

## Structure, Composition and Thermochemical Properties of C-(N)-S-H and N-A-S-H Gels

*Lauren Gomez-Zamorano<sup>1</sup>, Magdalena Balonis<sup>2</sup>, Bartu Erdemli<sup>3</sup>, Narayanan Neithalath<sup>4</sup> and Gaurav Sant<sup>5</sup>*

### Abstract

While trying to find a material that could potentially replace Ordinary Portland Cement (OPC) using wastes from several industries and at the same time reduce CO<sub>2</sub> emissions from the production of OPC, scientists around the world have been researching alkali activated cements, also known as geopolymers. During the past decades, alkali-activated and blended cements have attracted strong interest worldwide due to their advantages of low energy cost, high strength and good durability. Another major incentive for further development of such cements is generated by the great quantity of annual generation of wastes, which cause a need to find new uses for them. Nevertheless, the future of these materials could be influenced by a number of relevant concerns, such as, high drying shrinkage, compositional uniformity of the raw materials, quality control of the products, and long-term durability. Calcium silicate hydrates containing sodium [C-(N)-S-H], and sodium aluminosilicate hydrates [N-A-S-H] are the major reaction products of these alkali-activated binders. To gain insights into the thermodynamic stability of these phases and to tabulate self-consistent thermochemical datasets of such compounds, a series of synthetic C-(N)-S-H and N-A-S-H gels were synthesized with compositions:  $0.8 \leq \text{Ca/Si} \leq 1.2$  for the former, and  $0.25 \leq \text{Al/Si} \leq 0.50$  (molar units) for the latter. The gels were fully characterized using thermogravimetric analysis, scanning electron microscopy with energy dispersive X-ray microanalysis and X-ray diffraction. The solubility products of the phase pure gels were established.

<sup>1</sup> Associate Professor, Programa Doctoral en Ingeniería de Materiales, Facultad de Ingeniería Mecánica y Eléctrica, Universidad Autónoma de Nuevo León, San Nicolás de los Garza, 66450, México, Email: [lauren.gomezzm@uanl.edu.mx](mailto:lauren.gomezzm@uanl.edu.mx)

<sup>2</sup> Department of Materials Science and Engineering, Institute for Technology Advancement, University of California University of California, Los Angeles, CA, USA, Email: [mbalonis@ucla.edu](mailto:mbalonis@ucla.edu)

<sup>3</sup> School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ, USA, Email: [Narayanan.Neithalath@asu.edu](mailto:Narayanan.Neithalath@asu.edu)

<sup>4</sup> Laboratory for the Chemistry of Construction Materials(LC<sup>2</sup>), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA, USA

<sup>5</sup> Rice Endowed Chair in Materials Science, Laboratory for the Chemistry of Construction Materials(LC<sup>2</sup>), Department of Civil and Environmental Engineering, University of California, Los Angeles, CA, USA, Email: [gsant@ucla.edu](mailto:gsant@ucla.edu)

## I. INTRODUCTION

Alkali-activation of aluminosilicate minerals and industrial by-products had been the object of intensive study over the twenty years [1,2]. These materials are produced by means of a chemical reaction between a precursor and an alkaline activator, forming a hardened solid. The alkali-activated cements (AAC), with engineering properties similar to Portland cement systems, have a drastically lower carbon footprint, i.e., around 80% lower than cement [3]. When properly formulated and cured, alkali-activated binders or geopolymers can develop advantageous properties such as high mechanical strength, low permeability, and high resistance to aggressive environments [4,5]. However, it has been identified that these properties vary significantly from study to study, which could be associated with the chemistry differences between raw materials from different sources, dose and type of the alkaline activator, curing conditions, among other factors, that can significantly affect the reactivity of the precursors and the phase assemblage of the hardened materials [6]. The future of these materials could be influenced by a number of relevant concerns, such as, high drying shrinkage (mainly associated with slag-based cements, but it could be found also in fly ash based geopolymers), compositional uniformity of the raw materials, quality control of the products, and long-term durability.

Main products of reaction AAC systems are, depending on the raw materials used and the type and characteristics of the activator, CSH gel with Ca/Si ratio close to 1 [7], and/or N-A-S-H gel. Both products are in most of the cases amorphous and responsible of the physical, chemical and mechanical properties of these systems. For the case of blended cements with supplementary cementitious materials (SCMs), the product formed is mainly C-S-H gel with significantly low Ca content ( $\text{Ca/Si} \leq 1.5$ ) [8,9,10]. Although many articles have been published on synthesis of C-S-H gel in different media [11,12,13,14,15,16], the characteristics of synthetic N-A-S-H gels have been less studied (17,18,19). Those types of gels are mainly silicates but their structures and characteristics could present some variations. [20,21,22].

Unlike what happens with the C-S-H gel, the effect of raw materials, activators and processing in the composition and microstructure of gel N-A-S-H is an area yet to be explored. The study of such gels is relatively recent compared to the gel produced in traditional Portland cement systems. The majority of the studies are related with N-A-S-H gels derived from the alkali activation of fly ash or metakaolin. Although many of the macroscopic characteristics of inorganic polymers prepared from different sources appear similar the aluminosilicates, its microstructure and its physical, chemical, mechanical and thermal properties in fact depend largely on the raw material used, the conditions

of curing and the nature and concentration of the alkali activator [23].

The solubility studies could offer the preferred means of studying phase equilibrium in the geopolymer systems. Some studies have determined the effect of alkali and alkali plus aluminum and calcium additions on C-S-H gels and N-A-S-H gels. Nevertheless the solubility constants for these materials have not been widely studied yet. For the case of the C-S-H, Kulik and Kersten [24] described a thermodynamic model to predict pore solution compositions and hydrated Portland cement solid phase arrangement as a function of the chemistry of the cement. It is worth noting that the ability to account for the Al incorporation into these models is important because it would improve the confidence in predictions of the solid phases formed in the geopolymers systems.

Myers et. al. [10] presented a thermodynamic model for the C-(N)-A-S-H gel in AAC, which accounts explicitly for the structurally-incorporated Al and Na species in this phase. This model represents C-(N)-A-S-H gel as an ideal solid solution of tobermorite-like end-members with independent substitution of tetrahedral Al and Na species allowed in its formulation. A good fit was found, indicating that the model is suitable for thermodynamic modeling of these materials.

Regarding to the temperature effect, it has been observed that higher temperatures favor [25,26] the polymerization of C-S-H gel formed. The heating of the C-S-H gel removes water molecules and OH- groups of the space between layers, promoting the formation of more polymerized and disordered structures with lower basal spacing. In a regular process of hydration of Portland cement, C-S-H gel interacts with other components of cement, such as alkali cement itself. Indeed the literature indicates that some inorganic mixtures containing sodium oxide and aluminum play a significant role in the reaction mechanisms and kinetics of hydration of Portland cement [27]. Nevertheless, Grangeon et. al. [28] indicated that synthesis temperature (up to 110°C) has no significant influence on the three-dimensional structure of the gel found by XRD.

## II. EXPERIMENTATION

### A. Gel synthesis

Synthetic C-(N)-S-H gels of Ca/Si = 0.8, 1.0 and 1.2 (molar ratio) were prepared using the double decomposition of calcium nitrate with sodium silicate, as described by Chen et al. (29). A 0.10 M solution of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  (AR-grade) and 0.08 M, 0.10 M and 0.12M solutions of  $\text{Ca}(\text{NO}_3)_2$  (AR-grade) were prepared using ultrapure Milli-Q water. The solution pH was adjusted using NaOH buffer. In a  $\text{N}_2$ -atmosphere, 100 ml of  $\text{Ca}(\text{NO}_3)_2$  solution was added dropwise to 100 ml of  $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$  and 10 ml of 10 M NaOH

solutions. Stirring was continued for seven days in air-tight plastic containers.

N-A-S-H gels with Al/Si = 0.25 and 0.50 (molar ratio) were prepared using a procedure similar to that noted above. In a N<sub>2</sub>-atmosphere, 50 ml and 100 ml respectively, of a 0.1 M Al(NO<sub>3</sub>)<sub>2</sub> solution were added drop by drop to 100 ml of Na<sub>2</sub>SiO<sub>3</sub>·5H<sub>2</sub>O and 10 ml of 10 M NaOH solution's using an ice-bath during mixing. Stirring was continued for seven days in air-tight plastic containers. Following their precipitation, both the C-(N)-S-H and N-A-S-H gels were washed with 2L of Milli-Q water and then vacuum filtered under a continuous stream of nitrogen. After filtration, the samples were vacuum dried at room temperature, for fifteen days using CaCl<sub>2</sub> as a desiccant. Once dry, the gel samples were ground by hand using an agate mortar and pestle, prior to more detailed analytical studies. Syntheses of both gels were carried out from under-saturation.

#### B. Characterization

A Perkin Elmer STA 6000 simultaneous thermal analyzer (TGA/DTG/DTA) with a Pyris data acquisition interface was used to characterize the gels. The powder samples were heated under UHP-N<sub>2</sub> purge at a flow rate of 20 ml/minute and at a heating rate of 10°C/minute in pure aluminum oxide crucibles over a temperature range from 35-to-975°C. It should be noted that the samples were equilibrated at 40°C for 60 minutes to eliminate excess water. Qualitative X-ray diffraction analyses were carried out on the powdered gels using a Bruker-D8 Advance diffractometer in a  $\theta$ - $\theta$  configuration using Cu-K $\alpha$  radiation ( $\lambda=1.54$  Å). The samples were scanned on a rotating stage between 5-and-70° (2 $\theta$ ) in continuous mode with an integrated step scan of 0.021° (2 $\theta$ ) and a dwell time of 1 second using a VANTEC-1 detector. The total time required for acquisition of a complete X-ray diffraction pattern was around 50 minutes. X-ray structure information was sourced from the literature or standard databases (ICSD, JCPDS) [30]. The morphology of the gels and also their compositions were examined using scanning electron microscopy (SEM). Samples were prepared by dispersing the gel powders onto double-sided adhesive carbon tape held on an aluminum stub. The gels were sputter-coated with a gold film to reduce charging. The composition of the gels was determined by X-ray microanalysis (EDS) as averaged over  $\geq 50$  discrete points. To avoid inconsistencies in analysis [31], the same operational parameters were used.

Solubility data of the gels was determined by dispersing the solid gel powders in excess water at a solid-to-liquid ratio (mass basis) of 1:30. As such, 1 g of each sample was equilibrated in 30 mL of Milli-Q water in air-tight PTFE bottles. The samples were maintained at 25°C and 50°C respectively in shaking incubators for 90 days. After equilibration, the solutions were filtered using syringe filters,

and acidified with HNO<sub>3</sub> (15.8 N) to stabilize the solution. To avoid atmospheric carbonation, the preparatory process was carried out within a glove-box in a N<sub>2</sub>-atmosphere. The ion compositions of the six replicate solutions (Ca, Si, Na and Al species in solution) were analyzed using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and a Thermo iCAP6300 instrument. The measured solution concentrations were used to calculate the solubility constants (K<sub>so</sub>) of the gels.

### 3. RESULTS AND DISCUSSION

#### A. Gels characterization.

A SEM-EDS study was carried out to provide information about the particle morphology and the chemical composition of the synthetic gels. Figures 1 and 2 show the SEM images together with their microanalyses. Secondary electron images illustrate the globular morphology of both C-(N)-S-H and N-A-S-H gels, similar as previously reported elsewhere [23]. There is no significant difference between the two types of gels at the different compositions. No evidence of calcium or sodium carbonates (plate-like morphology) was found. For the C-(N)-S-H gels, the EDS results showed in the Ca/Si vs Na/Si histogram from the figure 1, indicated a chemical composition mainly based in Ca and Si, together with small amounts of Na. Systematic lower Ca/Si ratios compared to the predicted ones (see table 1) were observed. It has been reported that the calcium silicate hydrate formation and properties are affected by the presence of alkalis. The addition of NaOH to C-S-H could diminish the Ca/Si ratio [32]; a weak alkali-gel bonds were found by means of the analysis of cation adsorption and desorption on the gel [33]. The acceleration of the precipitation of the C-S-H gel in presence of alkalis was also reported, showing a poor crystallization [34]. In the case of alkali activated slags, sodium could go into a solid solution [26,35], partially occupying positions of calcium in the C-S-H gel (C-(N)-S-H gels), nevertheless, for the case of a cement paste, those alkalis may be free in the pore solution (located between C-S-H layers), if the cation:Ca in the C-S-H ratio is lower than 0.01, according with Taylor [36]. Garcia-Lodeiro suggested the formation of a new gel that incorporates sodium in its composition [**Error! Bookmark not defined.**].

For the case of the N-A-S-H gels, the Si/Al ratio obtained was a little above than the proposed one, with an average of 1.1 (%RSD 2.9) and 2.14 (%RSD 3.4). The formation of the N-A-S-H gel is a heterogeneous process, which includes the formation of two types of gels during the alkali activation; Gel 1, initially rich in aluminum, and Gel 2 rich in silicon. During the early stages of the process (between the first minutes of reaction and first 4-5 hours) the content of Al<sup>3+</sup> is greater since this element dissolves faster than silicon because the Al-O bonds are weaker than the Si-O. As the

reaction advances, more Si-O is dissolved, increasing the concentration of silicon and therefore producing a silicon-rich gel. The results indicated a similar composition of the N-A-S-H gels type 1 and 2 as described in the literature [37, **Error! Bookmark not defined.**]. According with Criado et. al. [38], the amount of soluble silica used in the activation process, helps to form polymerized structures to finally precipitate N-A-S-H gel when the saturation is reached. The degree of polymerization of the silica greatly influenced the reaction kinetics; with the increase of SiO<sub>2</sub>/Na<sub>2</sub>O ratio the reaction rate tends to decrease, affecting the kinetics of gelation and in some cases precipitating zeolites, but over time the system evolves to the thermodynamically more stable product. Table 1 presents the results of the composition of the gels estimated using simultaneously EDS-SEM and TGA results.

Fig. 3 shows the powder XRD patterns from the N-A-S-H and C-(N)-S-H gels. The TGA and XRD results showed the consistent absence of carbonation in all the gels evaluated. For the case of the N-A-S-H gels, both

Table 1: The calculated chemical formulas of the synthesized C-(N)-S-H and N-A-S-H gels.

	Target molar ratio (ID)	Chemical formula
Ca/Si	0.80	(Na <sub>2</sub> O) <sub>0.08</sub> · (CaO) <sub>0.74</sub> · (SiO <sub>2</sub> ) <sub>1</sub> · (H <sub>2</sub> O) <sub>1.9</sub>
	1.00	(Na <sub>2</sub> O) <sub>0.12</sub> · (CaO) <sub>0.97</sub> · (SiO <sub>2</sub> ) <sub>1</sub> · (H <sub>2</sub> O) <sub>2.1</sub>
	1.20	(Na <sub>2</sub> O) <sub>0.17</sub> · (CaO) <sub>1.16</sub> · (SiO <sub>2</sub> ) <sub>1</sub> · (H <sub>2</sub> O) <sub>2.2</sub>
Al/Si	0.50	(Na <sub>2</sub> O) <sub>0.45</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>0.45</sub> · (SiO <sub>2</sub> ) <sub>1</sub> · (H <sub>2</sub> O) <sub>2.5</sub>
	0.25	(Na <sub>2</sub> O) <sub>0.26</sub> · (Al <sub>2</sub> O <sub>3</sub> ) <sub>0.24</sub> · (SiO <sub>2</sub> ) <sub>1</sub> · (H <sub>2</sub> O) <sub>1.9</sub>

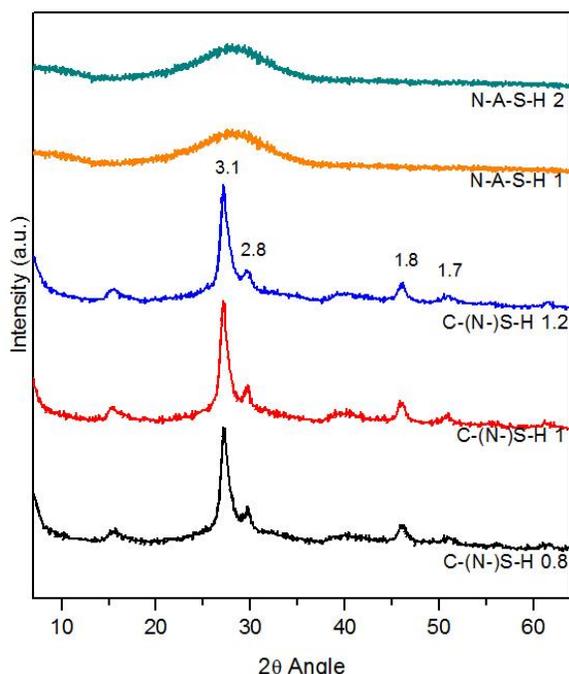


Fig 3. XRD patterns of the N-A-S-H and C-(N)-S-H gels

of the XRD patterns exhibit a broad halo between 20-35 2θ, indicating an amorphous phase similar to that observed in the alkali activated fly ashes [38]. There is no evidence of the presence of zeolitic-nature phases or other crystalline phases. No significant differences between both N-A-S-H gels were observed.

For the C-(N)-S-H gels, the XRD results (Fig. 3) indicate a low degree of order in the three different compositions of the gels, showing the same number of diffraction maxima, which similar positions and relative intensities; the only sharp peaks are those at 0.31, 0.28 and 0.19 nm, similar to those reported by Chen et. al [29]. Since, the reported crystalline C-S-H presents peaks in these regions, its difficult to determine the similarity with 1.4-nm tobermorite. Nevertheless, when comparing the patterns with those reported for 11 Å tobermorite [28], is possible to observe that all diffraction maxima in synthetic C-(N)-S-H gels have a position equivalent in the tobermorite pattern, and correspond to 11 Å tobermorite basal or hk0 reflections. A weak peak at 0.17 nm, and the presence of silica gel (marked by a broad band at 22-23° 2θ), were also observed. The significant peak broadening, compared to tobermorite XRD patterns published, suggests nanometer-sized domains in the gels and/or amorphous nature. There is not significant change in the XRD patterns with Ca/Si ratio.

#### B. C-(N)-S-H and N-A-S-H solubility results

While compiling the set of thermodynamic constants describing the equilibrium state of aqueous and mineral reactions over a defined range of temperature, pressure and ionic strength, is important to make a distinction between activity and concentration of solute species for non-ideal solutions. The theory of Debye and Huckel (Merkel et al. 2005<sup>39</sup>) includes the fundamental theoretical framework for the derivation of activity corrections. The original Debye–Huckel theory is valid for moderate concentrations (up to 0.1 mol/kg). Several extensions and approximations based on the Debye–Huckel theory have been presented in literature in order to extend it.

Reliable data are available for a large number of minerals and aqueous reactions over a very large range of temperatures in the range of validity of extended Debye–Huckel formulations. In particular, the Lawrence Livermore database (LLNL, Johnson et al. 1992<sup>40</sup>; Wolery 1992<sup>41</sup>), provided with the standard code of the PHREEQC software (Parkhurst et. al. 2001<sup>42</sup>), is valid in the range 0–300 °C and is adopted by several of modellers and applications (De Lucia et. al.<sup>43</sup>). The experimental data (ion activities and speciation) obtained for the solubility of C-(N)-S-H and N-A-S-H phases at 25°C and at 50°C, were calculated using the LLNL of the PHREEQC software. The experimental data from works already published were processed in the same database, in order to have more accurate results. The

thermodynamic properties of many aqueous complexes have been previously collected and selected for this work. The basis species for writing equilibria reactions were  $\text{OH}^-$ ,  $\text{AlO}_2^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{SiO}_4^-$ , using equations presented in table 2.

Fig. 4 shows the Ca vs. Si concentrations for the synthesized C-(N)-S-H gels equilibrated at 25 and 50°C for 3 months. The figure includes the curves published by Chen et. al. (2004) and proposed by Jennings et. al. (1986<sup>44</sup>). Curve A (lower Si concentrations), was considered to be the

Table 2: The dissolution reactions used to calculate solubility products for a given phase.

Phase ID	Dissolution reactions
C-(N)-S-H 0.8	$(\text{Na}_2\text{O})_{0.078}(\text{CaO})_{0.74}(\text{SiO}_2)_1(\text{H}_2\text{O})_{1.89} = 0.156 \text{ Na}^+ + 0.74 \text{ Ca}^{2+} + 1 \text{ HSiO}_3^- + 0.636 \text{ OH}^- + 1.072 \text{ H}_2\text{O}$
C-(N)-S-H 1.0	$(\text{Na}_2\text{O})_{0.12}(\text{CaO})_{0.97}(\text{SiO}_2)_1(\text{H}_2\text{O})_{2.1} = 0.244 \text{ Na}^+ + 0.973 \text{ Ca}^{2+} + 1 \text{ HSiO}_3^- + 1.19 \text{ OH}^- + 0.995 \text{ H}_2\text{O}$
C-(N)-S-H 1.2	$(\text{Na}_2\text{O})_{0.173}(\text{CaO})_{1.158}(\text{SiO}_2)_1(\text{H}_2\text{O})_{2.17} = 0.346 \text{ Na}^+ + 1.158 \text{ Ca}^{2+} + 1 \text{ HSiO}_3^- + 1.662 \text{ OH}^- + 0.839 \text{ H}_2\text{O}$
N-A-S-H 1	$(\text{Na}_2\text{O})_{0.45}(\text{Al}_2\text{O}_3)_{0.45}(\text{SiO}_2)_1(\text{H}_2\text{O})_{2.48} = 0.9 \text{ Na}^+ + 0.9 \text{ AlO}_2^- + 1 \text{ SiO}_2^0 + 2.48 \text{ H}_2\text{O}$
N-A-S-H 2	$(\text{Na}_2\text{O})_{0.26}(\text{Al}_2\text{O}_3)_{0.24}(\text{SiO}_2)_1(\text{H}_2\text{O})_{1.88} = 0.52 \text{ Na}^+ + 0.48 \text{ AlO}_2^- + 0.96 \text{ SiO}_2^0 + 0.04 \text{ HSiO}_3^- + 1.84 \text{ H}_2\text{O}$

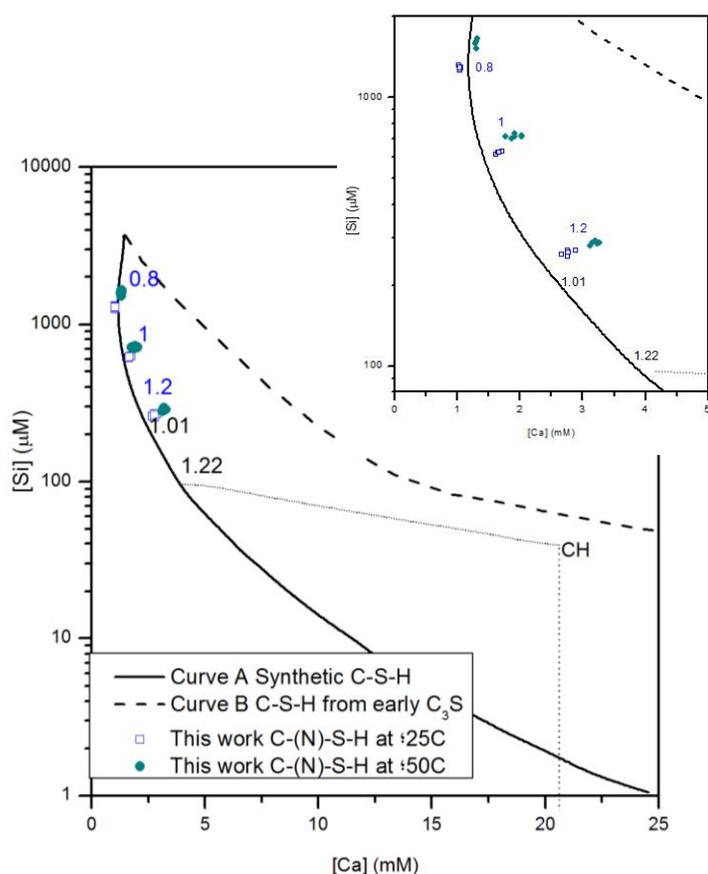


Fig. 4 Composition of the solutions at equilibrium with C-(N)-S-H gels equilibrated at 25 and 50°C. Lines from (Chen et. al. 2004)

metastable solubility curve for C-S-H(I), obtained from synthetic preparations using  $\text{CaO}$  and  $\text{SiO}_2$  or a double decomposition process, as prepared in this study. Curve B (higher Si concentrations), was obtained from experiments conducted during the first hours of  $\text{C}_3\text{S}$  hydration, which could involve the presence of a superficially hydroxylated surface on  $\text{C}_3\text{S}$ . Curve C, displays the effect of the insertion of  $\text{Ca-OH}$  groups into C-S-H, Chen et. al. suggested that these changes in solubility could be related with a changing from a purely tobermorite-like structure, to structures that include jennite-like characteristics.

Since the main goal in this study was to investigate the solubility in low Ca/Si ratios, similar to those observed in geopolymers, the results obtained do not reach curve C. In general is possible to observe that there is consistency in the equilibria of C-(N)-S-H with solubility results, following exclusively curve A, which implies that they do not contain  $\text{Ca-OH}$  and thus have structures based on 1.4-nm tobermorite, as was observed in the XRD results (Fig. 3); at CH saturation, these structures have a Ca/Si ratio of 1.5. The conditions under which the synthetic structures form is not well understood yet; however, it has been reported that the Ca/Si ratio in C-S-H made by double decomposition at room temperature, is limited to around 1.5; therefore synthetic C-S-H preparations thus tend to form tobermorite-like phases and equilibrate near curve A [29]. Nevertheless, they also discussed that the most significant variations in solubility of C-S-H phases occur at Ca/Si ratios above of 1, mainly due to the high Ca – OH content; this behavior was not observed in the results from the Figure 4. It is worth noting that the solubility of Ca and Na is in aqueous phase is thermodynamically related with the structure of the C-(N)-S-H gel.

Brown [45] found that for the sodium-substituted form of C-S-H, small content of  $\text{Na}_2\text{O}$  in the  $\text{C}_3\text{S}$  greatly increased the concentrations of  $\text{OH}^-$  and decreased those of  $\text{Ca}^{2+}$ . Following from that, is possible to observe that Fig. 4 exhibits a small deviation from curve A, caused by a lower Ca concentration than the predicted, together with an increase in the Si concentration. Unusually high aqueous Si and low Ca concentrations above certain of the precipitated products of the N-C-S-H system have been observed by Macphee et. al [46]; they established these precipitates were silica-rich, with respect to the bulk of the compositions encountered, and were tentatively considered to correspond to a stability field other than that of C-S-H, perhaps closer to sodium silicates, although the still significant  $\text{CaO}$  contents of the solids suggested an intermediate composition. According with Blanc et. al [47] the synthesis based on sodium metasilicate, which enables a quick C-S-H

dissolution, produces solutions located along the S curve, together with an uncertainty for the location of minimum solubility curves when sodium impurities are present,

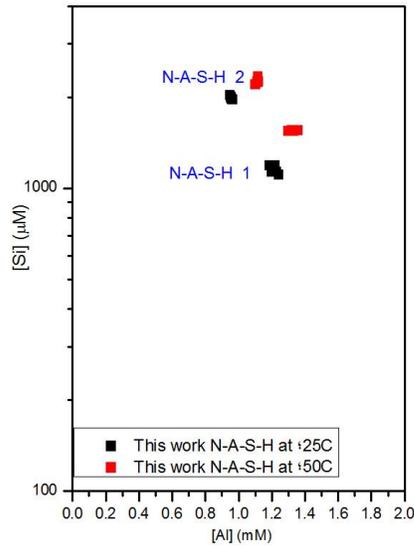


Fig. 5 Composition of the solutions at equilibrium with N-A-S-H gels equilibrated at 25 and 50°C

producing an uncertainty for the location of minimum solubility curves that interfere on the solubility models for C-S-H not fully characterized. The metastable equilibrium states mentioned by Chen et al. [29] and Blanc et. al. [47] also modified the behavior of the Ca/Si ratios of the gels.

One of the aims of this study was to investigate the temperature dependency of the thermodynamic functions associated with the synthetic gels, mainly due to the fact that most of the geopolymers are produced at temperatures above 50°C. Figure 4 displays the solubility results of all the gels equilibrated at two temperatures as a function of the Ca/Si ratio. The results followed the expected trend, nevertheless, Glasser et.al. [51] reported a diminution in the Ca concentration with the temperature, possible due to the crystallization of the gels, when maintained at temperatures around 55°C during long periods. In gels containing alkalis, the pH conditions could stabilize crystalline phases for C-S-H with low Ca/Si ratios as well as silica gels, and thus modify the ionic equilibrium of the aqueous phase and the solid, as observed in Fig. 4.

In figure 5, the results of the Si vs. Al concentrations for the synthesized N-A-S-H gels equilibrated at 25 and 50°C for 3 months are shown. It has been reported [48] that in dilute sodium aluminosilicate solutions near saturation with respect to zeolite A (with a Al/Si ratio  $\approx 1$ ), reactions among a host of silicate and aluminosilicate anions are fast. On a timescale of minutes each species may be considered in equilibrium with others. Hence, the solids and aqueous phase analyzed in

this study are considered to be in equilibrium, which indicates that the Al/Si ratio in both phases is the same, as observed in Fig. 5, therefore, concentrations of particular

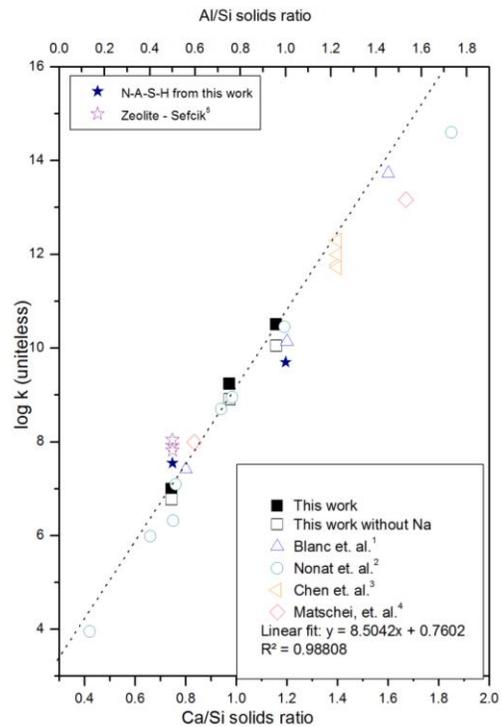


Fig. 5 Comparison of the 25°C equilibrium constants of synthetic C-(N)-S-H and N-A-S-H gels and using data from: (1) Blanc et. al. [47], (2) Haas et. al. [49], (3) Chen et. al. [29], (4) Matschei et. al. [50] and (5) Sefcik et. al. [48].

solution species are tied with the overall solution composition by a set of equilibrium relations and mass balances, following Eq. 3. To ensure charge balance in reactions, the stoichiometric cation proportion, has been set equal to the stoichiometric proportion of Al.

In order to predict the silicon or aluminum concentration with respect of the saturation concentrations Sefcik et. al. [48] analyzed the available experimental data for zeolite A at temperatures between 353 and 363 K, and compared the data with those obtained at room temperature. Their results present a wide range of concentrations for Al, Si and Na, since they were prepared from both under and oversaturation, but most of them follow the trend described above. There is not clear effect and/or trend of the temperature with the concentration of the ions in the aqueous phase. It is worth noting that there solubility concentrations will be affected with the amorphous content in a zeolite, thus a direct comparison between both results is not possible. Nevertheless, Fig. 6 presents the results of the  $K_{sp}$  values calculated with the results of Fig. 5 using Eq. 3 while

comparing the results with those reported by Sefcik et. al, showing a good correlation between both of the results at similar Al/Si ratio.

A large amount of solubility data is already available for C-S-H gels, as discussed above and it was established that there is generally good agreement between solubilities of gels prepared in a given way, although there is a slight variance between solubilities of hydration products from tricalcium silicates and precipitated gels. Nevertheless, the precipitated solids from the double decomposition synthesis (51), which give the lower solubilities at any given Ca/Si ratio, could represent a more steady-state quasi-equilibrium conditions. Fig. 6 presents the application of eq. 2 and 3 to calculate the  $K_{sp}$  values from an average of the C-(N)-S-H and N-A-S-H gels obtained in this study, a comparison of the data published by other authors and processed in the same way, using PHREEQC software and Eq. 2, is also showed in Fig. 6. The values of  $K_{sp}$  determined here decrease with increasing (Ca/Si) solid ratio, trend previously reported by several authors. Nevertheless, significant variations on the final values could be related from the mole definitions, here the gel is defined as containing only one silica unit per mole. However, appropriate conversion fails to bring sets of  $K_{sp}$  values for C-S-H to reasonable agreement when comparing data, since the initial chemical reaction must be set as the same, as presented in Figure 6. This figure shows the same tendency of all the data analyzed here, indicating that the chemical interaction proposed could be applied for a large range of Ca/Si and/or Al/Si compositions.

### III. CONCLUSIONS

A series of synthetic C-(N)-S-H and N-A-S-H gels were produced using a double decomposition method in order to analyze their compositions and solubility products. The XRD patterns of the N-A-S-H showed a broad halo previously reported for amorphous aluminosilicates and no evidence of any zeolite-like (crystalline) phases was found. For C-(N)-S-H gels, the XRD results indicated a low degree of ordering in the three different compositions of gels, showing peaks similar to those reported for 11 Å tobermorite. The compositions of the gels were calculated by SEM-EDS and the water content estimated using TGA data. The compositions thus estimated were used to write a dissolution equation for the gels. The concentrations of Ca and Si species in the aqueous phase, equilibrated with the solid gels, followed expected patterns in the case of C-(N)-S-H, with increasing incongruency in dissolution with increasing Ca/Si, and Na-content of the gels. For N-A-S-H gels, the solids and aqueous phase showed equivalent Al/Si ratios, therefore indicative of congruency in dissolution across the full range of compositions studied. Solubility constants were tabulated for the gels. The solubility

increased with temperature for N-A-S-H gels and decreased for C-(N)-S-H gels. Datasets of solubility products, or solubility constants ( $K_{so}$ ), density, Gibbs free energies of formation, and enthalpy of dissolution thus determined provide critical input data needed for calculation of mass and volume balances in the systems.

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