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Computational Study on the Al^{3+} Substitution and Porous Agent Effect on Geopolymer Foam Formation

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ABSTRACT

This work explores the replacement of Al^{3+} by Fe^{2+} or Fe^{3+} and the effect of porous agent on geopolymers foam formation, using DFT at the level of theory B3LYP/6-31G+(d, p). The obtained results show values of HOMO-LUMO gaps that are respectively 130.46 ; 93.3 and 14.38 kcal.mol^{-1} for $[Al(OH)_4]^-$, $[Fe(OH)_4]^-$ and $[Fe(OH)_4]^{2-}$ monomers and; 63.79, 5.65, 155.55 and 36.13 Kcal.mol-1 for oligomers$[(OH)_2Al–(O–Si(OH)_3)_2]^-$, $[(OH)_2Fe–(O–Si(OH)_3)_2]^-$,$[Al–(O–Si(OH)_3)_4]^-$ and $Fe–(O–Si(OH)_3)_4]^{2-}$. Calculations using thermodynamics parameter reveals the most favorable porous agent among the three (silica fume, aluminum powder and oxygenated water) tested. The results reveal that aluminum powder seems to be the best candidate with the lowest Δ_rG (-190.61 kcal.mol^{-1}) and ΔS (-82.94 cal/mol.Kelv).

1. Introduction

Geopolymers are considered as an alternative to Ordinary Portland Cement (OPC) in both construction and oil and gas applications. Geopolymers are three-dimensional network inorganic materials obtained through the polycondensation process when aluminosilicate source materials are mixed with silicate and alkaline solutions [1]. They were discovered by Davidovit in 1970 and are still considered relatively new. The aluminosilicate generally used include: fly ash, ground granulated blast furnace slag (GBFS) and metakaolin [2], as well as laterite. In general, the choice of the source materials for making geopolymers depends on factors such as availability, cost, type of application, and specific demand of the end users. Laterite is a raw material abundant and available in tropical zone [3,4]. For this reason laterite has been used for several decades. It is formed from the weathering of tropical rocks, enriched with iron and aluminum elements followed by the reduction of silica content. The solubility is enhanced in alkaline solution [5]. The particularity of this aluminosilcate is the presence of iron species in the structure as shown in the chemical formula (Fe_2O_3-Al_2O_3-SiO_2-H_2O). In this formula some of the Al^{3+} ions are replaced with Fe^{2+} or Fe^{3+} from the

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matrix of kaolinite clay [6]. The substitution of some Al^{3+} by Fe^{2+} or Fe^{3+} in laterite has attracted considerable attention in their potential as material for geopolymerization [7].

Geopolymer foam (highly porous materials) has emerged as one of the most exciting materials over the past few years due to their remarkable properties, low cost and green synthesis protocol. This has attracted their exploration in various high added-value applications [8] including: dye removal [9,10], waste water filtration [11], heavy metal absorption [12], and thermal insulation [13]. There are several methods used to synthetized geopolymer foam for instance: the use of sacrificial fillers (e.g., polymers) [14], the use of 3D printing sacrificial templates [15] and the incorporation of a foaming agent (e.g., hydrogen peroxide, fine metallic powders) [16, 17, 18] into the geopolymer slurry with the formation of bubbles (the most commonly used method).

Geopolymer foam formation from solid materials is a complex, multistep process roughly comprising of:

a) Alkaline depolymerization of the poly (siloxo) framework and dissolution of aluminum;

b) Formation of monomers and oligomers from ortho-sialate $(OH)_3 - Si–O–Al–(OH)_3$/$(OH)_3 - Si–O–Fe–(OH)_3$;

c) Polycondensation into higher oligomers and polymeric 3D networks [19, 20].

The most fundamental reaction in silica sol–gel chemistry is the dimerization of two neutral silicic species, $Si(OH)_4$, which react to produce a dimer, $(OH)_3SiOSi(OH)_3$, and a water molecule [21]. The DFT/CGMC methodology has successfully been used in silicate systems.

Katsoulakis et al. 2003 [22, 23] demonstrated that the atomic structures of silicate gels are complex, thus the simulation of molecular structures will require a relatively large simulation systems. This will require even more computational cost to capture the pseudo equilibrium state obtained through silica precipitation. Thus, coarse-grain method from atomic to molecular representation will be required to reduce the computational cost [21, 22].

The focus of this work is to evaluate the effect of substitution of Al^{3+} by Fe^{3+} and Fe^{2+} during the process of laterization. The results will reveal whether or not laterite can be used as potential aluminosilicate (able to reduce energy consumption) for geopolymerization reaction (condensation). A method like DFT will be used to study the reaction pathway of the pore formation during geopolymerization with the three porous agents (silica fume, aluminum powder and oxygenated water).

2. Computational Details

First, we opted for the semi-empirical PM6 method to carry out a preliminary study of the chosen system. This method is less computationally expensive, yet can assist in identifying the different obstacles that might affect a qualitative result. All the structures involved in this study were optimized by the B3LYP functional combined with the base 6-311 + G (d,p) implemented in the Gaussian 09 [24] software. The choice to perform calculations at the B3LYP/6-311 + G (d,p) level of theory was because the method is very effective for the geopolymerization modeling. The global minima were confirmed by the calculation of vibration frequencies.

An example of condensation reaction studied in this work is given below:

$$[Al(OH)_4]^- + Si(OH)_4 \rightarrow [(OH)_3Al\text{-}O\text{-}Si(OH)_3]^- + H_2O$$ The free enthalpy of the reaction ($\Delta_r G$) and the HOMO-LUMO gap ($\Delta\varepsilon$) are respectively presented in equations (1) and (2). For lower value of free enthalpy of the reaction, energy consumption is also low and therefore the reaction in question is thermodynamically favored. Knowledge of the properties of the frontier molecular orbitals notably their energy is very useful to gauge the chemical reactivity of molecules.

$$\Delta_r G = \sum \alpha \Delta G(product) - \sum \beta \Delta G(reactant) \quad (1)$$

$$\Delta\varepsilon = \varepsilon_{LUMO} - \varepsilon_{HOMO} \quad (2)$$

3. Results and Discussions

3.1. Effect of aluminum ion substitution by iron ions

Effect of Al^{3+}, Fe^{2+} and Fe^{3+} exchange during the oligomers formation has been study. In fact, geopolymerization is a very complex reaction, procuring in three steps which are: dissolution for the formation of monomers, condensation and polycondensation.

This work focus on the condensation which is a crucial step of geopolymerization and the one that can be easily be monitored. The starting point is therefore monomers and oligomers containing Al^{3+} and subsequently substituting Al^{3+} by Fe^{2+} and Fe^{3+} in order to evaluate the resulting free enthalpy of the reaction ($\Delta_r G$) and the HOMO-LUMO gap ($\Delta\varepsilon$). The results are shown in the table below:

Table 1. Gibbs energies of condensation reactions computed using B3LYP/6-311G +(d,p) method

N°	Condensation reactions	$\Delta_r G$ (Kcal.mol^{-1})
1	$[Al(OH)_4]^- + Si(OH)_4 \longrightarrow [(OH)_3Al–O–Si(OH)_3]^- + H_2O$	-33.30
2	$[Al(OH)_4]^- + \mathbf{2}Si(OH)_4 \longrightarrow [(OH)_2Al–(O–Si(OH)_3)_2]^- + \mathbf{2}H_2O$	-42.80
3	$[Al(OH)_4]^- + \mathbf{3}Si(OH)_4 \longrightarrow [(OH)Al–(O–Si(OH)_3)_3]^- + \mathbf{3}H_2O$	-53.30
4	$[Al(OH)_4]^- + \mathbf{4}Si(OH)_4 \longrightarrow [Al–(O–Si(OH)_3)_4]^- + \mathbf{4}H_2O$	-75.10
5	$[Fe(OH)_4]^- + Si(OH)_4 \longrightarrow [(OH)_3Fe–O–Si(OH)_3]^- + H_2O$	-43.60
6	$[Fe(OH)_4]^- + \mathbf{2}Si(OH)_4 \longrightarrow [(OH)_2Fe–(O–Si(OH)_3)_2]^- + \mathbf{2}H_2O$	-70.60
7	$[Fe(OH)_4]^- + \mathbf{3}Si(OH)_4 \longrightarrow [(OH)Fe–(O–Si(OH)_3)_3]^- + \mathbf{3}H_2O$	-163.40
8	$[Fe(OH)_4]^- + \mathbf{4}Si(OH)_4 \longrightarrow [Fe–(O–Si(OH)_3)_4]^- + \mathbf{4}H_2O$	0.64
9	$[Fe(OH)_4]^{2-} + Si(OH)_4 \longrightarrow [(OH)_3Fe–O–Si(OH)_3]^{2-} + H_2O$	-88.20
10	$[Fe(OH)_4]^{2-} + \mathbf{2}Si(OH)_4 \longrightarrow [(OH)_3Fe–O–Si(OH)_3]^{2-} + \mathbf{2}H_2O$	-46.90
11	$[Fe(OH)_4]^{2-} + \mathbf{3}Si(OH)_4 \longrightarrow [(OH)_3Fe–O–Si(OH)_3]^{2-} + \mathbf{3}H_2O$	-183.40
12	$[Fe(OH)_4]^{2-} + \mathbf{4}Si(OH)_4 \longrightarrow [Fe–(O–Si(OH)_3)_4]^{2-} + \mathbf{4}H_2O$	-209.20

Table 1 presents Gibbs energies computed using B3LYP/6-311G +(d,p) method. Starting with oligomers with Al^{3+}, results shows a correlation between drop in energy and substitution of OH by $Si(OH)_4$. This results show that $Si(OH)_4$ stabilizes the system by decreasing the free energy, rendering it more negative. These results also justify the favorability of experimental silica in the condensation and polycondensation reaction during the synthesis of geopolymers.

Regarding the reactant (monomer) $[Al(OH)_4]^-$, the energy of the system (zero point energy) is -546.10 Hartree. When Al^{3+} is replaced by Fe^{3+} and Fe^{2+}, the values are respectively -1567.20 and -1567.10 Hartree for $[Fe(OH)_4]^-$ and $[Fe(OH)_4]^{2-}$. These results indicate that the substitution of Al by Fe considerably reduces the energy of the system, leading to the conclusion that iron tends to stabilize the system. In addition, this result further explains why laterisation stabilizes rocks, which could justify the fact that there is no other material in nature resulting from the transformation of laterite into another material. The energy (zero point energy) of the $[(OH)_3Al\text{-}O\text{-}Si(OH)_3]^-$ $[(OH)_3Fe\text{-}O\text{-}Si(OH)_3]^-$ and $[(OH)_3Fe\text{-}O\text{-}Si(OH)_3]^{2-}$ oligomers system are respectively -1062.76, -2083.84 and -2083.82 Hatree. These zero point energy values of the various systems decreases considerably when Al^{3+} is replaced by Fe^{3+} and Fe^{2+}. This result corroborates with the previous one regarding the stabilization of the systems by iron. For the oligomers $[(OH)_2Al\text{-}(O\text{-}Si(OH)_3)_2]^-$, $[(OH)_2Fe\text{-}(O\text{-}Si(OH)_3)_2]^-$ and $[(OH)_2Fe\text{-}(O\text{-}Si(OH)_3)_2]^{2-}$ the results gave -1579.24; -2600.52 and -2600.34 Hartree respectively. Here again the substitution of Al^{3+} by Fe^{3+} and Fe^{2+} leads to stability of the system. The energy value for $[(OH)Al\text{-}(O\text{-}Si(OH)_3)_3]^-$ is -2095.99Hartree; when Al^{3+} is replaced by Fe^{3+} and $Fe^{2+}$the results are: -3117.27 and -3117.21 Hartree respectively. Finally for $[Al\text{-}(O\text{-}Si(OH)_3)_4]^-$, $[Fe\text{-}(O\text{-}Si(OH)_3)_4]^-$ and $[Fe\text{-}(O\text{-}Si(OH)_3)_4]^{2-}$ the results are respectively : -2612.625, -3633.61 and -3633.77Hartree.

Overall, the substitution of Al^{3+} by Fe^{3+} and Fe^{2+}stabilises the system because the energies decrease considerably. DFT results thus explain the choice of laterite as the raw material for geopolymerization. In fact as is known experimentally, laterite is a raw material obtained during the physico-chemical alteration of the parent kaolinitic rock under the effect of erosion. During this alteration, a part of Al atoms are substituted by Fe atoms. Quantum methods like DFT have the advantage of being able to predict reactions pathway and thus provide justification for their existence. Using DFT it was been demonstrated that laterite is a raw material use a source of aluminosilicate in the synthesis of geopolymers. The results obtained in the Table 1 show that laterite is indeed suitable, as the free enthalpy values of the reactions involving iron are lower than those involving aluminum. Thus looking at reaction 1, 5 and 9 in the Table 1, the values of $\Delta_r G$ are equal to -33.30, -43.60 and -88.20 Kcal.mol^{-1} respectively. The same observation is made for reactions 2, 6 and 10, where the values of $\Delta_r G$ are -42.80, -70.60 and -46.90 kcal.mol^{-1} respectively. This means that from an energy point of view, reactions with kaolinite consume more energy than those with laterite.

In addition, the molecular orbitals (HOMO and LUMO) of the reactants were used to calculate the energy gap between these orbitals. It should be noted that the energy gap is used to determine the reactivity index of molecules; the smaller it is, the more reactive is the molecule. The results are shown on Table 2 below:

Table 2. HOMO, LUMO and Gap energies for monomers and oligomers

Compounds	ε_{HOMO} (Hatree)	ε_{LUMO} (Hatree)	$\Delta\varepsilon$ (Hartree)	$\Delta\varepsilon$ (kcal mol^{-1})
$Si(OH)_4$	-0.33468	-0.05012	0.28456	178.5641033
$[Al(OH)_4]^-$	-0.09475	0.11315	0.2079	130.4592251
$[Fe(OH)_4]^-$	-0.05759	0.09109	0.14868	93.29811246
$[Fe(OH)_4]^{2-}$	0.14529	0.16821	0.02292	14.38251774
$[(OH)_3Al–O–Si(OH)_3]^-$	-0.09088	0.01802	0.1089	68.33578455
$[(OH)_2Al–(O–Si(OH)_3)_2]^-$	-0.05544	0.04622	0.10166	63.79261577
$[(OH)_2Fe–(O–Si(OH)_3)_2]^-$	-0.10602	-0.09701	0.00901	5.653860595
$[Al–(O–Si(OH)_3)_4]^-$	-0.18983	0.05805	0.24788	155.5470549
$Fe–(O–Si(OH)_3)_4]^{2-}$	0.07769	0.13527	0.05758	36.13199701

Table 2 highlights the results of HOMO, LUMO and Gap energies (reactivity index) of different compounds. After computing, results show that for the monomers used for condensation, the energy gap values of $Si(OH)_4$, $[Al(OH)_4]^-$, $[Fe(OH)_4]^-$ and $[Fe(OH)_4]^{2-}$ are 178.56, 130.46, 93.3 and 14.38 kcal.mol^{-1} respectively. This result shows that the substitution of Al^{3+} by Fe^{3+} makes the system more reactive. This result corroborates the previous results. It is observed that when Al^{3+} is replaced by Fe^{2+}, the molecule obtained is more reactive than when Al^{3+} is replaced with Fe^{3+}. These results also corroborate the experimental results where it was observed that the goethite present in non-calcined laterite is at the origin of its reactivity in the presence of an alkaline solution.

For the oligomers, the HOMO-LUMO gap of $[(OH)_2Al\text{-}(O\text{-}Si(OH)_3)_2]^-$ is 63.79261577 kcal.mol^{-1} and that of $[(OH)_2Fe\text{-}(O\text{-}Si(OH)_3)_2]^-$ is 5.653860595 kcal.mol^{-1}. This result implies that the substitution of Al^{3+} by Fe^{3+} makes the final compound more reactive. For another oligomer $[Al\text{-}(O\text{-}Si(OH)_3)_4]^-$ the value of the HOMO-LUMO gap is 55.5470549 kcal.mol^{-1} . When Al^{3+} is replaced by Fe^{2+}, this value is 36.13199701 kcal.mol^{-1} for $Fe\text{-}(O\text{-}Si(OH)_3)_4]^{2-}$. These results show that for a potential polycondensation reaction, oligomers containing iron elements are more favorable to the formation of the geopolymer network than oligomers containing only Al.

3.2. Energetic evaluation of pore-forming reactions by three porous-agents: hydrogen peroxide (H_2O_2), aluminum powder (Al) and silica fume (Si)

Porous materials are also being developed because of their potential applications. The synthesis of these materials requires the presence in the reaction system of a pore-forming agent (porous agent), capable of stimulating the formation of pores; there are several such agents, including silica fume, hydrogen peroxide and aluminum powder.

Since the aim of research and development is to reduce energy expenditure, it is necessary to rank the pore-forming agents available in order of their energy expenditure during the reaction. In this work, three pore-forming reactions were studied as shown in **Table 3** with their free enthalpy and entropy evaluated.

Note that, free enthalpy (Δ_rG) is a thermodynamic quantity that can be used to determine or define the energy required for a reaction to occur. When $\Delta_rG>0$, the reaction is endergonic and consumes energy (requiring external energy); when $\Delta_rG<0$, the reaction is exorgonic (releasing energy instead). It is therefore beneficial for the free enthalpy to be negative. Entropy characterizes the disorder of a reaction, so this value should be as small as possible. The results obtained are shown in the following table:

Table 3: Gibbs energies and Entropies pore-forming reactions

Pore-forming reactions	$\Delta_r G$ (kcal mol^{-1})	ΔS (cal/mol.Kelv)
$4H_2O + Si \rightarrow H_2 + Si(OH)_4$	-151.2291	-79.712
$Al + H_2O + OH^- \rightarrow Al(OH)_4^- + \frac{3}{2}H_2$	**-190.6075**	**-82.944**
$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$	-12.29008	13.789

Table 3 shows that the free enthalpy values of the pore-forming reactions from silica fume, aluminum powder and hydrogen peroxide are -151.2291, -190.6075 and -12.290087 kcal mol^{-1} respectively. These negative values indicate the endothermic nature of the three reaction types, which is in agreement with the experimental results. In addition, these results show that aluminum powder is the pore-forming agent whose use allows the lowest amount of energy. Theoretical calculations can therefore contribute in choosing a reaction component. Furthermore, the entropy values for the three previous reactions are respectively equal to -79.712, -82.944 and 13.789 cal/mol.Kelv. This result indicates that the reaction system leading to the formation of pores with aluminum powder is the weakest compared with the other two; a result that corroborates that of free enthalpy.

4. Conclusion

The aim of this work was first to study the impact of the substitution of Al^{3+} by Fe^{3+}/Fe^{2+} during the condensation step (formation of oligomers) and secondly to evaluate the reaction energy of the pore formation during geopolymer foams synthesis with three porous agents (silica fume, aluminum powder and oxygenated water). This was done using Density Functional Theory (DFT) calculations. Computational chemistry has enabled us to understand that laterite can be used as potential raw materials for geopolymerization since the reactions involved in these materials consume less energy compared with other raw materials such as metakaolin. The Gibbs energies involve $[Al(OH)_4]^-$, $[Fe(OH)_4]^-$ and $[Fe(OH)_4]^{2-}$ are -33.3, -43.6 and -88.2 cal/mol.Kelv. In addition, these results corroborate those obtained experimentally. Several experimental studies have shown that clay needs to be calcined at least 700°C to be activated, whereas for laterite, 550°C is sufficient to activate the system. On the other hand, the results show that the different energies converge towards the same conclusion, which is that, of the three pore-forming agents, silica fume, aluminum powder and hydrogen peroxide, the best in terms of energy is aluminum powder. This is because it consumes the smallest amount of energy, and the reaction it undergoes is the least disordered possible ($\Delta_r G$= -151.2291, -190.6075 and -12.29008 kcal mol^{-1} and ΔS= -79.712, -82.944 and 13.789 cal.mol^{-1}.Kelv for the reaction involving Si, Al and H_2O_2 respectively).

Highlights :

- DFT method was used to study the effect of Al^{3+} substitution by Fe^{3+}or Fe^{2+} and the reactions of pore formation during foams synthesis;
- Monomers and oligomers containing Al^{3+} are less reactive than those with Fe^{3+} or Fe^{2+} ;
- Foam synthesis reactions with Si, Al and H_2O_2 are all exothermic ;
- The pore-forming agent with the lowest energy consumption is Al powder.

Conflict of interest:

The authors do not have any conflict of interest with other entities or researchers.

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