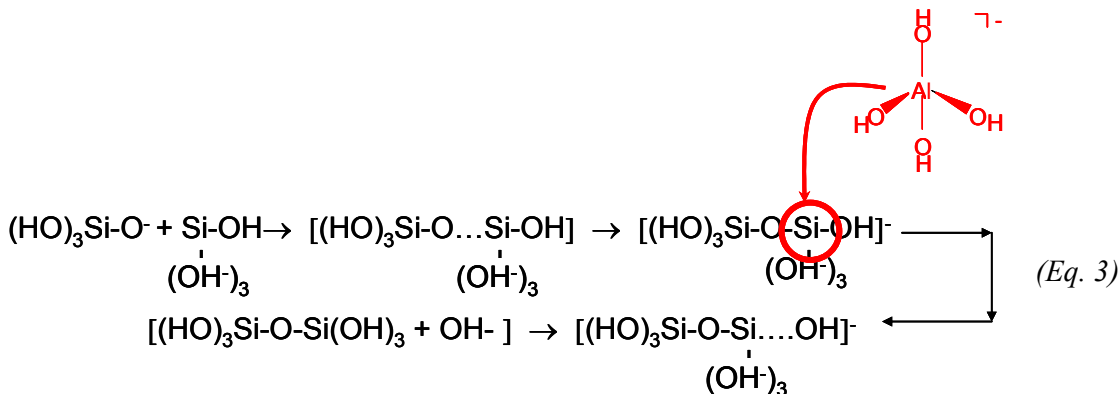
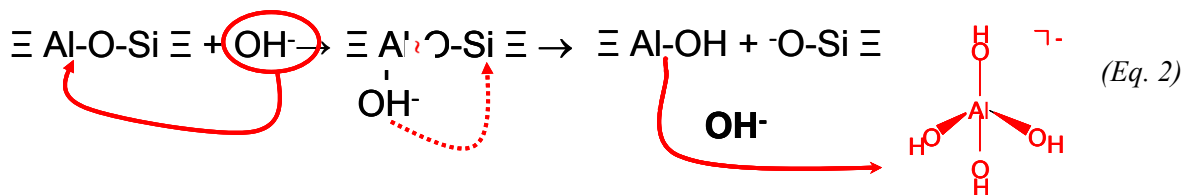
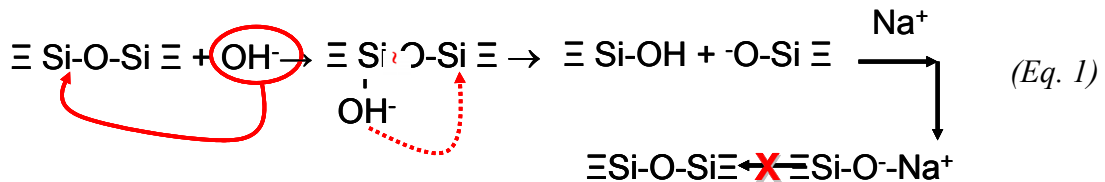
The structure of the gels forming in the alkaline activation of low calcium, aluminosilicates materials differs substantially from the gels formed in the activation of calcium-rich cements. These N-A-S-H gels are characterized by a three-dimensional structure (See Fig. 2(b)) in which the Si is found in a variety of environments, with a predominance of  $Q^4(3Al)$  and  $Q^4(2Al)$  units [4]. The  $Si^{4+}$  and  $Al^{3+}$  cations are tetrahedrally coordinated and joined by oxygen bonds. The negative charge on the  $AlO_4^-$  group is offset by the presence of alkaline cations (typically  $Na^+$  and  $K^+$ ).

The reaction mechanisms involved in the alkali activation of aluminosilicates differ substantially from the Portland cement hydration. This will be explained in detail below.

### 3. Reaction mechanisms in the alkali activation of aluminosilicates

Glukhovskiy [5] was one of the first authors to explore the reaction mechanisms involved in the alkaline activation of aluminosilicates. Based in the works of Carman and Iler [6] about the theory of silicic acid polymerization, *Glukhovskiy* [5] proposed a general mechanism for the activation reaction, consisting of three different stages: (a) Destruction-Coagulation; (b) Coagulation-Condensation; and (c) Condensation-Crystallization.

In the first stage, **destruction-coagulation**, the  $OH^-$  ions initiate the reaction with the rupture of the Si-O-Si bonds (Eq. 1). This takes place by the action of the  $OH^-$  redistributing the electron density around the silicon atom and rendering the Si-O-Si bond more susceptible to rupture. As consequence, silanol ( $-Si-OH$ ) and silates ( $-Si-O^-$ ) species are formed. The presence of alkaline metal cation neutralizes the resultant negative charge. The appearance of  $(Si-O-Na^+)$  bonds hinders the reverse reaction from forming siloxane bonds



Inasmuch as the hydroxyl groups affect the Al-O-Si bond in the same way, the aluminates in the alkaline solution form complexes, predominantly  $\text{Al}(\text{OH})_4^-$  (Eq. 2).

In the second stage, Coagulation-Condensation, accumulation enhances contact among the disaggregated products, forming coagulated structure where the polycondensation takes place (Eq. 3). This reaction is catalyzed by the  $\text{OH}^-$  ions. The clusters formed by the polymerization of silicic acid grow in all directions, generating colloidal particles. Aluminates also participate in the polymerization reaction, substituting isomorphously for silicate tetrahedra. While the alkaline metal catalyses destruction in the first stage, in the following two it is a structural component.

In the last stage, Condensation-Crystallization, the presence of particles in the initial solid phase promotes the precipitation of product whose composition is determined by the mineralogical and chemical composition of the initial phase, the alkaline component and the hardening conditions.

#### 4. Hybrid cements

Hybrid alkaline cements are complex cementitious blends with initial  $\text{CaO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  contents around 20 %, whose reaction products are intricate mixes of different gels (the type of product formed depends largely on the reaction conditions) [7-13].

The hybrid cementitious systems most frequently studied include:

- Portland cement – blast furnace slag blends
- Portland cement – phosphorous slag blends
- Portland cement – fly ash blends
- Portland cement – steel mill and blast furnace slag blends
- Portland cement – fly ash – blast furnace slag blends
- Multi-constituent cement blends

In 2005 Yip *et al.* [13] observed the coexistence of geopolymeric gel and a calcium silicate hydrate in the early reaction stages of alkaline activation of slag and metakaolin mixtures. The coexistence of these two phases was dependent on the alkalinity of the alkali activator and the MK/GGBFS mass ratio. The formation of C-S-H gel together with the geopolymeric gel occurs only in a system at low alkalinity, while in the presence of high concentrations of NaOH, the geopolymeric gel was the predominant phase formed with small calcium precipitates scattered within the binder.

In 2007 Palomo *et al.* [7] reported the results of research on hybrid cements containing 30 % Portland cement clinker and 70 % fly ash. Their characterization studies of the hardened matrices

showed that in all cases the reaction products consisted of a mixture of amorphous gels (C-S-H + N-A-S-H). These authors concluded that Portland cement hydration follows different pathways depending on the  $\text{OH}^-$  concentration and the presence of soluble silica in the medium. Another remarkable finding of these authors was that the fly ash activation at ambient temperatures is accelerated by the presence of Portland cement. The favourable effect of the presence of Portland cement on ash activation at ambient temperature may be explained by the heat released during OPC hydration reaction; the energy from this heat would in turn activate the chemical reactions that originate fly ash setting and hardening in highly alkaline media.

Summing up, prior studies have shown that the co-precipitation of these two gels in hybrid cements is possible [7,9,13], although recent research has revealed that the two products do not develop separately, as two separate gels, but that they interact, undergoing structural and compositional change in the process [14].

Consequently, the compatibility of the two cementitious gels, C-S-H/C-(A)-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.

#### 5. Co-precipitation of cementitious gels: C-S-H and N-A-S-H gels. Compatibility.

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 two main cementitious gels, N-A-S-H and C-S-H/C-(A)-S-H, is the object of considerable research today [11,14-16].

Research conducted on synthetic gels to determine the effect of the constituents of each on the other has led to the conclusion that high pH and the presence of aqueous aluminate impact C-S-H composition and structure [15]. Similarly, aqueous Ca modifies N-A-S-H gels, in which part of the sodium is replaced by calcium to form (N,C)-A-S-H gels [16]. Recent studies conducted by García-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 [14, See Fig. 3]. In the presence of sufficient calcium, pH values of over 12 favour the formation of a C-A-S-H rather than N-A-S-H gel. The experiments yielding these findings were conducted in equilibrium conditions, however, which are not normally present during binder hydration, particularly in the early stages of the reaction.

Recent studies carried out for the same authors in alkali activated "real binders" (70 % FA +30 % OPC mixtures) at short and long term (28 and 365 days respectively) showed that the C-S-H/N-A-S-H mix of gels precipitating did not precipitate in a pure state, but rather that their composition was affected by the presence of dissolved species (See Fig. 4) [11]. After one year of hydration, unreacted ash and cement particles co-existed in the cementitious matrix with secondary phases such as carboaluminae, along with a (N,C)-A-S-H /C-A-S-H gel mix with a tendency to form C-A-S-H gels. In any event, sight should not be lost of the fact that while close, the system was not in equilibrium.

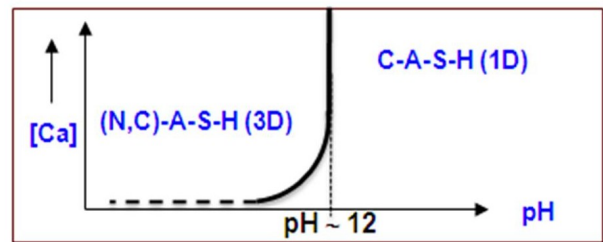


Fig. 3 - Model proposed for stability of N-A-S-H gel at high pH and in presence of Ca. At low pH,  $\text{Ca}^{2+}$  association with the 3D aluminosilicate framework is by ion exchange with  $\text{Na}^+$  up to saturation (broken line)[14] / Model propus pentru stabilitatea N-A-S-H gelici la valori mari ale pH și în prezența Ca. La valori mici ale pH, are loc înglobarea  $\text{Ca}^{2+}$  în rețeaua 3D aluminosilicatică, prin schimb ionic cu  $\text{Na}^+$ , până la saturare (linia întreruptă)[14].

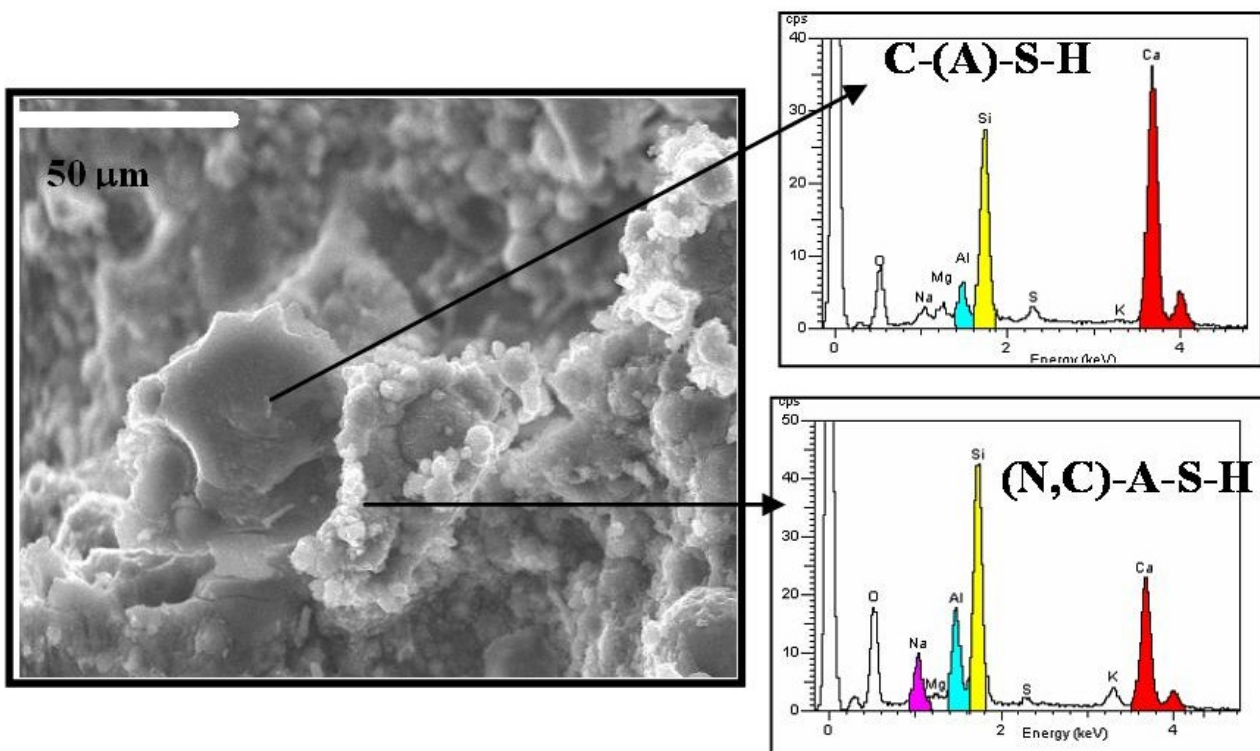


Fig. 4 - Co-precipitation of C-A-S-H and (N,C)-A-S-H in alkali activated blends (70 % FA + 30 % OPC) at 28 days / Co-precipitarea compușilor C-A-S-H și (N,C)-A-S-H în lianți micști, cu activare alcalină (70 % cenușă + 30 % ciment portland) la 28 zile.

## 6. Conclusions

The alkali activation of hybrid cements provides an alternative way to the use of traditional OPC mortars and concretes. The type of the final product depends on the reaction conditions (alkalinity, temperature...) and the percentage of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$ . The reaction mechanism involves a number of stages in which the original gels form in the OPC hydration, C-S-H gel and the gel precipitated in the alkali activation of aluminosilicates, N-A-S-H gel, evolve to C-A-S-H and (N,C)-A-S-H respectively. The characteristics of these new systems suggest that this new generation of cements can be consider as an alternative to the traditional OPC systems.

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## MANIFESTĂRI ȘTIINȚIFICE / SCIENTIFIC EVENTS



### 8<sup>th</sup> International Conference on Fracture Mechanics of Concrete and Concrete Structures 10-14 March 2013 University of Castilla LaMancha, Toledo, Spain

The major topics for FraMCoS-8 are as follows:

- Recent advances in fracture mechanics of concrete
- Fracture and cracking behavior of reinforced and prestressed concrete structures
- High-performance, high strength concretes and FRC
- Advances in structural design codes
- Structural monitoring and assessment
- Repair and retrofitting, practical application
- Durability and corrosion-induced cracking
- Interface fracture and debonding phenomena
- Constitutive relations, time-dependent effects, cyclic and fatigue behaviour
- Brick masonry, concrete-like and quasi-brittle materials
- Computational aspects in fracture mechanics of concrete

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