Synthesis, characterization and solubility of sodium aluminosilicate hydrate (N-A-S-H) gel

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ABSTRACT

Sodium aluminosilicate hydrate (N-A-S-H) gels with various Si/Al ratios are the dominant reaction products of geopolymer. However, their solubility products have not yet been fully determined, which hinders further investigation of thermodynamic modelling of geopolymer system. In this work, N-A-S-H gels with Si/Al ratios ranging from 1 to 3 were synthesized using the sol-gel method. The chemical composition of the synthesized N-A-S-H gels was determined by X-ray spectroscopy (XRF) and thermogravimetric analysis (TGA). The gel structure was characterized by X-ray diffraction (XRD). Dissolution experiments were further performed using the synthesized N-A-S-H gels to determine their solubility products. After dissolution, the aqueous concentrations of Na, Al, and Si were quantified by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and the solution pH was measured. It has been shown that N-A-S-H gels with various Si/Al ratios differ in atomistic structures and solubility products. The thermodynamic properties of N-A-S-H gels can be determined from the experimentally derived solubility products at different temperature, which are expected to complement the thermodynamic database.

KEYWORDS: *N-A-S-H gel, Si/Al ratio, Solubility product, Sol-gel method, Thermodynamics*

1. Introduction

The primary reaction product formed in geopolymer is sodium aluminosilicate hydrate (N-A-S-H) gel. The chemical composition of N-A-S-H gel can be expressed as $Na^+[AlO_2{\cdot}nSiO_2]^-{\cdot}mH_2O$, where n stands for Si/Al ratio and mainly varies from 1 to 3, depending on the raw materials and the curing regime (Pacheco-Torgal, Castro-Gomes, and Jalali 2008). As the principal phases, N-A-S-H gels with different thermodynamic properties are expected to control the geopolymerization reaction.
Several previous studies have reported the solubility product of synthesized N-A-S-H gel. Gomez-Zamorano et al. synthesized N-A-S-H gel with Si/Al ratios of 1 and 2 by sol-gel method and performed solubility test at 20 °C and 50 °C (Gomez-Zamorano et al. 2017). A similar route was adopted in Williamson's work to study the solubility of N-A-S-H gel (Williamson et al. 2019, 2020). However, N-A-S-H gels with high Si/Al were rarely synthesized in his study. As a result, only the solubility of N-A-S-H gel with a Si/Al of around 1 has been measured. In addition, Walkley et al. determined the solubility of

N-A-S-H gel obtained by alkali activation of synthesized aluminosilicate glass (Walkley et al. 2021). Again, the Si/Al ratio was below 2, which did not cover the domainant Si/Al ratios of the N-A-S-H gel formed in the geopolymer. To date, no solubility products of N-A-S-H with Si/Al above 2 have been reported. In addition, more data on the solubility of N-A-S-H gel at various temperatures are needed to build an accurate thermodynamic database of N-A-S-H gels.
This study aims to determine the solubility products of N-A-S-H gels with Si/Al ranging from 1 to 3 at different temperatures. First, N-A-S-H gels with various Si/Al compositions were synthesized using the sol-gel method. Next, the chemical composition of the N-A-S-H gel was determined by XRF and TGA, while the structural information of the N-A-S-H gel was obtained from XRD. Finally, dissolution experiments were performed at different temperatures to determine the solubility product of the N-A-S-H gel.

2. Experimental method

2.1 Synthesis of N-A-S-H gels

1M sodium silicate solution and 1M aluminum nitrate solution were used as the raw materials for the synthesis of the N-A-S-H gels. A 10 M NaOH solution and a HNO_3 solution (>65%) were used to maintain the pH when necessary. The sodium silicate solution was first mixed with a pH regulator and stirred for 30 minutes. A solution of aluminum nitrate was then added slowly to the stirring solution. The detailed synthesis conditions are given in Table 1 for all samples. The above procedure was performed in an N_2 filled glove box. After stirring for 1 day, the gel was obtained from the suspension by centrifugation and subjected to triple washing with deionized water. After that, the gel was dried in a vacuum desiccator for 14 days.

Table 1 Synthesis mixtures and conditions

Samples	Na_2SiO_3	$Al(NO_3)_3$	pH regulator	Target Si/Al	pH[(a)]
G1	50ml	50ml	20ml 10M NaOH	1	13.64
G2	280ml	100ml	-	2	13.46
G3	200ml	40ml	10ml HNO_3	3	13.40

(a) pH of filtrate referring to 25°C.

2.2 Characterization of synthesized N-A-S-H gels

XRF, XRD and TGA were used to characterize the gel. XRF measurement was performed with a Panalytical Axios Max WD-XRF spectrometer. XRD analysis was carried out at 45 KV and 40 mA using CuKα radiation, scanning from 8° to 60° 2θ at a rate of 2 seconds per step and a step size of 0.02° 2θ. TGA data were recorded at a heating rate of 10 ℃/min from 40 ℃-1000 ℃, except in the middle stage staying at 105 ℃ for 6h in order to determine the amount of non-evaporable water in N-A-S-H gel.

2.3 Solubility measurements

The resulting N-A-S-H gel was dispersed into deionized water with a solid-to-solution ratio of 20 g/L. The dissolution test was conducted in a shaker at 25 ℃ for 2 months, at 40 and 60 ℃ for 1 month, respectively. After equilibrium time, the suspension was filtered to obtain the aqueous phase. The pH of the filtrate was measured with a pH meter. Concentrations of Si, Al and Na in the filtrate were measured with an ICP-OES spectrometer. According to the element concentration and pH, the activities of the aqueous species, i.e., $\{Na^+\}$, $\{AlO_2^-\}$, $\{SiO_2^0\}$ and $\{OH^-\}$, were calculated out in GEMS (Kulik et al. 2013). Depending on the chemical composition of the N-A-S-H gels, their solubility products can be calculated. Note that the results in this work represent the average of three measurements.

3. Results and Discussion

3.1 Overview of the synthesized N-A-S-H gel

The chemical composition of the three types of synthesized N-A-S-H gels was determined by XRF. As shown in Table 2, the target Si/Al ratios, namely 1, 2 and 3, were successfully obtained. The amount of non-evaporable water was also determined, i.e. the amount of water that cannot be removed by D-drying or equivalent procedures, e.g. drying at 105 °C. In this work, drying at 105 °C was selected to determine the dry weight and calculate the amount of non-evaporable water based on TGA tests. According to TGA results, the amount of non-evaporable water, indicated by the weight loss between 105 °C to 1000 °C, was 5.59 %, 4.84 % and 4.90 % in G1, G2 and G3 respectively. Combining the XRF and TGA results, the chemical formula of the synthesized N-A-S-H gel can be determined, as summarized in Table 2.

Table 2 Chemical composition of synthesized N-A-S-H gel

Samples	Si/Al	Chemical composition
G1	1.10±0.01	$(Na_2O)_{0.46}(Al_2O_3)_{0.46}(SiO_2)_1(H_2O)_{0.48}$
G2	1.95±0.02	$(Na_2O)_{0.25}(Al_2O_3)_{0.25}(SiO_2)_1(H_2O)_{0.29}$
G3	2.81±0.02	$(Na_2O)_{0.18}(Al_2O_3)_{0.18}(SiO_2)_1(H_2O)_{0.26}$

The XRD patterns of N-A-S-H gels with various Si/Al ratios exhibit a single amorphous hump, as shown in Fig. 1. The hump was observed to shift towards lower angles as Si/Al increased, which aligns with previous observations in geopolymer pastes (Lee et al. 2017). This is the first time that such a shift towards lower 2θ with increasing Si/Al has been reported for N-A-S-H gels, indicating a difference in their chemical compositions.

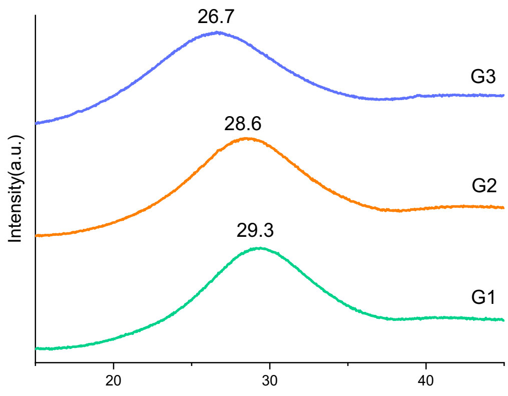

Fig. 1 XRD patterns for synthesized N-A-S-H gels with Si/Al from 1 to 3

3.2 Solubility products of N-A-S-H gels

The solubility product is defined based on the dissolution reaction. Using the dissolution reactions as listed in Table 3, the log K_{sp} values of the synthesized N-A-S-H gel at different temperatures were calculated, as shown in Fig. 2(a). The log K_{sp} values for each type of N-A-S-H gel increase with temperature. The log K_{sp} values of N-A-S-H gels with Si/Al of 1 and 2 are found consistent with (Gomez-Zamorano et al. 2017). N-A-S-H gels with different Si/Al ratios also show different solubility properties. In order to study the effect of Si/Al on the solubility, the log K_{sp} values were normalized by the sum of Si and Al as shown in Fig. 2(b). It can be seen that the log K_{sp} values increase with increasing Si/Al, especially from 2 - 3. Consistent trending was found in (Gomez-Zamorano et al. 2017). This indicates that N-A-S-H gel with higher Si/Al (e.g. up to 3) is less likely to form, which is in agreement with simulation result in (Chen et al. 2022). This may be one of the reasons why the synthesis of N-A-S-H gel with Si/Al of 3 has not been reported in the literature.

Table 3 The dissolution reactions used to calculate solubility products

Samples	Dissolution reactions
G1	$(Na_2O)_{0.46}(Al_2O_3)_{0.46}(SiO_2)_1(H_2O)_{0.48} \rightarrow 0.92\ Na^+ + 0.92\ AlO_2^- + SiO_2^0 + 0.48\ H_2O$
G2	$(Na_2O)_{0.25}(Al_2O_3)_{0.25}(SiO_2)_1(H_2O)_{0.29} \rightarrow 0.5\ Na^+ + 0.5\ AlO_2^- + SiO_2^0 + 0.29H_2O$
G3	$(Na_2O)_{0.18}(Al_2O_3)_{0.18}(SiO_2)_1(H_2O)_{0.26} \rightarrow 0.36\ Na^+ + 0.36\ AlO_2^- + SiO_2^0 + 0.36H_2O$

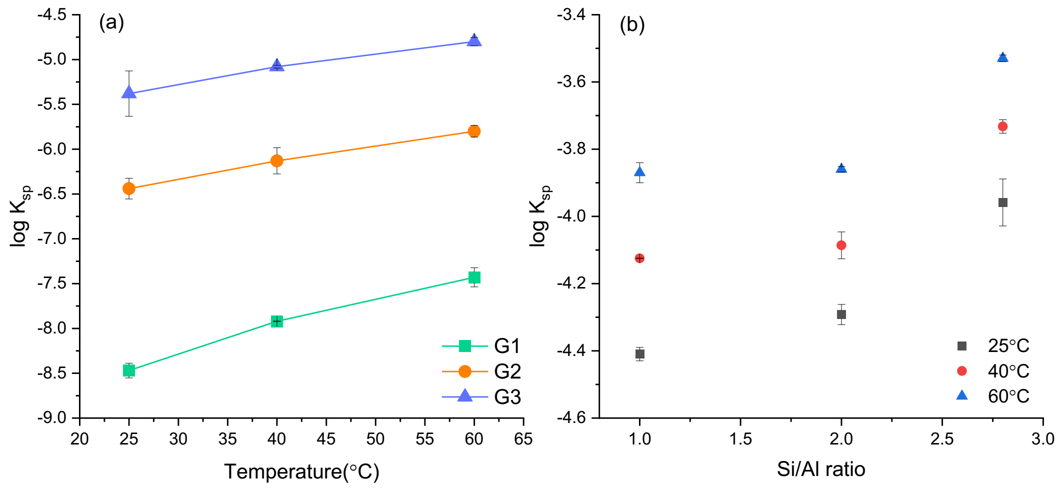

Fig. 2 Solubility products (log K_{sp}) of N-A-S-H gels with various Si/Al ratios at different temperatures

4. Conclusions

In this work, N-A-S-H gels with Si/Al ratios of 1, 2 and 3 were synthesized using the sol-gel method. XRF and TGA were used to determine the chemical composition of the N-A-S-H gel. XRD results also confirm the high purity of all the amorphous N-A-S-H gels. To the best of our knowledge, this is the first synthesis of N-A-S-H gels with high Si/Al ratios.

The solubility products of N-A-S-H gel with various Si/Al ratios were determined at 25, 40 and 60 °C and showed consistency with some literature values. Overall, this work has enriched and extended the solubility of N-A-S-H gels for a wide range of Si/Al ratios at various temperatures. The experimentally derived solubility products can be used to further calculate thermodynamic data for N-A-S-H gels, which are essential inputs for thermodynamic modelling to study chemical reactions in geopolymers.

Acknowledgements

The first author would like to acknowledge China Scholarship Council (Grant No. 201906150022) for financial support in this work.

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