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Activation of aluminosilicates - some chemical considerations

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Abstract

Apart from water, concrete is the most widely used material on earth, with the equivalent of nearly three tonnes per person being produced annually. However, the environmental sustainability of concrete is in the spotlight; its binding constituent, Portland cement, contributes about 5% of global CO₂ emissions during manufacture. In its pursuit of viable low-CO₂ alternatives, the cement research community is addressing process efficiency and alternative binders. To dilute Portland cement content, alkali activation of high volume aluminosilicate additions to Portland cement is being considered. This paper reviews the fundamental chemistry applicable to aluminosilicate reactivity, phase formation and phase compatibility in hybrid Portland cement-alkali-activated binders. The role of ion polarisability in phase (gel) formation is explored.

Introduction

Society's reliance on the conveniences of a modern built infrastructure and economic growth in developing countries has placed great demands on building materials, and in particular, concrete, which is already the world's most widely produced construction material at around 10 cubic kilometres per year. The corresponding demand on global cement manufacture is equally great yet each tonne of Portland cement produces around 0.83 tonnes of CO₂ to the atmosphere.¹ With the impact of CO₂ on global climate change now being widely recognised, the search for low-CO₂ cements as partial replacements or complete alternatives to Portland cement has prompted innovative thinking in the development of new binders and a review of existing systems for greater efficiencies.² Amongst the systems considered to offer reductions in CO₂ emissions are the alkali-activated aluminosilicates, on which considerable research literature has been generated in recent years, including some significant review articles.³⁻⁵

However, a complicating factor in rationalising the literature on alkali-activated systems has been the range of aluminosilicate materials which have been studied.

Properties of systems containing natural (kaolinite), processed (metakaolin) and industrial waste materials (coal combustion fly ash, blast furnace and ferro-nickel slags) have been reported and reviewed.^{4,6} Immediately, factors, which are known to influence set characteristics and strength development in conventional cement systems, can be identified, *e.g.* particle size distribution, glass content (reactivity), concentrations of interfering ions, *etc.* Further, various activating admixtures have been used to promote aluminosilicate reactivity (sodium or potassium hydroxide) and consolidation of microstructure through enhanced gel formation (sodium or potassium silicate solutions) in these studies. The variability in materials used, activator concentrations and mix proportioning means that interpreting the 'geopolymerisation' contribution to product performance from one system to another is particularly challenging.

If consistent performance of alkali-activated systems is to be addressed and exploited in constructional concretes, more emphasis must be placed on understanding the fundamental mechanisms which underlie the 'geopolymerisation' process and how these can be optimised in real systems. Fortunately, this challenge has been accepted by several groups in recent years and important insights into aluminosilicate reaction kinetics^{7,8} and the chemistry of gel formation and maturity have been reviewed.³ Whilst this knowledge is challenging to translate to physico-mechanical properties, important first steps have been taken.^{9,10}

It is unlikely that alkali activated aluminosilicate systems will completely replace Portland cement in constructional concretes but by providing additional activation potential to blends containing high volume of supplementary cementitious materials (SCM's), the required binder performance may be achievable with considerably reduced Portland cement contents and correspondingly reduced CO₂ emissions.

It is important to recognise that in conventional use, SCM's are activated by the alkali released by Portland cement (or lime) hydration, but significantly, the hydration process and ultimate products are similar to those of Portland cement hydration and are fundamentally different from those arising in 'geopolymer' systems. This paper discusses some of the fundamental chemistry, which defines the different hydration processes and products, and presents results of some recent studies on the equilibria established between the 'geopolymer' (N-A-S-H) gels and the C-A-S-H gels normally found in Portland and blended cement systems.

Reactivity and Hydrate Formation in Alkali-activated systems

Hydrolysis

The reaction mechanisms leading to phase formation in alkali-activated systems was discussed initially by Glukhovskiy¹¹ in 1959 and summarised more schematically in the review by Duxson *et al.*³ in 2007. The hydrolysis of silicates (and aluminosilicates) defines the initial reactivity of the substrate. The fundamental chemistry of aqueous silica and silicate systems were initially reviewed by Iler¹² in 1955 but even within the cement chemistry theme, there has been much interest, *e.g.* in the context of the alkali-silica reaction.¹³ Essentially, the alkaline hydrolysis of an aluminosilicate can be described schematically as follows:^{13,14}

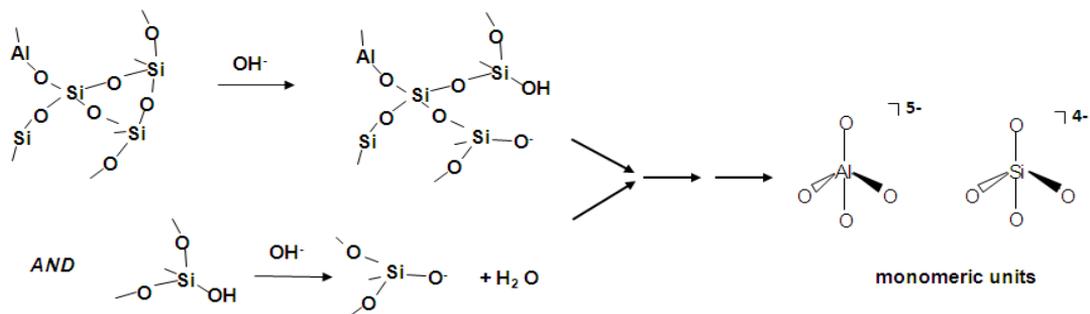


Figure 1: Hydrolysis of aluminosilicates leading to fragmentation and ultimately to aqueous monomeric silicate and aluminate species

There has been some discussion of the factors which control the rate of aluminosilicate hydrolysis (reactivity) and this can be linked to the mainly glassy 'structure' of the substrates used. In a review of alkali-activated metakaolin and blast furnace slag studies, Li⁶ concludes that, although important, glass content does not correlate with reactivity. Instead, structural heterogeneity within the glass is thought to be important.¹⁵⁻¹⁷ Moesgaard *et al.*¹⁵ proposed a heterogeneous structure with domains of highly polymerised aluminate and silicate and domains of predominantly silicate in their synthetic lime-alumina-silica glasses and correlated higher reactivity in cement systems with this heterogeneity.¹⁸ This is consistent with attributing the observed higher rates of solubility of aluminosilicate minerals to the more energetically favourable hydrolysis of the $-\text{Al}-\text{O}-\text{Si}-$ linkages over $-\text{Si}-\text{O}-\text{Si}-$ ^{19,20} and may be explained given that, due to polarisation by the different cations, the electron density around the bridging oxygen in an aluminosilicate linkage experiences uneven distribution offering a preferred site for hydrolytic attack. Consequently, a higher aluminate content in an aluminosilicate glass might be expected to offer higher dissolution rates and consequently better reactivity as indicated for observations of Class F fly ashes relative to other substrates.¹⁷

Condensation and the effect of cations

Condensation reactions are ubiquitous in inorganic cementing reactions, leading to the elimination of water and extended gel networks such as C-S-H gel, the principal binder in Portland cement pastes. The open framework 3D structure identified as the product in Figure 2 is a proposed structure for the N-A-S-H gel arising from the ‘geopolymerisation’ of kaolinite²¹ in which the degree of condensation is somewhat greater than that found in hydrated Portland cement systems, *i.e.* involving more of the four T-O- linkages in the tetrahedral TO₄ building units of the structure, where T is Al or Si. This degree of condensation is strongly influenced by the nature of the available cations. In ‘conventional’ geopolymer systems, the cations are typically Na⁺ or K⁺. These ions are of particular interest because they mark a differentiation in coagulation behaviour of silica sols^{22,23} due essentially to differences in their ionic size and, consequently, to tendencies to hydration. Cations in an aqueous environment establish an association between their positive charge and the partial negative charges on the oxygens of the surrounding water molecules; this configuration (Figure 3) is a response to the Lewis acidity of the cation with the oxide ion (from water) being the Lewis base. It has been shown that the relatively high charge density of Li⁺ and Na⁺ (Z/r in Table 1) ensures that these ions remain hydrated, even at high pH, whereas K⁺ and larger alkali metal ions are less strongly hydrated and can shed hydration water to associate with negatively charged silicate surface sites; the less negative ΔH_{hyd} indicates less tightly bound water. It is suggested that Li⁺ and Na⁺ promote gelling because this ‘structural’ water co-ordinates hydrogen bonding between silicates²³ whilst the weakly hydrated K⁺ and larger alkali metal cations cannot.

Table 1: Cation characteristics relevant to hydration chemistry in cementitious systems

	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺
Radius, Å	0.68	0.97	1.33	0.66	0.99
Z/r	1.47	1	0.75	3	2
$\Delta H_{\text{hyd}}^{\circ}/\text{kJmol}^{-1}$	-519	-406	-322	-1921	-1577

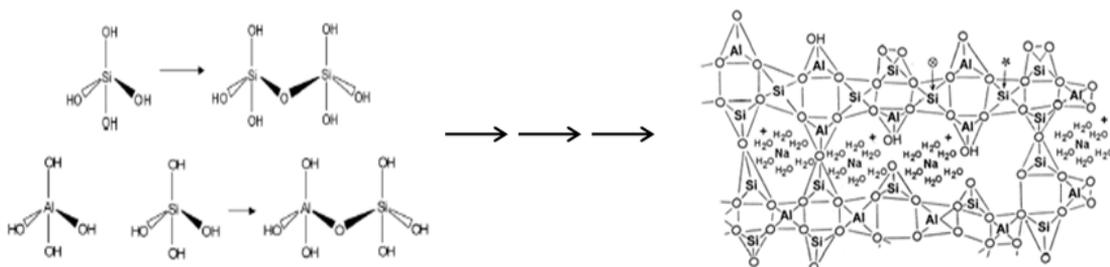


Figure 2: Condensation of silanol/aluminol groups to reform –Si-O-Si– or –Si-O-Al– linkages in the formation of bonded networks

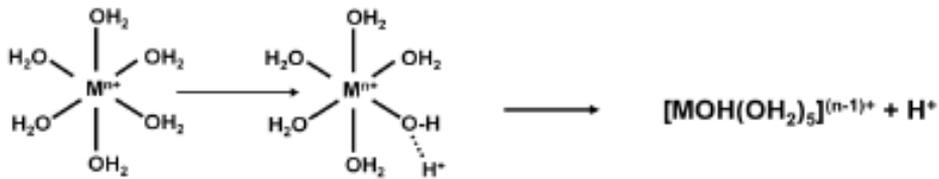


Figure 3: Hydrolytic dissociation of a hydrated cation as a function of increasing pH

Silica sols provide a reasonable model for cement-related systems in which the reacting surface may be only partially dissolved but the same situation has been observed by McCormick *et al.*²⁴ when suspended solids are fully solubilised. This dependency of coagulation/gelling tendency on the polarisability (acidity) of the metal cation offers some explanation for the observed differences between geopolymer systems activated by Na and K hydroxide/silicates.^{25,26}

The effect of Ca^{2+}

There is already considerable evidence that the presence of Ca strongly influences the alkali-activation process and the hydration products formed. Indeed, the products of alkali activation of blast furnace slags (BFS), which contain appreciable Ca, are typically more similar to C-S-H gel found in the hydration of Portland cements.^{27,28} From the discussion above, and the ion size and corresponding hydration enthalpy data listed in Table 1, it can already be suggested that aqueous Ca^{2+} (or Mg^{2+}) will have a stronger influence on gelling than the alkali metal cations but, as Figure 3 illustrates, increasing pH further increases polarisation of electron density into the M-O bond which weakens the O-H bonds, eventually releasing a proton by hydrolytic dissociation. This leads to the formation of M-OH ion-pair species such as $[\text{CaOH}]^+$, the concentration of which increases with pH as shown in Figure 3. The increasing strength of the M-O interaction is therefore summarised in Figure 4 (as $[\text{M}^{n+}\text{-OH}]/[\text{M}^{n+}]$ increases) and illustrates additional gelling potential,

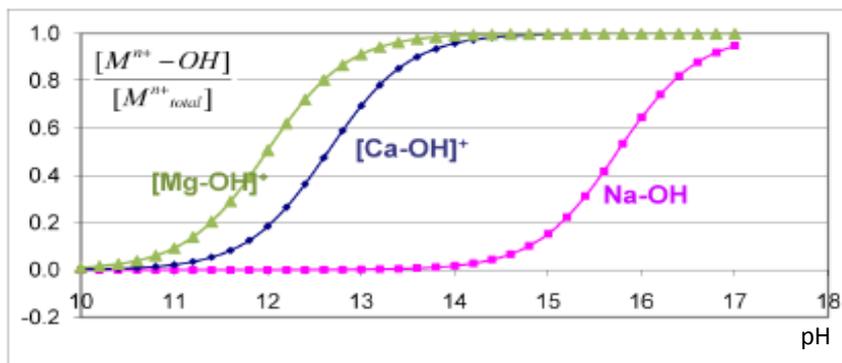


Figure 4: Formation of M-OH ion pairs as a function of pH; formation constants for $[\text{NaOH}(\text{OH}_2)_5](\text{aq})$, $[\text{CaOH}(\text{OH}_2)_5]^+(\text{aq})$ and $[\text{MgOH}(\text{OH}_2)_5]^+(\text{aq})$ as $10^{-0.4}$, $10^{-1.36}$ and $10^{-2.01}$ respectively

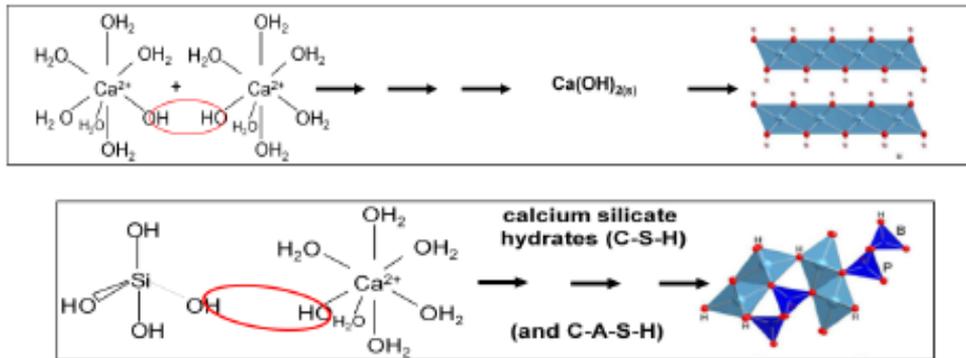


Figure 5: Proposed mechanisms for precipitation through condensation of cement-relevant phases

either *via* increased hydrogen bonding brought about by the increase in polarity of the remaining O-H bond, or *via* enhanced condensation reactions as illustrated in Figure 5. Consequently, $\text{Ca}^{2+}(\text{aq})$, at sufficiently high pH, may be predicted to have a high tendency towards precipitating silicates (or aluminosilicates) from solution through such mechanisms, its effectiveness limiting the higher degree of directional polymerisation which would arise if Li^+ or Na^+ were co-ordinating gel formation.

Phase Equilibria in the $\text{Na}_2\text{O-CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ system

Recent studies by Garcia-Lodeiro *et al.* have explored equilibria between the N-A-S-H gels typical of alkali-activated fly ash or metakaolin, and aqueous Ca^{2+} ,²⁹ and also the effect of alkalis on C-S-H gel.^{30,31} However, their study on equilibria between the different gel types has only recently been completed.³² Figure 6 summarises the phase relations observed at 25°C.

All phase compositions indicated are of solids precipitated from solution and aged until constant aqueous phase composition was observed with time as an indicator of equilibrium. Phase development in the CaO-rich region of the diagram includes aluminium-substituted C-S-H, gehlenite hydrate, AF_m phases (including hemi- and mono-carboaluminate as it was difficult to completely exclude CO_2 from these experiments) and $\text{Ca}(\text{OH})_2$. The clustering of compositions together with information from the literature, *e.g.* on the C-A-S-H phase field,³³ informed phase assemblage identification as indicated in Figure 6. It should be noted that all phases were precipitated under different concentrations of NaOH, the Na_2O content being represented towards the Na_2O apex above the plane of the image. Correspondingly, all compositions are projected onto the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ plane of the diagram. However, for the CaO-rich phases discussed, the residual Na_2O associated with them was negligible and so compositions lie virtually on the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ plane.

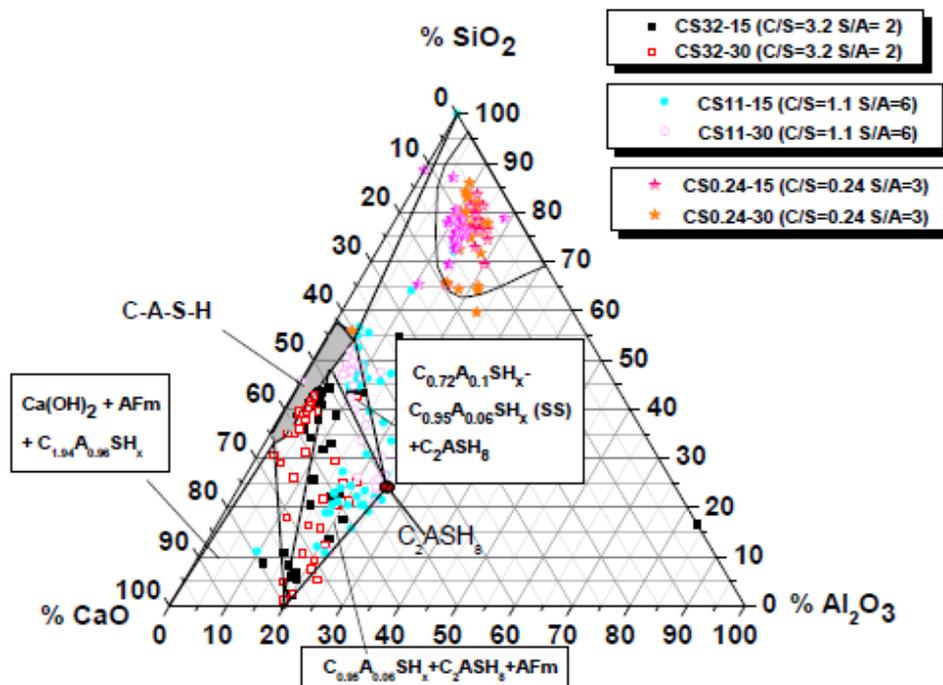


Figure 6: CaO-Al₂O₃-SiO₂-H₂O projection diagram showing tentative phase field boundaries; compositions are expressed in mole %. The highlighted area indicates the probable extent of C-A-S-H gels. Original bulk aqueous compositions are indicated in the figure legend by the label format CS(CaO/SiO₂)-(mol% Na₂O); e.g. CS32-15 indicates CaO/SiO₂ = 3.2, Na₂O content = 15 mol%.

Towards the SiO₂-rich region, the cluster of compositions highlighted represents N-A-S-H gels, confirmed by structural analysis, with associated Ca. Here the Na₂O content is not always negligible but examination of the experimental data showed that the solution pH for these systems was less than 12 (and typically less than 11.5). Given that N-A-S-H gels have zeolitic characteristics, the possibility of Ca adsorption by ion exchange was considered and it was shown that the Ca loading on these precipitates corresponded to between 67 and 100% of the exchange capacity depending on the Si/Al ratio of the N-A-S-H gel. These products were designated (N,C)-A-S-H gels. However, where higher pH was maintained (pH > 12), as in systems in which C-S-H gel was precipitated, N-A-S-H gels, if forming at all, were unstable, undergoing pozzolanic activity similar to that expected and observed for zeolites.³⁴ Further, in a parallel approach, FTIR data (Figure 7³²) showed that direct mixing of N-A-S-H and C-A-S-H gels in an aqueous suspension yielded a tendency towards C-A-S-H structure.

These observations appear to validate the observed prominence of C-A-S-H in systems where Ca is present^{27,28} but suggest that a critical pH is necessary to activate Ca participation in complexation and precipitation. A pseudo-phase diagram was proposed³² to summarise the situation (Figure 8).

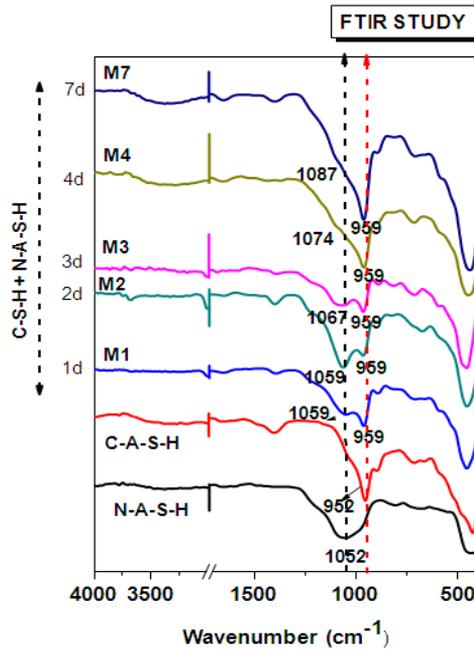


Figure 7: FTIR data of products derived from the direct mixing of pre-synthesised C-A-S-H and N-A-S-H gels for up to 7 days. Starting material spectra are included to show the prominent character of the parent gel in the absorbance between 960 and 1100 cm^{-1} .

With reference to Figure 4, it may be suggested that the precipitating influence of aqueous Ca is correlated with the quantitative polarisation characteristics discussed above and that the phase relations reported in Figure 6 are a response to the aggressive reactivity of aqueous Ca at pHs in excess of 11.5-12. There, it is shown that high CaO phases, *e.g.* lime-rich C-S-H, are incompatible with N-A-S-H gels at these pHs, the reaction products being a low CaO C-A-S-H gel with gehlenite hydrate and an aqueous phase. Only C-A-S-H gels of minimum Ca/Si can be compatible with N-A-S-H at high pH. If pH is allowed to fall, Ca^{2+} is insufficiently polarising to degrade the N-A-S-H structure and may adsorb onto its surface in an ion exchange with Na^+ to give (N,C)-A-S-H gels.

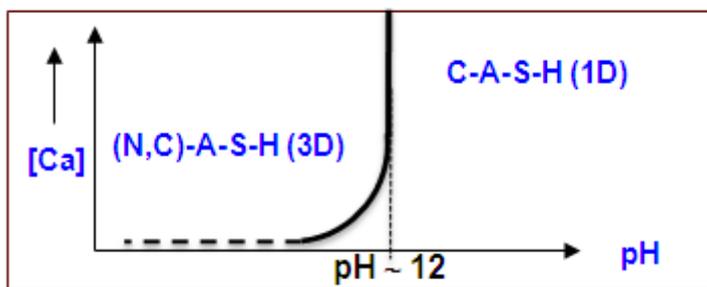


Figure 8: Schematic to illustrate the stability of N-A-S-H gels in the presence of Ca. At low pH, below the broken line, N-A-S-H is capable of adsorbing Ca by ion exchange for Na until saturated (broken line).

Conclusions

The discussion above is focused on equilibrium conditions. It is recognised that real cement systems represent systems which can be a long way from equilibrium but such an approach shows the direction in which a system will go assuming kinetic limitations can be overcome. The main conclusions of this study are that:

- Gel formation is dependent on the state of hydration of the participating cations as well as the 'normal' condensation mechanisms active in aluminosilicate structure formation; cation hydration character is pH dependent, leading to hydrolytic dissociation and ion-pair formation at high pH;
- The high charge density of Ca^{2+} (and consequently, its state of hydration) ensures that C-S-H or C-A-S-H precipitation will dominate whilst there is sufficient availability of Ca and alkalinity;
- $\text{Ca}^{2+}(\text{aq})$ is not sufficiently aggressive at pH lower than about 11.5 to degrade N-A-S-H gel and associates with the gel by ion exchange with Na^+ .

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