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A MOLECULAR DYNAMICS STUDY OF N-A-S-H GEL WITH VARIOUS Si/Al RATIOS

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Abstract

The understanding of sodium aluminosilicate hydrate (N-A-S-H) gel is still limited due to its complex and amorphous structure. Recently, molecular dynamics simulation has provided a unique opportunity to better understand the structure of N-A-S-H gel from nanoscale. In this work, the N-A-S-H gel structure was obtained by simulating the polymerization of Si and Al monomers by molecular dynamics. The simulated polymerization process is in good agreement with the experimental results especially in terms of the reaction rate of Si and Al species. The atomic structural features of the N-A-S-H gel were analyzed in terms of bond length and bond angle information, simulated X-ray diffraction (XRD) and Q^n distribution. A significant finding is the existence of pentacoordinate Al in all simulated N-A-S-H structures, indicating that pentacoordinate Al in geopolymer does not only come from raw material. Besides, the results show that a smaller Si/Al ratio led to a more crosslinked and compacted structure of N-A-S-H gel.

Keywords: molecular dynamics, N-A-S-H gel, atomic structures, Si/Al ratio

1. INTRODUCTION

Sodium aluminosilicate hydrate (N-A-S-H) gel is the primary reaction product of geopolymers [1]. It is known as a three-dimensional disordered structure consisting of interconnected Si and Al tetrahedrons, Na^+ ions and absorption water [2]. Some basic knowledge of N-A-S-H gel has been obtained through commonly used materials characterization techniques, including X-ray diffraction (XRD) analysis, Fourier transform infrared (FTIR) spectroscopy and nuclear magnetic resonance (NMR) spectroscopy, etc. [3–5].

However, due to the complex nature of N-A-S-H gel, these experimental techniques are not able to fully unravel the mysteries of N-A-S-H gel.

Recently, molecular dynamics (MD) simulation has offered an exciting opportunity to understand the N-A-S-H gel structure down to nanoscale. Lolli proposed a new molecular model of N-A-S-H gel based on sodalite framework [6]. A sodium aluminosilicate glasses model was built from an initial configuration of silica glass to investigate the properties of geopolymer binders by Sadat [7]. Zhang carried out reactive molecular dynamics to build N-A-S-H gels following a geopolymerization process [8]. From these researches, it is not hard to find that they all performed molecular dynamics in different ways to model N-A-S-H gel. Most of these simulations started from an available structure (e.g. sodalite) which is analogous to N-A-S-H gel structure. Zhang is the only one employing reactive molecular dynamics to form N-A-S-H gel, which is closer to the reality. Besides, some contradictory findings have been found in terms of the effect of Si/Al ratio [6,7,9]. Further effort is required to gain a deeper understanding of N-A-S-H gel with a wide range of Si/Al ratios.

In this study, the formation and structure of N-A-S-H gels with Si/Al ratios from 1.0 to 4.0 are investigated by molecular dynamics simulation. Unlike most of the researches mentioned above, the N-A-S-H gels were obtained from the reaction of Si monomers and Al monomers in this study. This methodology to construct N-A-S-H model was derived from the polymerization of silica sols introduced by Feuston [10]. Reactive force field (ReaxFF) was adopted in this work to carry out molecular dynamics simulation. This is the main difference compared with Zhang's research, in which FG potential (a reactive potential developed by Feuston and Garofalini) was used. ReaxFF can yield more accurate and reliable results compared with FG potential. The main reason is that ReaxFF divides the system energy up into ten partial energy contributions [11], while FG potential only contains a two-body and a three-body interaction terms [12]. With ReaxFF, the process of polymerization was simulated in this study. Detailed structural analysis was performed on the final simulated structure.

2. METHODOLOGY

A simulation box containing individual $Si(OH)_4$, $Al(OH)_3$ and NaOH molecules was built by software PACKMOL [13] as the initial structure for molecular dynamics simulation. The size of the simulation box was 25×25×25 Å and the density of the system was set at around 2 g/cm^3. Table 1 shows the composition and density of all the initial configurations. The composition of the initial configuration covers a wide range of Si/Al ratio from 1.0 to 4.0 with a fixed Na/Al ratio at 1.

Table 1 The composition and density of initial configurations

Si/Al	Number of $Si(OH)_4$	Number of $Al(OH)_3$	Number of NaOH	Density(g/cm^3)
1.0	92	92	92	2.10
2.0	120	60	60	1.98
3.0	138	46	46	1.99
4.0	144	36	36	1.93

Molecular dynamics simulation was executed on the large-scale atomic/molecular massively parallel simulator (LAMMPS) [14]. The whole simulation was run under the Canonical ensemble (NVT) condition. The system was first relaxed at 300 K for 100 ps. Then, the temperature was raised linearly up to 2000 K for the next 100 ps and subsequently kept at 2000 K for 1 ns to accelerate the reaction. This was followed by a cooling process at a rate of 2.2 K/ps. Finally, the system was equilibrated at 300K for 200 ps. The total duration for the whole process was 2.15 ns with a time step of 0.25 fs. ReaxFF was employed in all simulations to describe the interatomic interactions among the atoms [11]. The detailed potential functions and parameters can be found in the literature [6].

The N-A-S-H structure was then extracted from the final configuration to analyze its structural features. Visual Molecular Dynamics (VMD) software [15] was used to view the snapshot. Based on the coordinate information, bond length and bond angle were calculated. The XRD patterns were simulated in LAMMPS. Q^n distribution was calculated to reveal the topology of the N-A-S-H gel.

3. RESULTS AND DISCUSSION

3.1. Polymerization process

Fig.1 shows the simulation process in terms of the evolution of Q^n, including Si sites and Al sites. The superscript n refers to the number of bridging oxygens that a Si or Al atom is bonded. Fig. 1 only shows the simulation with the Si/Al ratio of 1.0 as the other Si/Al ratios have an almost identical trend. As can be seen in Fig. 1, all Si and Al in the system existed as Q^0 at the beginning, because all of them were separated monomers. For Si sites, Q^0 decreased immediately with the simulation time. Meanwhile, Q^1 emerged first, followed by Q^2, Q^3 and Q^4 in sequence. That means Q^0 reacted and transferred to higher polymerized sites Q^n (n=1-4). This simulated process is consistent with geopolymerization reaction in practice [16], where monomers reacted to form oligomers and then oligomers polymerized to form large clusters.

The evolution of Al sites followed a similar pattern to that of Si sites, which also experienced polymerization process. However, two major differences can be observed. First, all Al^0 sites were consumed completely at the end regardless of Si/Al ratios. Second, some Al^5 sites (pentacoordinate Al) and traces quantities of Al^6 sites were formed besides Al^1, Al^2, Al^3 and Al^4. The presence of the pentacoordinate Al will be further discussed in Section 3.2.3.

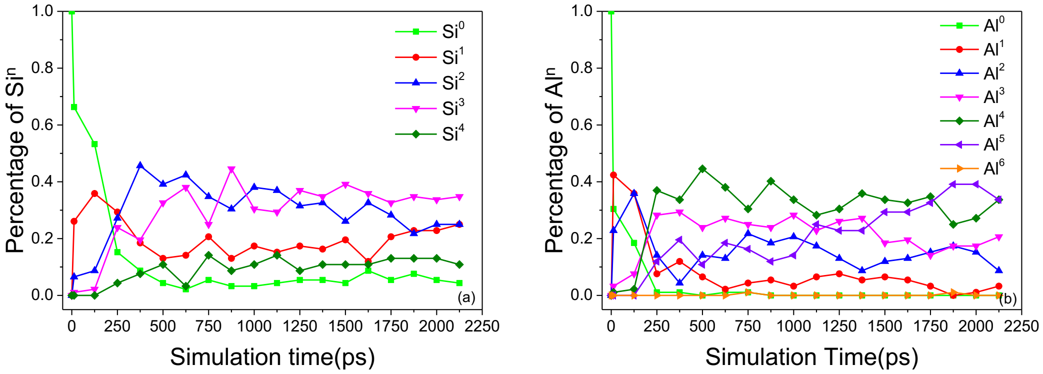

Fig. 1 Evolution of Q^n sites for (a) Si sites and (b) Al sites (only shown a Si/Al ratio at 1.0)

3.2 Atomic structure of N-A-S-H model

3.2.1 Bond length and bond angle

To describe the atomic structure of the obtained N-A-S-H gel, the average bond length for Si-O and Al-O was calculated in Table 2. Si-O bond length is mainly located at 1.61-1.63 Å, while Al-O bond length is a bit longer (1.83-1.85 Å). These results are in line with the simulation results in [9,17] and experimental results in [18]. As Si/Al ratio increases, both Si-O bond and Al-O bond become longer.

Table 2 Average bond length of N-A-S-H model compared to other work

Bonds	This work	Sadat et al.[17]	Wang et al.[9]	White et al.[18]
Si-O	1.61-1.63 Å	1.61 Å	1.65-1.67Å	1.63 Å
Al-O	1.83-1.85 Å	1.77 Å	1.75-1.77Å	1.80 Å

Besides bond length, bond angle is another key parameter to reveal the details of N-A-S-H gel structure. Fig. 2 (a) and (b) show the distribution of O-Si-O bond angle and O-Al-O bond angle for all N-A-S-H gel structures, respectively. The distribution of O-Si-O bond angle has a main peak at around 110° regardless of the Si/Al ratios. This indicates all Si in N-A-S-H gel are tetrahedral. For O-Al-O bond angle, a much wider range can be observed in Fig. 2(b). More specifically, the distribution of O-Al-O bond angle has two peaks at around 95° and 150°, respectively. These two peaks indicate Al environment in N-A-S-H gel is not as single as Si environment, which will be further explained.

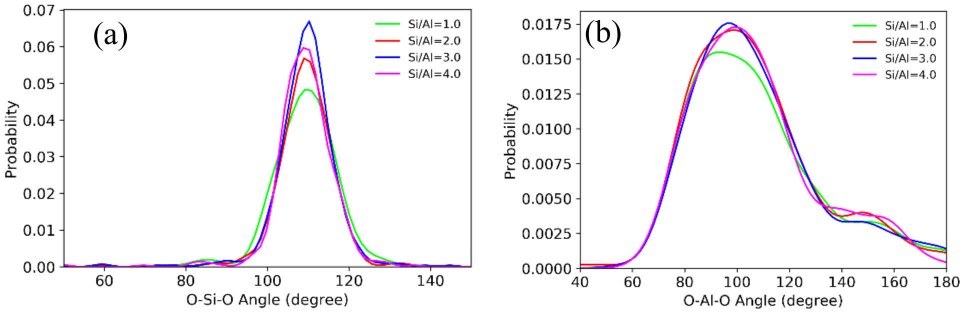

Fig. 2 Bond angle distribution for O-Si-O (a) and O-Al-O (b) for all N-A-S-H models

3.2.2 X-ray diffraction

X-ray diffraction pattern can further determine the amorphous nature of the obtained N-A-S-H. In geopolymers, the typical hump for N-A-S-H gel is located from 25°-40° (2θ) [3]. A well-matched hump from 20°-40° can be found for all XRD patterns with different Si/Al ratios in Fig. 3. The Si/Al ratio has an apparent effect on the structure of N-A-S-H gel structure. As Si/Al ratio increases, the hump shifts to smaller angle. Similar results were obtained in Lee's research [20], where the typical hump is located at 28.54°, 26.85°, and 26.27° (2θ) for the geopolymer paste with Si/Al ratio of 1.5, 3.5 and 4.0, respectively. According to Bragg's law, a smaller angle corresponds to a larger interplanar spacing. That means N-A-S-H gel structure with higher Si/Al ratio has a larger interplanar spacing, indicating a less compact structure. This result can be supported by the relationship between bond length and Si/Al ratio, as mentioned in Section 3.2.1.

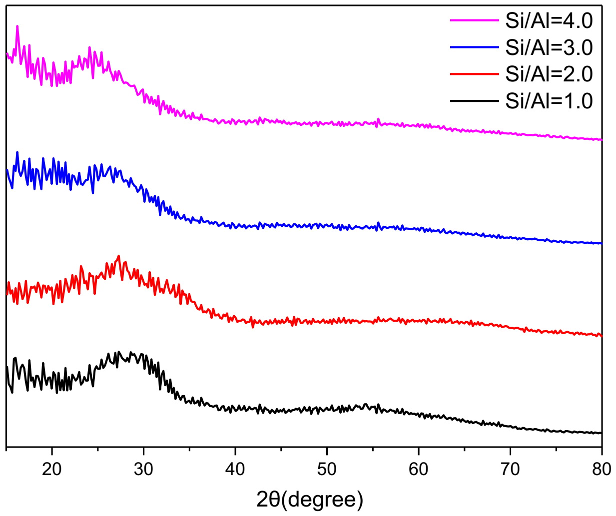

Fig. 3 Simulated XRD patterns for all N-A-S-H models with different Si/Al ratios

3.2.3 Q^n distribution

Q^n distribution is the most important structural parameter to explain how Si and Al are linked in N-A-S-H gel framework. Fig. 4 shows the Si sites (Si^n) distribution for all N-A-S-H structures with different Si/Al ratios. Four types of Si^n units, Si^1, Si^2, Si^3, Si^4, were found in all N-A-S-H gel structures. According to these studies [21,22], Si mainly exists in the form of Q^4 in N-A-S-H gel framework as N-A-S-H gel is a 3D network structure. Q^1 and Q^2, present at the surface of the gel, are supposed to be only occupied a small amount. However, 30%-56% of Si^1 and Si^2 can be found in the simulated N-A-S-H gels, which is higher than that in experiments [23]. This is due to the surface effect. The simulations took place in a very small box. As a result, the surface atom to bulk atom ratio far greater than that in a real material. That is why more Q^1 and Q^2 were found in the simulated structures. Besides, the effect of Si/Al ratio on the Si^n sites distribution can be observed obviously. With lower Si/Al ratio, N-A-S-H gel structure has more Si^3 and Si^4 and less Si^1 and Si^2, which means the structure is more crosslinked. This result has confirmed the fact that lower Si/Al ratios tends to form a 3D network (more Si^3 and Si^4), while higher Si/Al ratios prefer to a 2D crosslink structure (more Si^1 and Si^2) [24].

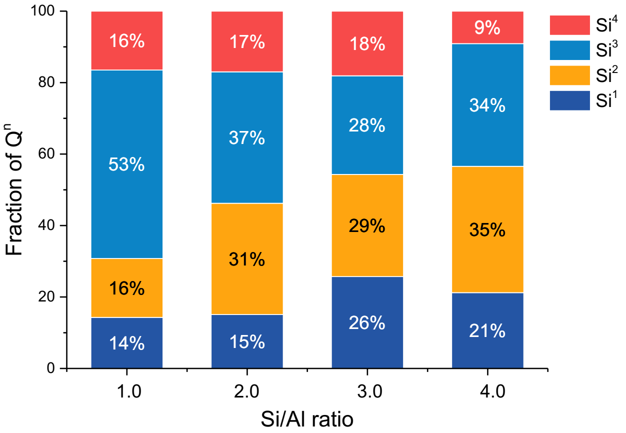

Fig. 4 Distribution of Si^n sites within all N-A-S-H models with different Si/Al ratios

The distribution of Al sites within all N-A-S-H gel structures is shown in Fig. 5. Al^4 and Al^5 are two main Al sites for all the simulated structures with different Si/Al ratios. It is generally accepted that Al always stays tetrahedrally coordinated [21]. Al^4 is the main existing form based on NMR results [5,21]. Pentacoordinate Al and six coordinated Al were once believed to only come from the unreacted raw materials in geopolymer pastes [5,19] until Walkley proposed a N-A-S-H model containing six coordinated Al for the first time [22]. Actually, pentacoordinate Al and six coordinated Al have been found as the charge-balance roles in aluminosilicate glass system in many early reports [25,26]. The presence of Al^5 is also detected in some N-A-S-H structures built by molecular dynamics [27,28]. These tetrahedral Al and non-tetrahedral Al can explain why the O-Al-O bond angle has a wide range from 60°-180°.

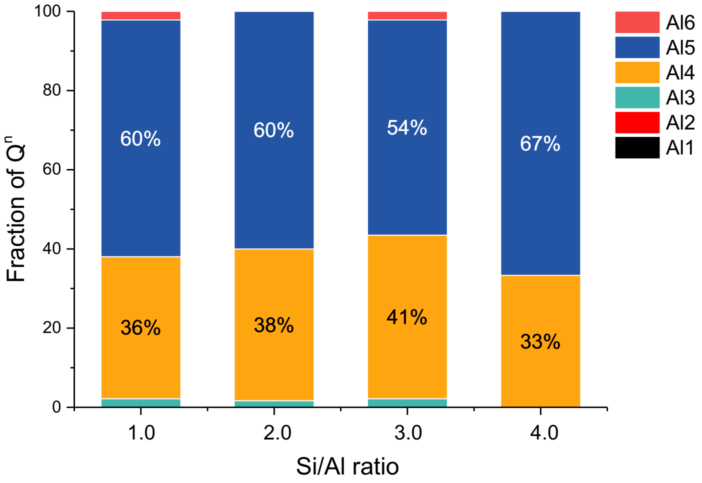

Fig. 5 Distribution of Al^n sites within all N-A-S-H models with different Si/Al ratios

4. CONCLUSIONS

The N-A-S-H atomic model was built successfully by reactive molecular dynamics simulation in this paper. During the simulation, the system went through a polymerization process similar to what happened in real geopolymer. At the end, a 3D network structure (N-A-S-H gel) was obtained. The pentacoordinate Al found in N-A-S-H model demonstrate Al does not 100% exist as tetrahedra forms. Furthermore, Si/Al ratio can affect the structure of N-A-S-H gels in terms of bond length, XRD patterns, Qn distribution. N-A-S-H gel with a lower Si/Al ratio has a denser structure.

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