

Basic Principles of Hybrid Alkaline Cements

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Abstract. A line of research of particular interest being pursued at this time is the development of new cements known as **blended or hybrid alkaline cements**. These cements form when blends containing low proportions of cement and high proportions (60-70 %) of mineral additions (such as blast furnace slag, fly ash or metakaolin) are alkali activated. The reaction products precipitating in these systems are very complex and actually comprise a mix of gels: C-(A)-S-H type gels (similar to the gels obtained during cement hydration, but with aluminium in their composition) and (C,N)-A-S-H gels (similar to the N-A-S-H gels obtained during the alkaline activation of aluminosilicates, but with calcium in their composition). The prevalence of one or the other gel depends on a number of factors, including the concentration of the initial species in the solution, type of activator used, pH values and reaction time. The paper reviews the fundamental chemistry governing these new systems and the activation mechanisms involved. It also analyses the nature of the reaction products formed and their compatibility under different reaction conditions.

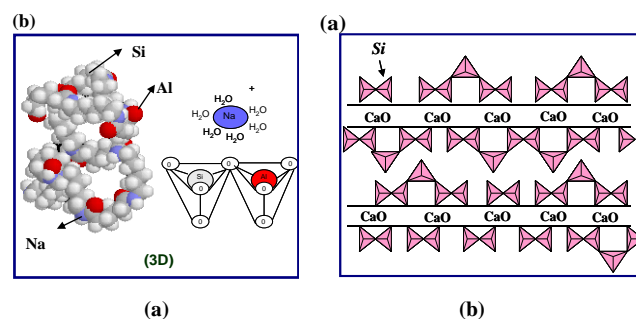
1 Introduction

Portland cement concrete is today's construction material per excellence. It owes this pre-eminence to its mechanical strength, low cost 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 CO₂ and NO_x.

Concerns around the CO₂ 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 a series of binders generically known as alkaline cements [1].

The alkaline activation of aluminosilicates is a line of research that has delivered very promising results in terms of the properties of the resulting cements. The main differences between this procedure and normal Portland cement hydration lie in the high alkaline content and the substantially lower total calcium content in the materials. In these systems the main reaction product and the one to which mechanical strength development and durability are attributed is a N-A-S-H gel (see Fig. 1(a)), a three-dimensional alkaline aluminosilicate structure very different from the calcium silicate hydrate (C-S-H gel) obtained in OPC hydration (See Fig. 1(b)).

Fig. 1 (a) N-A-S-H gel structure (b) C-S-H structure



Today, there is an innovative option, a new type of binder known as a blended or **hybrid alkaline cement** [2], formed as the result of the alkaline activation of materials with CaO, SiO₂ and Al₂O₃ 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 aluminosilicates, See Fig. 1(a)) and C-S-H or C-A-S-H (C-S-H containing aluminium in its compositions, see Fig. 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 are explained below.

2 Alkali activation of aluminosilicates

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 ($M_n-(SiO_2)-(AlO_2)_n \cdot wH_2O$) known as N-A-S-H gel [1] (See Fig. 2(a)). The secondary reaction products in this type of systems are zeolites (See Fig. 2(b)) such as hydroxysodalite, zeolite P, Na-chabazite, zeolite Y and faujasite [1].

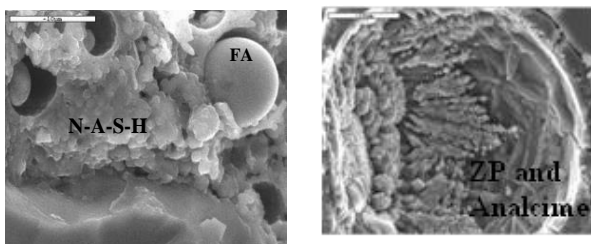


Fig. 2 (a) N-A-S-H gel (b) Zeolites (ZP and analcime)

The reaction mechanisms involved in the alkali activation of aluminosilicates differ substantially from Portland cement hydration.

N-A-S-H gel formation entails a series of stages (basically hydrolysis and condensation reactions) that can be summarized in Fig. 3[3]. When the source of aluminosilicates comes into contact with the alkaline solution it dissolves into several species, primarily silica and alumina monomers. These silica monomers react with more monomers to form dimers, with the formation of Si-O-Si bonds (a). But these species can also react with aluminate species, forming Si-O-Al bonds. The aluminate species enhance polymerization due their tendency to form bridging tetrahedra between silica units (b). As a consequence of the continuous polymerization process we will finally have 3D type structures (c).

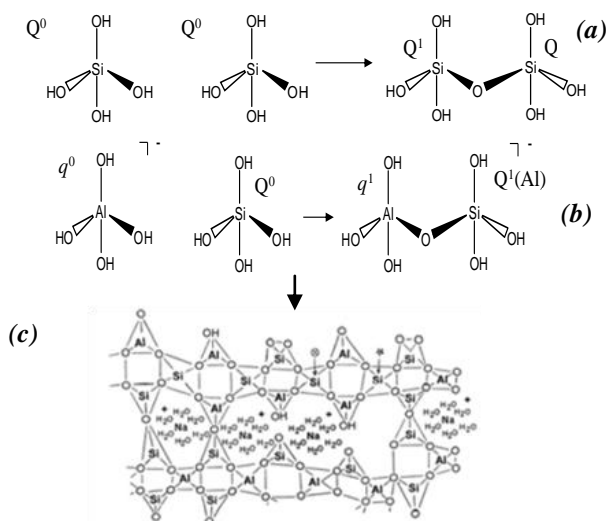


Fig. 3 Condensation of silanol/aluminol groups to form Si-O-Si and Si-O-Al linkages [3]

3 Hybrid Alkaline Systems

Hybrid alkaline systems are complex cementitious blends with a total $CaO + SiO_2 + Al_2O_3 \geq 80-90\%$ of the total weight, in which each individual component

represents at least 20%. In these systems the type of the product formed largely depends on the reaction conditions, including the chemical composition of the prime materials, alkaline activator type and concentration and curing temperature.

The hybrid cementitious systems most frequently studied included mixtures of Portland Cement (OPC) with Blast Furnace slag blends (BFS), with Fly Ashes (FA) or with even both [2]. The specific composition for these hybrid cements will depend on the initial proportions of the prime materials used.

In general terms, in systems containing Portland clinker (OPC), C-S-H gel normally prevails as the main reaction product in slightly alkaline media (i.e 2N NaOH) [2], whereas a N-A-S-H type gel prevails in highly basic environments (such as 10N NaOH). Consequently, the compatibility of the two cementitious gels, C-S-H and N-A-S-H is the object of considerable research today[2].

3.1. Co-precipitation of cementitious gels

Different studies have shown that the co-precipitation of these two gels in hybrid cements is possible [4-5], 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 changes in the process [6]. 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 affects C-S-H composition and structure [7]. Similarly, aqueous Ca modifies N-A-S-H gels, in which part of the Na is replaced by Ca to form (N,C)-A-S-H gels [8].

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 [6, See Fig. 4]. In the presence of sufficient calcium, pH values above 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.

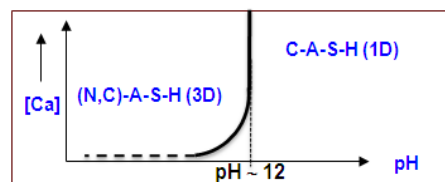


Fig. 4 Model proposed for stability of N-A-S-H gel at high pH and in presence of Ca[9].

Research carried out for the same authors in alkali activated “real binders” (70 % FA +30 % OPC mixtures) over the medium 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 [6]. A conceptual model to describe the variation over time in this hybrid cements was proposed (see Fig. 5) [6].

The process begins with the dissolution of Si, Ca and Al sources providing Si, Al and Ca ions which are not uniformly distributed (*Stage A*). Silica monomers react with other silica monomers to form dimers, but also with $\text{Al}(\text{OH})_4^-$ type species. The result is the precipitation of an aluminosilicate compound, a N-A-S-H gel (which is rich in Aluminium, Type I). Analogously, the Ca^{2+} and silicate species resulting from the dissolution of Portland cement react to form a C-S-H type gel (*Stage B*).

As the reaction progresses, more Si-O groups dissolve from the original aluminosilicate (fly ash) increasing the silica content in the medium. This allows the evolution of the N-A-S-H gel type I (rich in Al) to a gel type II (rich in Si). But Si can be incorporated into C-S-H gel structure, which enhances the C-S-H polymerization degree (*Stage C*).

With time, the Ca^{2+} and $\text{Al}(\text{OH})_4^-$ ions present in the aqueous solution begin to diffuse through the already hardened cementitious matrix. A small fraction of Ca^{2+} 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. Similarly, the C-S-H gel forming from the silicates in cement takes aluminium into its composition (preferably) in bridge positions yielding C-(A)-S-H \rightarrow C-A-S-H gels as the aluminium content rises.

Where a sufficient store of the element is available Ca^{2+} continues to diffuse in N-A-S-H gel structure \rightarrow The polarising effect of Ca^{2+} distorts the Si-O-Al bonds, inducing their rupture (less polymerized structures) (*Stage D*).

After one year of hydration, unreacted ash and cement particles co-existed in the cementitious matrix with secondary phases such as carboaluminates, 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 yet in equilibrium (*Stage E*).

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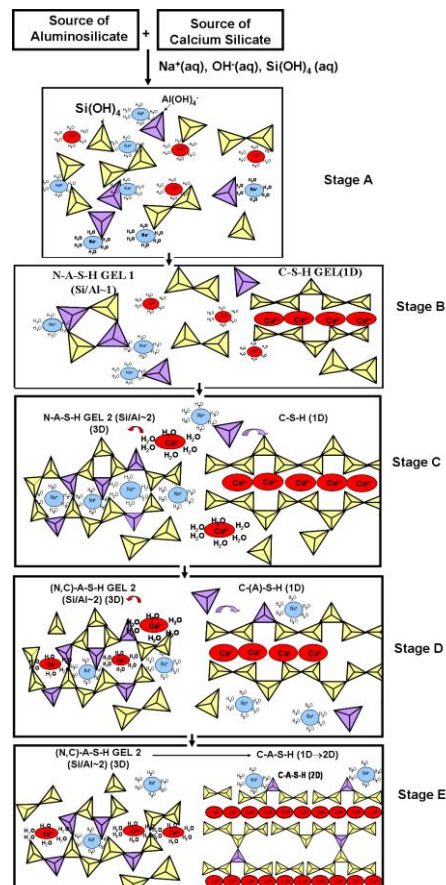


Fig. 5 Conceptual model proposed to describe the variations in hybrid cements over time [6]

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