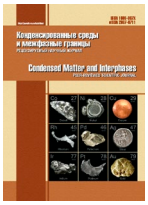

ISSN 1606-867X (Print)
ISSN 2687-0711 (Online)
Condensed Matter and Interphases
Kondensirovannye Sredy i Mezhfaznye Granitsy
https://journals.vsu.ru/kcmf/

Short communication

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https://doi.org/10.17308/kcmf.2025.27/12493

Monte Carlo simulation of interfacial adhesion between geopolymer binders and mineral aggregates

Y. M. Ermolov[1], A. A. Vasilchenko[2]✉, V. B. Mischinenko[2]

[1]Platov South-Russian State Polytechnic University (NPI),
132 Prosveshcheniya st., Novocherkassk 346428, Russian Federation

[2]Rostov State Transport University,
2 Rostovskogo Strelkovogo Polka Narodnogo Opolcheniya sq., Rostov-on-Don 344038, Russian Federation

Abstract

Silico-aluminophosphate and alkali-aluminosilicate geopolymers are increasingly popular as a green alternative to traditional Portland cement concrete used in the construction industry. In geopolymer concretes and mortars, the aggregate-matrix interface plays a major role in the fracture mechanisms. The adhesion strength between the mineral aggregate and the geopolymer matrix is mainly determined by the chemical nature of the components of the aggregate-geopolymer interface. However, this aspect remains insufficiently studied. Therefore, we used a Monte Carlo simulation to investigate adhesive behavior and interfacial interaction mechanisms of a cyclic aluminosilicate oligomer forming the structure of a geopolymer gel with mineral aggregates.

The study determined the low-energy equilibrium configurations of the structure of oligomers adsorbed on the surface of quartz, calcite, albite, and microcline, as well as the adsorption energies.

Keywords: Geopolymer, Interfacial adhesion, Mineral aggregate, Quartz, Calcite, Albite, Microcline, Monte Carlo method

Funding: The study was supported by the Russian Science Foundation grant No. 19-79-10266, https://rscf.ru/project/19-79-10266/.

For citation: Ermolov Y. M., Vasilchenko A. A., Mischinenko V. B. Monte Carlo simulation of interfacial adhesion between geopolymer binders and mineral aggregates. *Condensed Matter and Interphases*. 2025;27(1): 154–159. https://doi.org/10.17308/kcmf.2025.27/12493

Для цитирования: Ермолов Я. М., Васильченко А. А., Мищиненко В. Б. Моделирование межфазной адгезии между геополимерным вяжущим и минеральными заполнителями методом Монте-Карло. *Конденсированные среды и межфазные границы*. 2025;27(1): 154–159. https://doi.org/10.17308/kcmf.2025.27/12493

✉ Andrey M. Vasilchenko, e-mail: zmandr@mail.ru

1. Introduction

Over the past few years, silico-alumino-phosphate and alkali-aluminosilicate geopolymers [1] have been considered as a green alternative to traditional Portland cement concrete used in the construction industry [2–4] and as promising binders for a wide range of applications [5, 6]. The adjustable pore microstructure of geopolymers makes them promising materials for thermal, acoustic, and vibration insulation [7–9]. Geopolymers also exhibit effective immobilization properties and can thus be used for the utilization and disposal of radioactive waste [10–12]. Owing to their strong bonding properties, geopolymers can also be used as repair binders for concrete and reinforced concrete structures [13, 14].

In geopolymer concretes and mortars, the aggregate-matrix interface plays a major role in the fracture mechanisms and hence determines the mechanical properties of the aggregate. The properties of the interface affect the process of deformation of geopolymer materials, which typically deteriorate within the interfacial layer. A weak interfacial adhesion between geopolymer binders and mineral aggregates often results in inferior mechanical properties [15]. The adhesion strength between the mineral aggregate and the geopolymer matrix is determined by frictional forces at the aggregate-geopolymer interface and the chemical nature of these components. The impact of the latter factor on the final adhesion strength is more significant. However, this aspect remains insufficiently studied.

In our study, we used a Monte Carlo simulation to investigate the adhesive behavior and the mechanism of interfacial interaction between a cyclic aluminosilicate oligomer forming the structure of a geopolymer gel and characteristic minerals in the structure of an inorganic aggregate (α-SiO_2, β-SiO_2, calcite, albite, and microcline). The article presents low-energy equilibrium configurations of the aluminosilicate oligomer on the surface of the considered minerals and the results of a comparative analysis of adsorption energies.

2. Experimental

To study the interfacial interaction between the geopolymer obtained by means of low-temperature alkali activation of aluminosilicates [16] and mineral aggregates, we used a cyclic aluminosilicate oligomer (CAO) with a ratio of Si/Al = 3 shown in Fig. 1a. The structure of the CAO was optimized using the Dmol3 software package [17]. The calculations were performed by means of exchange-correlation functional approximations using the Perdew–Burke–Ernzerhof (RPBE) functional [18]. The electron density was determined using a double numerical plus polarization (DNP) basis set [19]. In order to account for the van der Waals forces, we used a dispersion-corrected DFT (DFT-D) suggested by Grimme [20, 21].

The following surfaces were used for the simulation of the adsorption behavior of the CAO: (100) quartz (α-SiO_2) [22]; (100) quartz (β-SiO_2) [23], (010) calcite ($CaCO_3$) [24], (100) albite

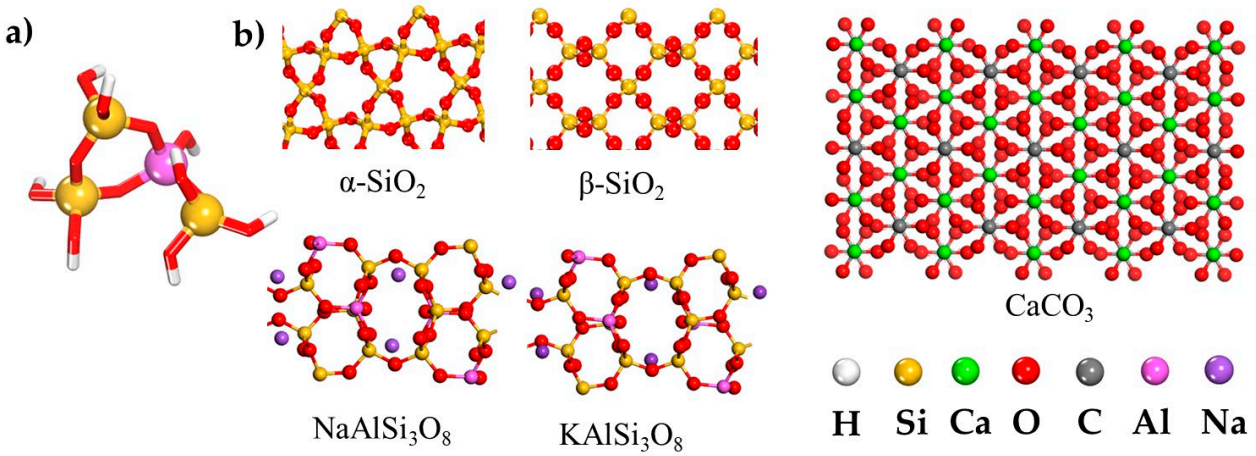

Fig. 1. (a) model of a ring-type aluminosilicate oligomer defining the structure of the N-A-S-H geopolymer gel; (b) surface models: (100) α-SiO_2; (100) β-SiO_2; (010) $CaCO_3$; (100) $NaAlSi_3O_8$; (100) $KAlSi_3O_8$

($NaAlSi_3O_8$) [25], and (100) microcline ($KAlSi_3O_8$) [26] shown in Fig. 1b. In order to eliminated the effect of the atomic layers associated with periodic boundary conditions when simulating a mineral surface, we used a 40 Å vacuum layer. The simulation was performed by means of the Monte Carlo technique in a gas phase using the Adsorption Locator software unit [17]. The calculations were based on the Metropolis–Hastings algorithm and involved simulated annealing with 20 measurement cycles at different temperatures and 2×10^5 steps for each cycle [27]. The energies were calculated using the COMPASS force field [28]. The van der Waals energy was calculated using the atomic method. The cut-off distance of the Lennard-Jones potential was 14 Å. The electrostatic interaction was described using the Ewald summation technique [29].

3. Results and discussion

The interfacial adhesion between the geopolymer binder and the aggregate was assessed based on the results of the Monte Carlo simulation of the adsorption of the cyclic aluminosilicate oligomer on the analyzed surfaces. In our study, we determined the most stable adsorption configurations of the CAO and its adsorption energies.

The adsorption energy (E_{ads}) was determined using the formula:

$$E_{ads} = E_{Total} - (E_{Adsorbate} + E_{Surface}),$$

where E_{ads} is the energy of the mineral surface-adsorbate configuration, $E_{Adsorbate}$ and $E_{Surface}$ are energies of the CAO and the mineral surface respectively.

The low-energy equilibrium configurations of the structure of the CAO adsorbed on mineral surfaces (α-SiO_2, β-SiO_2, $CaCO_3$, $NaAlSi_3O_8$, $KAlSi_3O_8$) determined as a result of the Monte Carlo simulation are demonstrated in Fig. 2. We can see that as a result of the adsorption, the CAO is oriented parallel to the mineral surface. This spatial conformation of the CAO allows for maximum number of interactions with the mineral surface. To determine the main types of interactions between the adsorbate and the mineral surface, we performed an analysis of bond lengths. The shortest distances between the atoms of the mineral surface and the nearest aluminum and silicon atoms of the adsorbed oligomer in the equilibrium state are given in Table 1. The distances were calculated based on the difference in the Cartesian coordinates. To calculate the number of bonds between the surface oxygen atoms and the hydroxyl groups of the oligomer, we used a geometric criterion, according to which the distance between the atoms forming the hydrogen bond cannot be more than 2.45 Å [30]. In our study, practically all the shortest bonds were less than 2.5 Å, which indicates the formation of a strong bond between chemisorbed oligomers and the mineral surface.

Fig. 3 presents the calculated E_{ads} for all the studied systems. Significantly negative E_{ads} values indicate the strongest and most stable adsorption. Fig. 3 demonstrates that the absolute values of the adsorption energy of the CAO on the studied

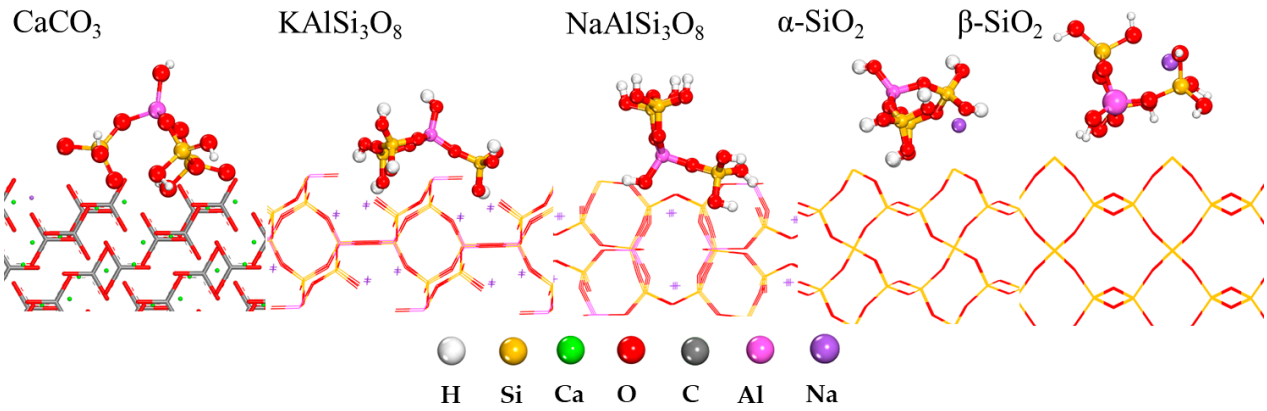

Fig. 2. Most stable low-energy configurations calculated by MC simulations for the adsorption of oligomer on the mineral surfaces of aggregate

Table 1. The distance (Å) between the layer of near-surface atoms and the atoms of the oligomer, as well as the number of bonds formed, calculated by the Monte Carlo method

Mineral aggregate	Al	Si	Si	Si	Number of bonds
$CaCO_3$	3.22	5.72	3.36	3.09	5
$KAlSi_3O_8$	2.78	1.99	2.52	4.83	4
$NaAlSi_3O_8$	5.07	2.04	5.32	5.67	3
α-SiO_2	3.89	1.49	6.61	2.97	2
β-SiO_2	2.52	4.31	2.05	4.31	2

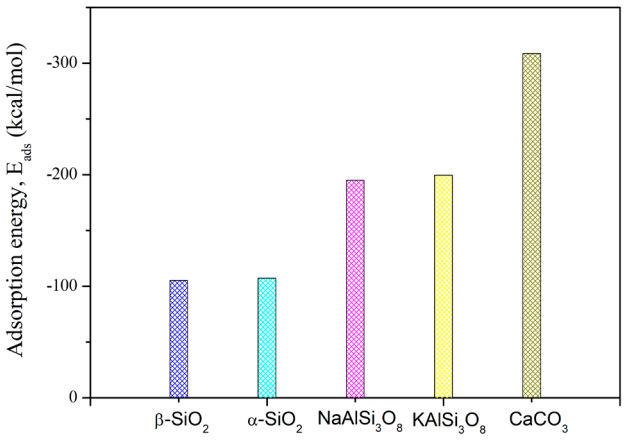

Fig. 3. Adsorption energies obtained from Monte Carlo simulations for oligomer adsorption on the surface of mineral aggregates in the gas phase

mineral surfaces decrease in the following order: $CaCO_3$ > $KAlSi_3O_8$ > $NaAlSi_3O_8$ > α-SiO_2> β-SiO_2. This tendency correlates well with the number of formed OH-bonds (Table 1). The calculated E_{ads} demonstrated that the best adhesion is observed during the interaction of the CAO with calcite, which is confirmed by the experimental data presented in [31, 32].

4. Conclusions

This study presents Monte Carlo simulation results investigating the adhesive behavior and the mechanism of interfacial bonding of a cyclic aluminosilicate oligomer and mineral aggregates. The study determined low-energy equilibrium configurations of the structure of oligomers adsorbed on the surface of (100) α-SiO_2, (100) β-SiO_2, (010) $CaCO_3$, (100) $NaAlSi_3O_8$, (100) $KAlSi_3O_8$, as well as the adsorption energies. The simulation demonstrated that cyclic aluminosilicate oligomers can be chemisorbed. The absolute values of the adsorption energy of the aluminosilicate oligomer on the studied surfaces are characterized by the following sequence: $CaCO_3$ > $KAlSi_3O_8$ > $NaAlSi_3O_8$ > α-SiO_2> β-SiO_2. This result is in good agreement with the number of the OH-bonds formed between the aluminosilicate oligomer and the mineral surface. The best adhesion effect was observed for calcite.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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Information about the authors

Yakov M. Ermolov, Cand. Sci. (Tech.), Engineer of the Fuel Energy Waste Recycling Laboratory, Platov South-Russian State Polytechnic University (Novocherkassk, Russian Federation).

https://orcid.org/0000-0002-2065-6168

mr.yak.erm@gmail.com

Andrey A. Vasilchenko, Head of the Research Testing Laboratory "Testing and monitoring in civil and transport construction", Rostov State Transport University (Rostov-on-Don, Russian Federation).

https://orcid.org/0000-0001-6336-4379

zmandr@mail.ru

Vasily B. Mischinenko, Assistant at the Department of Transport Machines and Tribotechnics, Rostov State Transport University (Rostov-on-Don, Russian Federation).

https://orcid.org/ 0000-0002-9799-0519

m.vasbor@bk.ru

Received 02.04.2024; approved after reviewing 03.05.2024; accepted for publication 15.05.2024; published online 25.03.2025.

Translated by Yulia Dymant