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MOLECULAR DYNAMICS SIMULATION OF THE STRUCTURE AND PROPERTIES OF GEOPOLYMER GEL

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ABSTRACT

Fly ash captured by power plant can be mechanically grounded, activated, and then stimulated with strong alkali to produce a chemical reaction called geopolymer. Geopolymer gel is a material with a 3D network structure, which is widely used in architecture and material science. This research aims to study the structure and properties of geopolymer gel through modeling and molecular dynamics simulation. Firstly, this paper describes the molecular structure of geopolymer gel in detail using advanced modeling techniques, including the Compass force field and molecular dynamics calculation. The molecular dynamics method studied six geopolymer gel systems with different structures, and their elastic modulus, radial distribution function, and XRD patterns were deeply discussed. The results show that the elastic modulus of the geopolymer gel simulated in this study is 22.9~39.1 GPa, close to the experimental result of 47.2 GPa. The first peak positions of H-O bond, Si-O bond, Al-O bond, and O-O bond in the radial distribution function is approximately 0.097, 0.161, 0.177, and 0.263 nm, respectively, which are consistent with the experimental values. In the XRD spectrum, the dispersion peaks are distributed within the 2 θ range of 10 ° to 40 °, consistent with the distribution characteristics of the dispersion peaks observed in the experiment. The values obtained from molecular dynamics simulations align closely with those derived from experimental data, which not only verifies the validity of the structural model built but also provides a possibility for further in-depth research on the geopolymer gel system.

Keywords:
Fly ash geopolymer, Gel structure model, Molecular dynamics, Molecular structure characteristics

INTRODUCTION

With the acceleration of global industrialization and urbanization, the demand for building materials has sharply increased, which poses enormous pressure on the exploitation of natural resources and environmental protection. Therefore, the field of building materials science is undergoing unprecedented changes aimed at developing more environmentally friendly, efficient, and sustainable new materials. In this context, geopolymer materials, as a type of green building material, have gradually attracted widespread attention from academia and industry due to their wide range of raw material sources, simple preparation processes, and excellent performance. Geopolymer materials are usually made from industrial waste (such as fly ash, slag, etc.) through specific processes, which not only realize the resource utilization of waste but also significantly reduce energy consumption and carbon emissions in the production process of building materials (Vishnuram et al., 2023; Zhao et al., 2024). However, despite the enormous potential of geopolymer materials in the field of sustainable construction, there are still many challenges and unknowns in terms of their microstructure, performance control mechanisms, and performance in practical applications (Duan et al., 2024; Rashad et al., 2024). Therefore, in-depth research on the relationship between the composition, structure, and properties of geopolymer materials, and exploring new methods for optimizing and modifying their properties, is of great significance for promoting the progress of materials science and the development of sustainable architecture.

Fly ash geopolymer cementitious material refers to a new type of building structural material that is an inorganic non-metallic material featuring a spatial network structure generated by the polymerization reaction of aluminum silicate minerals with volcanic ash activity or potential cementitious activity and alkaline compounds (Sasi Rekha & Sumathy, 2022). Geopolymer gel, characterized by its

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unique inorganic polymer structure, has become an important class of materials, with a variety of applications from architecture to environmental restoration (Alsaif et al., 2022). These gels are synthesized by alkaline activation of aluminosilicate precursors and are expected to become sustainable substitutes for traditional cement-based materials. Although the performance issues of fly ash geopolymers have received widespread attention, traditional research methods mostly focus on macroscopic performance testing and evaluation, such as physical and mechanical properties, durability, etc. (Rashad et al., 2024). Although these methods provide valuable information, they have limitations in revealing deep-seated mechanisms such as the microstructure evolution and intermolecular interactions of fly ash. Geopolymer gel is the main reaction product and cementation phase of fly ash-based polymer materials. Its microstructure and performance are the basic units that determine the service performance of fly ash-based polymer materials (Guo et al., 2024; J. Li, Liu, et al., 2024; Y. Luo, Klima, et al., 2022). However, the structure and properties of geopolymer gel at the molecular scale have not yet been clarified (H. Wang et al., 2021).Therefore, to gain a deeper understanding of the properties and behaviors of fly ash and its geopolymer materials, more sophisticated research methods need to be introduced, and molecular dynamics (MD) simulation is such a powerful tool that can simulate the dynamic behavior of materials at the molecular scale, providing microscopic insights for explaining macroscopic properties. As a widely used computational method, molecular dynamics (MD) simulation can establish correlations between microscopic and macroscopic quantities or measurable properties. The motivation for this research is that there is a gap in our understanding of the structure of geopolymer gel at the molecular scale. MD simulation is a powerful computing tool, that provides an opportunity for an in-depth study of the complex details of the formation and behavior of geopolymer gel and provides a molecular-level perspective to supplement experimental observations (L. Li et al., 2023).

To fully understand the fly ash geopolymer gel, this study attempts to bridge the gap between macro-observation and molecular scale phenomena. By combining advanced modeling technology and MD simulation, this study aims to reveal the fine structure of geopolymer gel and the complexity of its molecular structure and mechanical properties. The main contribution of this study is to build the NASH molecular structure model of 6 fly ash geopolymer gel with different calcium silicon ratios and characterize the mechanical properties and physical properties at the molecular structure level. The molecular dynamics simulation method was used to optimize the simulation process and verify the accuracy of the model, providing a new approach for the research of geopolymer materials. The accuracy of the NASH model was verified by comparing existing literature, revealing the model characteristics of different calcium silicon ratios and their impact on mechanical properties. The research results have broad application potential in the fields of building materials, environmental protection, and resource recycling, which can help improve material performance and reduce costs.

REVIEW OF MOLECULAR STRUCTURE RESEARCH ON FLY ASH GEOPOLYMERS

FORMATION MECHANISM OF FLY ASH GEOPOLYMER GEL

The intrinsic complexity of fly ash geopolymer gel stems from the complex interaction of chemical reactions in its formation process. The formation mechanism of geopolymer gel at nanometer scale is a complex and precise process, involving multi-step physical and chemical interactions. This process is usually realized by alkali excitation reaction, and its core steps include the dissolution of raw materials, the formation of polymers, and the development of three-dimensional gel networks (S. Chen et al., 2022; J. Li, Ma, et al., 2024).

The starting point of forming geopolymer gel is the dissolution of fly ash. Alkaline activators and silicate components in fly ash dissolve in water, forming solutions containing silicon, aluminum, oxygen, and alkaline substances. In alkaline environments, the tetrahedra and hexahedra of silicon and aluminum in silicates begin to undergo hydrolysis and polymerization reactions. During this process, hydroxide ions and water molecules participate, promoting the rearrangement of silicon and aluminum atoms to form polymers (Yuan et al., 2021). The formation of polymer is a key step in the formation of geopolymer gel, which is composed of chain or ring polymers of silicon oxide tetrahedron and aluminum oxide hexahedron. As the polymers form, they gradually connect to form a 3D network structure (J. Li et al., 2022; H. Y. Zhang et al., 2021). The stability and strength of this network depend on the shape, size, and interconnectivity of the polymers. At the same time, water molecules are also incorporated into the network structure in this process, increasing the water content of the gel. Water molecules combine with silicon-oxygen and aluminum oxygen bonds in the gel network to form hydrogen bonds and hydration bonds, further improving the stability of the gel. As the reaction continues, the geopolymer gel gradually becomes harder and more stable from the initial fluid or colloidal state. On a nanometer scale, the microstructure of gel is affected by many factors, including the nature of raw materials, the type and concentration of activator, reaction temperature, etc. The formation mechanism of geopolymer gel at the nanometer scale is a process of dynamic equilibrium, involving the synergism of various physical and chemical reactions (S. Chen et al., 2022; Wu et al., 2024). The microstructure directly affects the gel's pore structure and mechanical properties (Ge et al., 2024).

MOLECULAR STRUCTURE OF GEOPOLYMER GEL

The geopolymer obtained through the polymerization reaction is composed of a 3D network structure composed of [SiO4]4- and [AlO4]5- tetrahedra bonded alternately by bridging oxygen. According to Davidovits' (2020) research, the structural monomer products generated by polymerization reactions in geopolymers have three forms: polysialate (PS), Si: Al=1:1; polysialatesiloxo (PSS), Si: Al=2:1; polysialatedisiloxo (PSDS), Si: Al=3:1. Geopolymer gel network structure is mainly formed by condensation and connection among PS, PSS, and PSDS. The condensation process of Si-O tetrahedron and Al-O tetrahedron in the polymerization process differs from cement materials' hydration process. Water is only used as a reaction medium in the geopolymer reaction, and most of the water will be removed to become solid gel in the final system of the reaction (Frasson & Rocha, 2023; Liang et al., 2023). Majidi (2009) research believes that both Si and Al elements in the geopolymer gel structure exist in the form of IV coordination, in which the [AlO4]5-tetrahedron needs to rely on the cations (Na+, Ca2+, etc.) in the structural pores to balance the overall electronegativity of the structure. The research of geopolymer gel generally involves the synthesis of calcium aluminosilicate hydrate (CASH) and sodium aluminosilicate hydrate (NASH) in the laboratory. The mineral composition and microstructure of the synthesized gel are studied using XRD, SEM/EDX, and HREM, and then the macro performance of the geopolymer is predicted (Walkley et al., 2021; Y. Wang et al., 2022, 2023; Yan et al., 2023).

MOLECULAR STRUCTURE OF FLY ASH GEOPOLYMER GEL

Existing studies have proved that the reaction products of geopolymer gel are mainly an amorphous structure formed by silicon tetrahedron and aluminum tetrahedron structure. According to the different calcium content, they can be divided into high-calcium and low-calcium systems. The hydration product of a high calcium system is generally CASH gel, and the hydration product of a low calcium system is generally NASH gel (Y. Wang et al., 2023).

On the research of NASH gel, Y. Chen et al. (2022) showed that in geopolymer, Si mainly exists in the form of SiQ4 (2Al) and SiQ4 (4Al), and Al exists in the form of AlQ4 (4Si). Guan et al. (2022) successfully constructed a geopolymer gel model with 7 different Si/Al ratio groups as basic units and simulated the geological polymerization process through the condensation reaction between hydroxyl groups to generate water and form an aluminosilicate network.

In the research of CASH gel, Kalousek (1957) proposed for the first time that Al [4] (four coordinated Al atoms) can replace Si on the Si-O chain of the Tobermorite structure to form an Al-doped Tobermorite. Faucon et al. (1999) prepared CASH gel with Ca/Si=0.66~1.7, Al/Si=0.1, and 0.3 by hydrothermal synthesis. The substitution position and coordination distribution of Al in CASH gel were analyzed by NMR. Scholars have pointed out that Al can exist in 3 types of coordination: Al [4], Al [5], and Al [6]. Al [4] exists on the Si-O chain to replace the Si-O tetrahedra, which can increase the degree of polymerization of the Si-O tetrahedra. The negative charge generated by substitution is balanced by hydrogen atoms or alkali metal ions.

SELECTION OF SIMULATION TECHNOLOGY AND MODELING METHOD FOR GEOPOLYMER GEL

Quantum mechanical calculation and MD simulation have been increasingly used to model the structure and behavior of geopolymer gel. These techniques enable researchers to simulate the evolution of gel structure over time and provide information on the formation of molecular bonds, spatial arrangement, and dynamic characteristics (Guan et al., 2022). Choosing appropriate modeling techniques is crucial for capturing the unique characteristics of geological polymer structures. Recently, the advancement of computational simulation techniques has enabled traditional descriptive models to be transformed into predictive models. The establishment of models can not only verify or explain the information obtained from experiments but also predict some properties of materials, such as mechanical properties and transport properties, from the perspective of atomic size (Y. Chen et al., 2022).

Abdolhosseini Qomi et al. (2012) used the first-principal method to simulate the doping of Al in CSH gel. The results show that Al can exist in the CASH gel in the form of Al [4], Al [5], and Al [6], where Al [4] exists in the silica chain to bridge the broken silica chain, increasing the degree of polymerization of the silica-alumina chain. Al [5] and Al [6] exist in the interlayer space to connect silicate chains on different main layers, forming the CASH 3D network structure. First principles are more inclined towards theoretical calculations, as almost all properties of molecules can be obtained through computation. However, the computational complexity is usually very large, and can only be calculated on large computer clusters, greatly limiting research application scenarios. Molecular dynamics relies on Newtonian mechanics to simulate the motion of molecular systems, requiring much lower computational power than first principles and can observe the dynamic evolution process of the system. Relatively speaking, the current application of molecular dynamics is more extensive and mature.

CONSTRUCTION AND APPLICATION OF GEOPOLYMER GEL MODEL BY MOLECULAR DYNAMICS METHOD

Bagheri et al. (2017) constructed a NASH model using Si-O-Al oligomers, sodium ions, and water molecules, tested its mechanical and structural properties, and compared the model with experimental results to demonstrate its rationality. The geopolymer model is constructed using oligomers, which are easy to operate and can yield reasonable results. Y. Chen et al. (2022) obtained the NASH gel model by polymerizing Si (OH)4 and Al (OH)3 monomers using a reaction field (ReaxFF). Molecular structural characteristics obtained through simulation, including bond length, bond angle, and X-ray diffraction pattern of the gel, align well with test results reported in the literature. Chitsaz & Tarighat (2020) considered different silicon aluminum ratios and conducted MD simulations using the NASH model of structural aluminum silicate molecule Q4 [4Al] Si with various charge balance modes. Tang et al. (2024) reacted oligomers to form a 3D network structure of NASH under the ReaxFF force field, and studied the changes and degradation mechanisms of NASH performance in corrosive environments. The ReaxFF force field has been widely used in silicon aluminum polymer systems, but its simulation calculation process requires more precise control, computational resources, and computation time. More suitable for characterizing the kinetic properties of different substance reaction interfaces. Hou et al. (2018, 2020) analyzed the structure of NASH in geopolymers and found that the structure of N-A-S glass is highly similar to that of NASH. They constructed a NASH molecular model using existing N-A-S glass models and inserted H2O molecules. Due to the similarity in molecular structure between water glass and NASH, Wang et al. (2020) randomly replaced Si atoms with Al atoms in the existing water glass molecular model and successfully constructed a NASH model. Zhang et al. (2023) used a similar method to construct a NASH model based on the sodium silicate molecular model, and conducted in-depth research on the adsorption behavior of cations at the NASH interface, analyzing the impact of Si/Al ratio, ion concentration, and ion type on this behavior. Because NASH gel is amorphous at room temperature and has low crystallinity, it is difficult to accurately measure and describe its structural morphology under the current experimental conditions, so the general silicate crystal system, space group, and its parameters are still different from the structure of NASH gel.

In summary, there are three main methods for researchers to construct NASH models: first, modifying the NASH molecular model using sodium silicate or NAS glass models with similar structures to NASH; second, combining oligomer molecular models to obtain NASH molecular models; third, using reactive force fields (ReaxFF) based on the second method to obtain NASH models with three-dimensional network structures. The relevant physical and mechanical properties of these three models are consistent with real experimental results. Considering the consumption of computer computing resources, this study uses the method of combining oligomer molecular models to obtain NASH molecular models.

Table 1: Previous research on Molecular Simulation of NASH Geopolymer gel

Study	Platform	Model	Density /(g/cm^3)	Si/Al	Potential	Ensemble	Research Target
Bagheri et al.(2017)	Materials Studio	NASH oligomers	2.00	1	Dreiding	NPT	Gel Properties
Chitsaz & Tarighat (2020)	Materials Studio	NASH gel	1.7	2	COMPASS	NPT, NVT	Gel modulus
Guan et al. (2022)	LAMMPS	NASH gel	1.92~2.05	1,2,3	ReaxFF	NVT	Gel properties
Y. Chen et al.(2022)	LAMMPS	NASH glass	2	1~4	ReaxFF	NVT	Gel Properties
Tang et al.(2024)	LAMMPS	NASH gel	2.05	3	ReaxFF	NVT, NPT	Gel properties
Fang et al.,(2024)	LAMMPS	Si,Al,O ,Na atoms	2.42	3	ReaxFF	NVT	Gel properties
R. Wang et al.(2020)	Materials Studio	Na2SiO5 glass	2.69,2.94	1,2	COMPASS	NPT, NVT	Gel Structure
W. Zhang et al.(2023)	LAMMPS	Na2SiO5 glass	-	1,2,3	ClayFF	NVT	Gel properties
R. Wang et al.(2024)	LAMMPS	Na2SiO5 glass	2.18~2.23	3,4,5	ClayFF	NVT	Gel properties
Hou et al.(2018)	LAMMPS	NAS glass	2.59	3	ReaxFF	NVT, NPT	Polymerization & gel properties
Hou et al.(2020)	LAMMPS	NAS glass	2.41	3	ClayFF	NVT	Ion immobilization
Z. Li et al.(2020)	LAMMPS	NAS glass	2.57~2.74	1,2,3	ReaxFF	NVT, NPT	Structure and mechanical properties

MODELING OF GEOPOLYMER GEL STRUCTURE MODEL AND EVALUATION OF MECHANICAL PROPERTIES

BASIC UNIT STRUCTURE MODEL

Referring to the method proposed by Wang Q et al.(2020), they constructed the structural models of PSS type and PSDS type geopolymer gel in the molecular simulation software *Materials Studio* with Ca, Na, H_2O, Si_2AlO_{10}, and Si_3AlO_{13} as the basic units. When building the geopolymer gel structure, the models of Na, Ca, H_2O, OH, $Si_2AlO_{10,}$ and Si_3AlO_{13} are clearly defined in the *Materials Visualizer* module and carried out geometric optimization in the *Forcite* module to ensure the accuracy and stability of the model. The specific forms of the optimized basic unit structure models are shown in Figure 1.

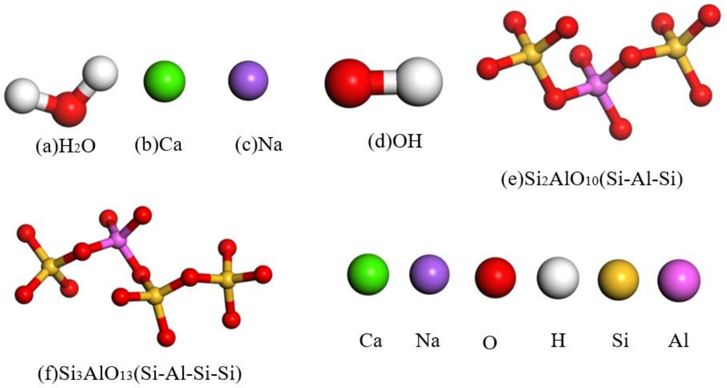

(a)H_2O (b)Ca (c)Na (d)OH (e)Si_2AlO_{10}(Si-Al-Si)
(f)Si_3AlO_{13}(Si-Al-Si-Si)

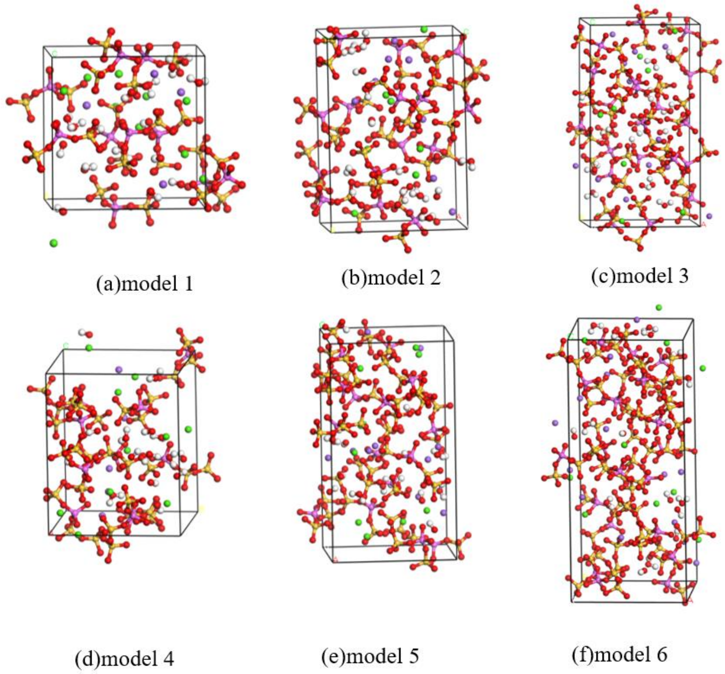
Figure 1: The basic unit of geopolymer gels

STRUCTURAL MODEL OF GEOPOLYMER GEL

Considering the influence of different Ca/Si ratios and Si/Al ratios on the mechanical properties of the model, the number of basic structural units when building the gel structure model is shown in Table 2. For the initial structure model of the gel that has been constructed, the *Focrcite* module is used for geometric optimization and MD simulation. First, the Geometry optimization in the *Focrcite* module is used, and the maximum number of optimization steps is 10000. The system is optimized in two steps (Steepest and Quasi-Newton methods). Afterward, *Energy* was used to minimize the energy of the system, and *Dynamics* was used for MD simulation. At a temperature of 298 K and a pressure of 0.001 GPa, the initial structure was equilibrated for 500 ps in the NPT ensemble with a time step of 1 fs, and then the structural system was further optimized for a duration of 500 ps in the NVT ensemble, to achieve a stable equilibrium state of the system molecules. Because the system simulated in this study is a mixed system composed of metal oxides and non-metal oxides, belonging to a generalized inorganic covalent bond system, the parameters obtained from ab initio calculations are reliable, and the COMPASS force field has the widest applicability in covalent bond simulation systems(Chitsaz & Tarighat, 2020). In this experiment, the *Compass* force field was chosen for all modeling and calculations. The *Universal* force field covers the universal force field of the entire periodic table, but the accuracy is average. This article will also compare the mechanical performance simulation results under the *Compass* force field and *Universal* force field. The final gel structure model after structural optimization and MD simulation is shown in Figure 2.

Table 2: Basic unit of geopolymer gel structure model

NO.	Ca/Si	Si/Al	Na	Ca	Si_2AlO_{10}	Si_3AlO_{13}	H_2O	OH
NASH-1	1:2	2:1	5	10	10	0	6	10
NASH-2	1:3	2:1	10	10	15	0	7	10
NASH-3	1:4	2:1	15	10	20	0	8	10
NASH-4	1:3	3:1	5	10	0	10	6	10
NASH-5	1:4.5	3:1	10	10	0	15	7	10
NASH-6	1:6	3:1	15	10	0	20	8	10


(a)model 1 (b)model 2 (c)model 3

(d)model 4 (e)model 5 (f)model 6

Figure 2: The structure model of geopolymer gel

MECHANICAL PROPERTIES OF MOLECULAR STRUCTURE OF GEOPOLYMER GEL

The mechanical properties program in the *Focrcite* module can be used to simulate and calculate the elastic modulus of the geopolymer gel system. The mechanical properties of the optimized structural model can be calculated under the *Compass* force field, and compared with the simulation results of the *Universal* force field. The simulation results of the elastic modulus after NVT MD optimization are shown in Table 3.

Luo et al.(2020) used nanoindentation technology to test the micromechanical properties of fly ash-based polymers and calculated the elastic modulus of amorphous NASH gel to be 47.2GPa. By comparison, it can be seen that the simulation value of the Universal force field is larger than that of the *Compass* force field, but the simulation results of both methods are consistent with the actual test results. Due to differences in the initial model, types, and proportions of oligomers, and ensemble parameter settings, the simulation results of molecular dynamics models may be affected to a certain extent. Different calcium silicon ratios and silicon aluminum ratios affect the products of geopolymer reactions, such as PS, PSS, and PSDS (Davidovits, 2020). These different types of geopolymers exhibit significant differences in structure and performance. From the results, the elastic modulus of NASH gel decreases with the decrease of calcium silicon ratio.

Table 3: The elastic modulus (GPa) of the geopolymer structure model

Structure type	Under *COMPASS*	Under *Universal*(Wang Q et al., 2020)
Model 1	39.01	46.45
Model 2	33.53	41.91
Model 3	28.84	33.54
Model 4	36.40	-
Model 5	27.62	-
Model 6	22.96	-

RADIAL DISTRIBUTION FUNCTION OF MOLECULAR STRUCTURE OF GEOPOLYMER GEL

The radial distribution function (RDF) (Allen & Tildesley, 2017), as an effective parameter for characterizing the structural characteristics of a system, can intuitively reflect the structural features of the system. Its physical meaning is the ratio of the local atomic density of the system to the average density of the system. When MD simulation is carried out for the gel structure model, the system movement trajectory can be obtained, and the RDF of the system can be calculated from the movement trajectory of the structure model system. The RDF g (r) is commonly used to characterize the spatial correlation between atoms, which represents the ratio of local density to the overall density of atoms. If there is a clear peak in the radial distribution function, it indicates stable nonbonding interactions between atoms, and the peak position can be used to analyze bond length information. The RDF g (r) is as follows:

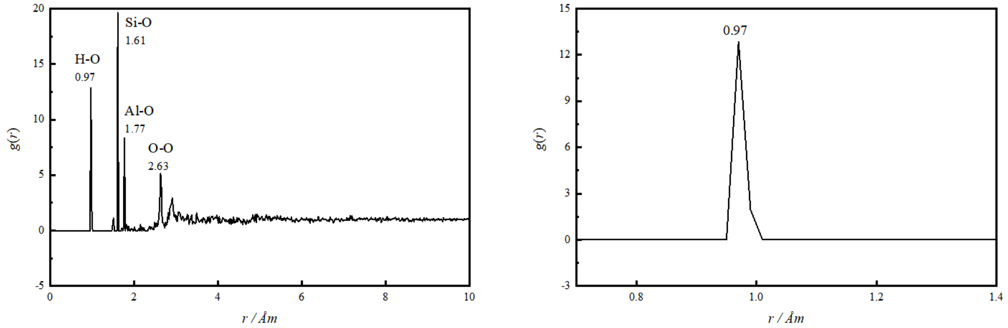
$$g(r) = \frac{dN}{\rho 4\pi r^2 dr} \tag{1}$$

Where N is the total number of atoms of this class; ρ is the system average density of this type of atom; r is the distance from the reference atom to other atoms.

For NASH, an amorphous system, due to its close-range order and long-range disorder, its radial distribution function usually only has peaks within the close range. When the radius approaches infinity, the local atomic density of the entire system is equal to its average density, and the value of the radial distribution function will tend to be 1. The difference in radial distribution function caused by this structural difference can serve as an important reference for determining the crystallization state of the system.

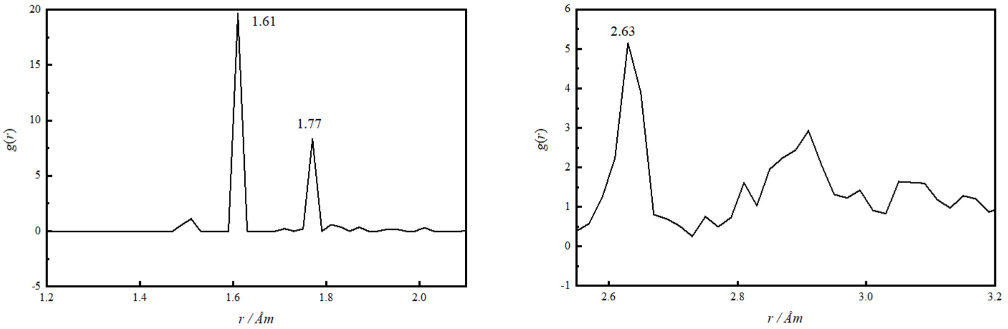
The total RDF of the NASH gel system in the range of 0~1.0 nm, as well as the RDF of the H-O bond, Si-O bond, Al-O bond, and O-O bond in the system was obtained through *Forcite* module calculation, as shown in Figure 3. As shown in Figure 3 (a), the total RDF of NASH gel will only have an obvious peak in the short range. With the increase of atomic spacing (>0.35 nm), the peak will gradually disappear. In a larger radius range, its value will gradually tend to 1, which is consistent with the characteristics of short-range order and long-range disorder that the amorphous system structure should show. From the radial distribution function diagrams of each atomic pair (Figure 3 (b) - (d)), it can be observed that the first peak positions of H-O bond, Si-O bond, Al-O bond, and O-O bond is around 0.097, 0.161, 0.177, and 0.263 nm, respectively.

White et al. (2011)used neutron scattering to determine the structural factors of metakaolin-base polymers in a 90-day-old and calculated the corresponding RDF curve. The comparison between the calculated results and the simulated values in this paper is shown in Table 4. According to Table 4, the RDF values obtained from the simulation calculations in this paper are in good agreement with the experimental values of White et al. The model Al-O bond, O-O bond, Si-O bond, and Ca-O bond are close to the experimental values, so the structure model constructed under the COMPASS force field and obtained by structural optimization and molecular dynamics simulation meets the structural requirements of geopolymer gel.



(a) The total radial distribution function of NASH model

(b) The first peak of H-O bond



(c) The first peak of (Si,Al)-O bond

(d) The first peak of O-O bond

Figure 3: RDF of NASH gel system, (a) is the total RDF of NASH, the peak appears between 0.97 and 3.5 Å, (b) is the first peak of H-O bond, (c) is the first peak of (Si, Al)-O bond, (d) is the first peak of O-O bond,

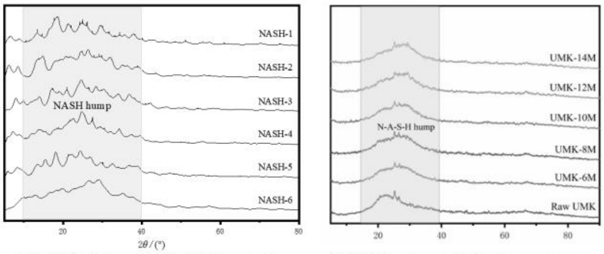
Table 4: RDF value of each atom pair of NASH gel /nm

Atomic pair type	H-O	Si-O	Al-O	O-O
Experimental value (White et al., 2011)	0.095	0.163~0.167	0.175~0.180	0.23~0.50
This study	0.097	0.161	0.177	0.263

XRD ANALYSIS

Because NASH gel is amorphous at room temperature and has low crystallinity, in its XRD pattern, the diffraction peak widens and forms a dispersion peak, which is generally distributed in the range of 2θ from 10° to 30°. The XRD patterns of amorphous NASH gel were calculated by *Materials Studio* software and compared with the XRD analysis results of UMK geopolymer samples cured for 28 days (Y. Luo, Jiang, et al., 2022). In the 28-day UMK geopolymer, the main component is an amorphous phase (2θ is the dispersion peak in the range of 20~35°). It is believed that the dispersion peak in this range is caused by the amorphous NASH gel. In the simulated XRD spectrum of NASH gel in this study, the dispersion peak is distributed in the range of 2θ from 10° to 40°, which indicates that NASH gel is an amorphous substance. But there is a deviation of about 10 ° from the dispersion peak in UMK geopolymer. The occurrence of this difference is due to the superposition of diffraction peaks of impurity minerals and dispersion peaks of amorphous phases in UMK geopolymers, resulting in a shift of dispersion peaks towards higher angles. The crystals used in simulation calculations are affected by simulation conditions, which may cause fluctuations or noise in the XRD pattern of the simulation results. However, in real experiments, due to the uniformity and anisotropy of the samples, as well as differences in sample preparation, some peaks may become weaker or stronger. If some peaks become weaker, they may disappear from the instrument noise, thereby reducing the number of peaks.

As shown in Figure 4, the simulated XRD patterns of NASH gel are consistent with the test values, indicating that the microstructure of the amorphous NASH gel system established in this study is consistent with the actual situation.



(a) XRD patterns (simulated values) of amorphous NASH gel in this study

(b) XRD patterns of UMK geopolymers (Y. Luo et al., 2022)

Figure 4: XRD patterns of amorphous NASH gel (simulation value) and UMK geopolymer, molecular models showing different combinations of geopolymers exhibit distinct crystal structure characteristics, with simulated and experimental dispersion peaks ranging from 10 ° to 40 °

DISCUSSION ON THE LIMITATIONS OF THE MODEL

Although the model in this study showed good consistency with the experimental results in the literature in terms of radial distribution function (RDF), XRD simulation pattern, mechanical properties, etc., it still has some limitations. First of all, this study assumes that the initial geopolymer gel structure model constructed can reasonably reflect the microstructure characteristics of actual materials. This includes correct atomic ratios, chemical bond types, and spatial network structures. However, due to limitations in real-world computing resources, we have reduced the model size to simplify calculations, which may result in bias when evaluating mechanical performance. Based on limited simulation research data, the selection of oligomer molecular models has a single type, short molecular chains, and some discrepancies with real polymers, which increases the uncertainty of the results. Future research should focus on improving models to more comprehensively reflect the complexity of real systems. Secondly, this study assumes that the selected molecular dynamics simulation parameters (such as force field, temperature, pressure, time step, etc.) can accurately describe the dynamic behavior of geopolymer gel. The selection of these parameters is based on existing research results, ensuring the applicability and correctness of the simulation results. In the future, various parameter adjustments will be made to improve the accuracy of the simulation.

The results of this study have certain significance for the field of sustainable materials science and engineering. By revealing the performance of polymer molecular models based on fly ash with different calcium-to-silicon and silicon-to-aluminum ratios, a theoretical basis can be provided for the development of more efficient and environmentally friendly geopolymer materials. This study is also consistent with the current trend in materials science to regulate material properties through microstructure design.

CONCLUSION

This study successfully verified the accuracy of the initial structure model of fly ash geopolymer gel based on the experimental and existing simulation data and provided a clear perspective for an in-depth understanding of the relationship between the structure and performance of geopolymer gel at the molecular level. This contribution provides significant reference value for the development of high-performance and environmentally friendly geopolymer materials and helps promote innovation and sustainable development in the fields of architecture and materials science.

Based on the initial structural model constructed concerning the experimental data, according to the structural characteristics of fly ash geopolymer gel system, Na atom, H_2O molecule, Si_2AlO_{10}, and Si_3AlO_{13}group are selected as the basic unit to construct the geopolymer gel model NASH. According to the movement track of the system in the simulation process, several optimization simulation operations were carried out, and the radial distribution function (RDF), XRD simulation atlas, mechanical properties, and other relevant parameters of the NASH gel system were calculated. The good agreement between these parameters and experimental data proves the effectiveness and reliability of the model. The establishment of this model provides important experience for the subsequent research on the mechanical properties, durability, and environmental adaptability of geopolymer gel. Based on the NASH gel model established in this study, we can further explore the microstructure evolution of geopolymer gel under different process conditions, and optimize its mechanical properties and environmental adaptability.

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REFERENCES

Abdolhosseini Qomi, M. J., Ulm, F. J., & Pellenq, R. J. M. (2012). Evidence on the dual nature of aluminum in the calcium-silicate-hydrates based on atomistic simulations. *Journal of the American Ceramic Society*, *95*(3), 1128–1137. https://doi.org/10.1111/j.1551-2916.2011.05058.x

Allen, M. P., & Tildesley, D. J. (2017). Computer simulation of liquids: Second edition. In *Computer Simulation of Liquids: Second Edition*. https://doi.org/10.1093/oso/9780198803195.001.0001

Alsaif, A., Albidah, A., Abadel, A., Abbas, H., & Al-Salloum, Y. (2022). Development of metakaolin-based geopolymer rubberized concrete: fresh and hardened properties. *Archives of Civil and Mechanical Engineering*, *22*(3), 144. https://doi.org/10.1007/s43452-022-00464-y

Bagheri, A., Nazari, A., Sanjayan, J. G., Rajeev, P., & Duan, W. (2017). Fly ash-based boroaluminosilicate geopolymers: Experimental and molecular simulations. *Ceramics International*, *43*(5), 4119–4126. https://doi.org/10.1016/j.ceramint.2016.12.020

Chen, S., Wang, K., Wei, E., Muhammad, Y., Yi, M., Wei, Y., & Fujita, T. (2022). Preparation of Al2O3-2SiO2/geopolymer powder by hydrolytic sol-gel method and its activity characterization and research on the reaction mechanism. *Powder Technology*, *397*, 117026. https://doi.org/10.1016/j.powtec.2021.11.070

Chen, Y., Dolado, J. S., Li, Z., Yin, S., Yu, Q., Kostiuchenko, A., & Ye, G. (2022). A molecular dynamics study of N–A–S–H gel with various Si/Al ratios. *Journal of the American Ceramic Society*, *105*(10), 6462–6474. https://doi.org/10.1111/jace.18597

Chitsaz, S., & Tarighat, A. (2020). Molecular dynamics simulation of N-A-S-H geopolymer macro molecule model for prediction of its modulus of elasticity. *Construction and Building Materials*, *243*, 118176. https://doi.org/10.1016/j.conbuildmat.2020.118176

Davidovits, J. (2020). Geopolymer Chemistry and Applications. 5-th edition. In *J. Davidovits.–Saint-Quentin, France* (Issue April).

Duan, S., Guo, H., Sun, H., Zhou, X., Lu, G., Guo, Y., & Ma, Z. (2024). Effect of synthesis conditions on mechanical properties and microstructure of coal gasification slag-based geopolymer. *Construction and Building Materials*, *443*, 137736. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2024.137736

Fang, M., Wang, T., Guo, T., Shi, P., Jiang, B., Wang, C., Tu, Y., Sas, G., & Elfgren, L. (2024). Compressive reactive molecular dynamics on mechanical and structural behaviors of geopolymers: Imposing lateral constraints and varied temperatures. *Applied Clay Science*, *249*, 107257. https://doi.org/10.1016/j.clay.2024.107257

Faucon, P., Delagrave, A., Petit, J. C., Richet, C., Marchand, J. M., & Zanni, H. (1999). Aluminum incorporation in calcium silicate hydrates (C-S-H) depends on their Ca/Si ratio. *Journal of Physical Chemistry B*, *103*(37), 7796–7802. https://doi.org/10.1021/jp990609q

Frasson, B. J., & Rocha, J. C. (2023). Drying shrinkage behavior of geopolymer mortar based on kaolinitic coal gangue. *Case Studies in Construction Materials*, *18*, e01957. https://doi.org/10.1016/j.cscm.2023.e01957

Ge, X., Hu, X., & Shi, C. (2024). The long-term development in the micro- and macro-properties of geopolymers made from different fly ashes. *Cement and Concrete Composites*, *152*, 105637. https://doi.org/https://doi.org/10.1016/j.cemconcomp.2024.105637

Guan, X., Jiang, L., Fan, D., Garcia Hernandez, A., Li, B., & Do, H. (2022). Molecular simulations of the structure-property relationships of N-A-S-H gels. *Construction and Building Materials*, *329*, 127166. https://doi.org/10.1016/j.conbuildmat.2022.127166

Guo, L., Liu, J., Zhou, M., & An, S. (2024). Effect of an alkali activators on the compressive strength and reaction mechanism of coal gangue-slag-fly ash geopolymer grouting materials. *Construction and Building Materials*, *426*, 136012. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2024.136012

Hou, D., Zhang, J., Pan, W., Zhang, Y., & Zhang, Z. (2020). Nanoscale mechanism of ions immobilized by the geopolymer: A molecular dynamics study. *Journal of Nuclear Materials*, *528*, 151841. https://doi.org/10.1016/j.jnucmat.2019.151841

Hou, D., Zhang, Y., Yang, T., Zhang, J., Pei, H., Zhang, J., Jiang, J., & Li, T. (2018). Molecular structure, dynamics, and mechanical behavior of sodium aluminosilicate hydrate (NASH) gel at elevated temperature: A molecular dynamics study. *Physical Chemistry Chemical Physics*, *20*(31), 20695–20711. https://doi.org/10.1039/c8cp03411g

KALOUSEK, G. L. (1957). Crystal Chemistry of Hydrous Calcium Silicates: I, Substitution of Aluminum in Lattice of Tobermorite. *Journal of the American Ceramic Society*, *40*(3), 74–80. https://doi.org/10.1111/j.1151-2916.1957.tb12579.x

Li, J., Liu, X., Cai, C., Li, F., Jin, H., Zhang, S., Sheng, N., Wang, T., & Ngo, T. (2024). Microstructure, strength development mechanism and CO2 emission assessments of molybdenum tailings collaborative fly ash geopolymers. *Case Studies in Construction Materials*, *21*, e03608. https://doi.org/https://doi.org/10.1016/j.cscm.2024.e03608

Li, J., Ma, Z., Guo, Y., & Feng, Z. (2024). In-depth analysis of macro-properties and micro-mechanism of eco-friendly geopolymer based on typical circulating fluidized bed fly ash. *Journal of Building Engineering*, *95*, 110074. https://doi.org/https://doi.org/10.1016/j.jobe.2024.110074

Li, J., Mailhiot, S., Kantola, A. M., Niu, H., Sreenivasan, H., Telkki, V. V., & Kinnunen, P. (2022). Longitudinal single-sided NMR study: Silica-to-alumina ratio changes the reaction mechanism of geopolymer. *Cement and Concrete Research*, *160*, 106921. https://doi.org/10.1016/j.cemconres.2022.106921

Li, L., Wei, Y., Feng, Q., Liu, F., Liu, B., & Pu, B. (2023). A Review: Progress in Molecular Dynamics Simulation of Portland Cement (Geopolymer)—Based Composites and the Interface between These Matrices and Reinforced Material. In *Buildings* (Vol. 13, Issue 7, p. 1875). https://doi.org/10.3390/buildings13071875

Li, Z., Zhang, J., & Wang, M. (2020). Structure, Reactivity, and Mechanical Properties of Sustainable Geopolymer Material: A Reactive Molecular Dynamics Study. *Frontiers in Materials*, *7*, 69. https://doi.org/10.3389/fmats.2020.00069

Liang, G., Yao, W., & She, A. (2023). New insights into the early-age reaction kinetics of metakaolin geopolymer by 1H low-field NMR and isothermal calorimetry. *Cement and Concrete Composites*, *137*, 104932. https://doi.org/10.1016/j.cemconcomp.2023.104932

Luo, Y., Jiang, Z., Wang, D., Lv, Y., Gao, C., & Xue, G. (2022). Effects of alkaline activators on pore structure and mechanical properties of ultrafine metakaolin geopolymers cured at room temperature. *Construction and Building Materials*, *361*, 129678. https://doi.org/10.1016/j.conbuildmat.2022.129678

Luo, Y., Klima, K. M., Brouwers, H. J. H., & Yu, Q. (2022). Effects of ladle slag on Class F fly ash geopolymer: Reaction mechanism and high temperature behavior. *Cement and Concrete Composites*, *129*, 104468. https://doi.org/https://doi.org/10.1016/j.cemconcomp.2022.104468

Luo, Z., Li, W., Gan, Y., Mendu, K., & Shah, S. P. (2020). Applying grid nanoindentation and maximum likelihood estimation for N-A-S-H gel in geopolymer paste: Investigation and discussion. *Cement and Concrete Research*, *135*, 106112. https://doi.org/10.1016/j.cemconres.2020.106112

Majidi, B. (2009). Geopolymer technology, from fundamentals to advanced applications: A review. *Materials Technology*, *24*(2), 79–87. https://doi.org/10.1179/175355509X449355

Rashad, A. M., Mohamed, R. A.-E., Zeedan, S. R., & El-Gamal, A. A. (2024). Basalt powder as a promising candidate material for improving the properties of fly ash geopolymer cement. *Construction and Building Materials*, *435*, 136805. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2024.136805

Sasi Rekha, M., & Sumathy, S. R. (2022). Engineering properties of Self-cured Geopolymer concrete binded with supplementary cementitious materials. *Materials Today: Proceedings*, *69*, 879–887. https://doi.org/10.1016/j.matpr.2022.07.357

Tang, Q., Sun, M., Lu, X., Hou, D., Li, M., & Wang, P. (2024). Understanding erosion resistance mechanisms of sodium aluminate silicate hydrate in erosion environments: a molecular dynamics study. *RSC Advances*, *14*(15), 10397–10408. https://doi.org/https://doi.org/10.1039/d4ra00302k

Vishnuram, B. G., Muthupriya, P., Dhanalakshmi, A., & Leema Margret, A. (2023). Fly-ash and GGBS based geo-polymer concrete with granite powder as partial replacement of M-Sand for sustainability. *Materials Today: Proceedings*. https://doi.org/https://doi.org/10.1016/j.matpr.2023.09.196

Walkley, B., Ke, X., Hussein, O., & Provis, J. L. (2021). Thermodynamic properties of sodium aluminosilicate hydrate (N-A-S-H). *Dalton Transactions*, *50*(39), 13968–13984. https://doi.org/10.1039/d1dt02202d

Wang, H., Wu, H., Xing, Z., Wang, R., & Dai, S. (2021). The effect of various si/al, na/al molar ratios and free water on micromorphology and macro-strength of metakaolin-based geopolymer. *Materials*, *14*(14), 3845. https://doi.org/10.3390/ma14143845

Wang Q, Kang SR, Wu LM, Zhang Q, & Ding ZY. (2020). Structural Modeling and Molecular Dynamics Simulation of Geopolymers Gel. *Materials Reports*, *34*(4), 4056–4061. https://dx.doi.org/10.11896/cldb.19030097

Wang, R., Wang, J., Dong, T., & Ouyang, G. (2020). Structural and mechanical properties of geopolymers made of aluminosilicate powder with different SiO2/Al2O3 ratio: Molecular dynamics simulation and microstructural experimental study. *Construction and Building Materials*, *240*, 117935. https://doi.org/10.1016/j.conbuildmat.2019.117935

Wang, R., Zhou, X., Zhang, W., Ye, J., & Wang, J. (2024). Transport mechanism of uranyl nitrate in nanopore of geopolymer with different Si/Al ratios: Molecular dynamics simulation. *Journal of Solid-State Chemistry*, *331*, 124542. https://doi.org/10.1016/j.jssc.2023.124542

Wang, Y., Cao, Y., Zhang, Z., Huang, J., Zhang, P., Ma, Y., & Wang, H. (2022). Study of acidic degradation of alkali-activated materials using synthetic C-(N)-A-S-H and N-A-S-H gels. *Composites Part B: Engineering*, *230*, 109510. https://doi.org/10.1016/j.compositesb.2021.109510

Wang, Y., Cao, Y., Zhang, Z., Zhang, P., Ma, Y., Wang, A., & Wang, H. (2023). Intrinsic sulfuric acid resistance of C-(N)-A-S-H and N-A-S-H gels produced by alkali-activation of synthetic calcium aluminosilicate precursors. *Cement and Concrete Research*, *165*, 107068. https://doi.org/10.1016/j.cemconres.2022.107068

White, C. E., Provis, J. L., Llobet, A., Proffen, T., & Van Deventer, J. S. J. (2011). Evolution of local structure in geopolymer gels: An in-situ neutron pair distribution function analysis. *Journal of the American Ceramic Society*, *94*(10), 3532–3539. https://doi.org/10.1111/j.1551-2916.2011.04515.x

Wu, H., He, M., Wu, S., Cheng, J., Wang, T., Che, Y., Du, Y., & Deng, Q. (2024). Effects of binder component and curing regime on compressive strength, capillary water absorption, shrinkage and pore structure of geopolymer mortars. *Construction and Building Materials*, *442*, 137707. https://doi.org/https://doi.org/10.1016/j.conbuildmat.2024.137707

Yan, Y., Bernard, E., Miron, G. D., Rentsch, D., Ma, B., Scrivener, K., & Lothenbach, B. (2023). Kinetics of Al uptake in synthetic calcium silicate hydrate (C-S-H). *Cement and Concrete Research*, *172*, 107250. https://doi.org/https://dx.doi.org/10.1016/j.cemconres.2023.107250

Yuan, J., Li, L., He, P., Chen, Z., Lao, C., Jia, D., & Zhou, Y. (2021). Effects of kinds of alkali-activated ions on geopolymerization process of geopolymer cement pastes. *Construction and Building Materials*, *293*, 123536. https://doi.org/10.1016/j.conbuildmat.2021.123536

Zhang, H. Y., Liu, J. C., & Wu, B. (2021). Mechanical properties and reaction mechanism of one-part geopolymer mortars. *Construction and Building Materials*, *273*, 121973. https://doi.org/10.1016/j.conbuildmat.2020.121973

Zhang, W., Li, J. shan, Huang, X., Chen, Z., Lang, L., & Huang, K. (2023). Unraveling the cation adsorption of geopolymer binder: A molecular dynamics study. *Chemosphere*, *335*, 139118. https://doi.org/10.1016/j.chemosphere.2023.139118

Zhao, L., Zaborowski, E., Bordoloi, S., Rajagopalan, N., Sharma, B. K., Baroi, C., Xing, W., & Zhang, L. (2024). Characterization of novel polysulfide polymer coated fly ash and its application in mitigating diffusion of contaminants. *Environmental Pollution*, *347*, 123706. https://doi.org/https://doi.org/10.1016/j.envpol.2024.123706