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Research Article

Atomistic study on silica-based superhydrophobic material interaction with calcium ion in concrete industry

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Abstract: The interaction between calcium ions and hydrophobic silica-based material plays a critical role in understanding the durability and interfacial properties of protective coatings within concrete. In this study, Density Functional Theory (DFT) computations are utilized to investigate the interaction between calcium ions and model compounds within a silica-based hydrophobic material. These model compounds include 3-aminopropyltriethoxysilane (APTES), triethoxy(octyl)silane, Bisphenol A, and silicon dioxide. Geometry optimizations and electronic structure computations are carried out for these model compounds. The DFT computations are performed with the B3LYP/6-311++G(d,p) method with Grimme's D3 correction. Molecular Electrostatic Potential (MEP), Reduced Density Gradient (RDG), and Non-Covalent Interaction (NCI) analyses are performed to investigate the charge distribution and intermolecular interactions. The results obtained from DFT computations show that calcium ion stabilization increases progressively from isolated organic modifiers to a complex silica-based material. While APTES, Bisphenol A, and triethoxy(octyl)silane make a contribution to calcium ion stabilization by weak to moderate intermolecular interactions, silicon dioxide shows the strongest interaction with calcium ions. Silicon dioxide seems to be the major contributor to calcium ion stabilization. However, the strong interaction between calcium ions and water points to hydration as a major competing effect.

Keywords: *Silica-based materials; Superhydrophobic coatings; Density Functional Theory (DFT); Advanced materials, Road construction; Mechanical properties; Environmental Resistance.*

1 Introduction

Concrete is the most widely used construction material globally; however, its long-term durability remains strongly influenced by water transport, ionic diffusion, and chemically driven microstructural degradation processes [1], [2]. Among the ionic species governing cement chemistry, calcium ions (Ca^{2+}) play a fundamental role in hydration reactions, calcium silicate hydrate (C–S–H) formation, and overall mechanical strength development [3], [4]. At the same time, calcium leaching and redistribution under aggressive environmental conditions contribute to increased porosity, reduced cohesion, and progressive durability loss in cementitious systems [2], [5]. Therefore, controlling water ingress and calcium mobility is central to enhancing the service life of concrete infrastructures.

To combat the issue of water penetration, silica-based superhydrophobic coatings have been identified as one of the promising approaches in the field of surface engineering techniques [6], [7], [8]. Superhydrophobic coatings mimic the hierarchical structures found in natural surfaces and have the capability to attain high contact angles with reduced wettability [9]. In cement-based materials, silica nanoparticles and silica fume particles are used to improve the interfacial transition zone, refine the pore structure, and improve the mechanical properties of the material [10], [11], [12]. Surface functionalization with organosilane-based compounds, including 3-aminopropyltriethoxysilane (APTES), long-chain alkoxysilanes, and epoxy-based coatings, including Bisphenol A, is used to improve the adhesion properties of silica-based substrates. These coatings have the capability to chemically graft with hydroxylated silica surfaces [13], [14], [15].

Although considerable progress has been achieved in the experimental study of superhydrophobic silica-based materials, the atomic-level mechanisms of interaction with Ca^{2+} ions remain poorly understood. It has been demonstrated in previous research that Ca^{2+} in aqueous solution possesses a strongly stabilized hydration shell, including six to eight water molecules in the coordination shell, with considerable interaction energies [16], [17], [18], [19]. On the other hand, theoretical and experimental research on Ca^{2+} adsorption onto oxide surfaces, including silica, has revealed that Ca^{2+} may react with surface oxygen atoms in an inner-sphere manner, depending on the surface hydroxylation degree and coordination [20], [21], [22].

However, a systematic atomistic analysis of the following aspects: (i) the hydration of calcium, (ii) the interaction with organosilane-based modifiers, and (iii) adsorption at silica-based superhydrophobic structures under solvated conditions, has not been extensively explored. Specifically, the question remains whether the silica-based functional groups have the capacity to counteract the high affinity of the hydration shell of the calcium cation, and how the organic–inorganic hybrids may affect the affinity of the calcium cation.

Elucidating this competition is essential for rationalizing materials design. In the context of surface immobilization mechanisms, if calcium ions prefer to interact with silica-based superhydrophobic coatings rather than maintaining their hydrated state, then surface immobilization mechanisms may play an important role in ion transport, interfacial stability, and long-term durability in the context of coated concrete systems. Alternatively, if hydration effects are dominant, then surface functionalization may not play an important role with respect to calcium ion redistribution.

In order to bridge this knowledge gap, this study aims to apply Density Functional Theory (DFT) calculations to investigate the interactions between calcium in increasingly complex silica-based superhydrophobic systems. The systems include APTES, triethoxy(octyl)silane, Bisphenol A, silicon dioxide clusters, and their combined systems with the addition of Ca^{2+} ions in hydrated states. DFT calculations can reveal the optimized geometry, electronic structure, molecular electrostatic potential distribution, non-covalent interaction regions, and quantum topological features of calcium coordination [23], [24].

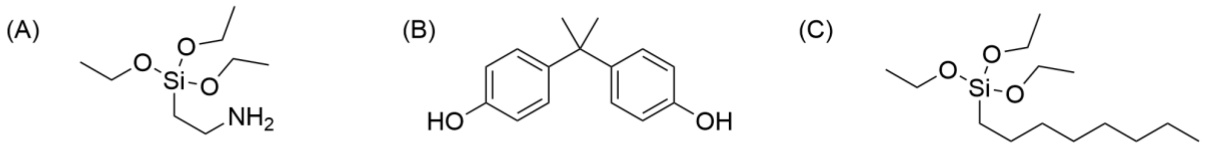

Figure 1. Chemical structures of (a) APTES, (b) Bisphenol A, and (c) Triethoxy(octyl)silane.

By integrating electronic-level characterization with statistical mechanical modeling, this work establishes a hierarchical comparison of calcium binding from isolated organosilane coordination to silica-surface adsorption within hybrid superhydrophobic matrices. The findings provide mechanistic insight into competitive hydration versus surface immobilization and offer guidance for the design of durable, silica-based superhydrophobic coatings aimed at improving the environmental resistance of concrete structures. To better position the present study within the existing body of literature, a comparison with representative recent works is summarized in Table 1.

Table 1. Comparison of recent studies on Ca^{2+} interactions with silica-based systems and the contribution of this work.

Study	System Studied	Methodology	Key Findings	Limitation
[6]	Water + Ca^{2+} on quartz surface	DFT	Demonstrated adsorption behavior and ion–surface interaction energetics	Focused only on simple oxide surface, no organics, no hybrid systems
[18]	Ca^{2+} on mineral surfaces	DFT + experiments	Identified adsorption mechanisms on mineral surfaces	No silica-based hydrophobic coatings or organic modifiers
[12]	APTES-functionalized silica	DFT	Showed surface functionalization improves adsorption	No Ca^{2+} hydration competition studied
[16]	Polymer–Ca^{2+} interactions in concrete	Atomistic simulations	Provided insight into admixture–Ca^{2+} interactions	Focused on polymer systems, not hydrophobic silica coatings
[24]	Ca–silicate complexes	Ab initio MD	Studied early-stage C–S–H formation	No organic modifiers, no coating context
[26]	C–S–H + epoxy interface	MD	Studied interfacial binding energies	No explicit Ca^{2+} hydration or NCI analysis
This Work	APTES + BPA + OTES + SiO_2 + Ca^{2+} + water	DFT + multi-component system analysis	Reveals competition between hydration and surface immobilization, and role of silica vs organics	—

2 Methodology

Density Functional Theory (DFT) calculations were performed to investigate the ground-state structures, electronic properties, and intermolecular interactions of silica-based superhydrophobic systems with calcium ions. The systems include isolated 3-aminopropyltriethoxysilane (APTES), Bisphenol A, Triethoxy(octyl)silane, calcium ion, silicon dioxide, APTES + Ca^{2+}, APTES + Bisphenol A + Triethoxy(octyl)silane, and the complex with SiO_2 (Chemical structures of APTES, Bisphenol A, and Triethoxy(octyl)silane were given in figure1).

All calculations were performed with the B3LYP hybrid functional [22] with 6-311++G(d,p) basis set. Empirical dispersion corrections were performed with Grimme's D3 correction (Empirical Dispersion = GD3) to include weak non-covalent interactions not accounted for in the exchange-correlation functional.

The DFT calculations yield important quantum properties: optimized structures, Mulliken charge distributions, Molecular Electrostatic Potential (MEP) surfaces, Non-Covalent Interactions (NCI) plots, and Reduced Density Gradient (RDG) analyses. These calculations will provide valuable insight into the binding affinity, electronic changes, and stabilization mechanisms upon calcium ion interaction with the superhydrophobic surface-modifying agents.

In DFT studies, the following systems were modeled: (i) calcium ion, (ii) silicon dioxide, (iii) APTES, (iv) Bisphenol A, (v) Triethoxy(octyl)silane, (vi) APTES + Ca^{2+}, (vii) APTES + Bisphenol A + Triethoxy(octyl)silane + Ca^{2+}, and (viii) the full complex with SiO_2.

All DFT calculations were carried out using GAUSSIAN 16 software. Visualization and post-processing were conducted via GaussView (v6.0) for structural inspection, Multiwfn for wavefunction analysis and VMD for Non-Covalent Interactions (NCI) analysis [27], [28].

3 Results and discussion

Optimized structures

Figure 2 shows a stepwise evolution of a silica-based superhydrophobic system, optimized using DFT calculations, as more functional groups are added to it. In the first structure, the APTES molecule coordinates with a calcium ion through a series of coordination bonds to its nitrogen and ethoxy oxygen atoms.

The second optimized structure consists of a series of functional groups added to it, i.e., Bisphenol A and triethoxy(octyl)silane. This results in a complex structure with a branched chain, where a number of hydroxyl and ether oxygen atoms are oriented towards the calcium ion.

The third structure consists of silicon dioxide clusters, mimicking the formation of an inorganic matrix, i.e., silica. In this structure, the calcium ion is stabilized even further through extensive coordination with hydroxyl groups on the silica surface [6], [9], [24], in addition to its interaction with the organic additives. The third structure, therefore, represents the optimized structure, emphasizing the synergistic effect of combining silane coupling agents, hydrophobic modifiers, and inorganic fillers. The calcium ion is still in the center, emphasizing the high binding affinity [6], [24].

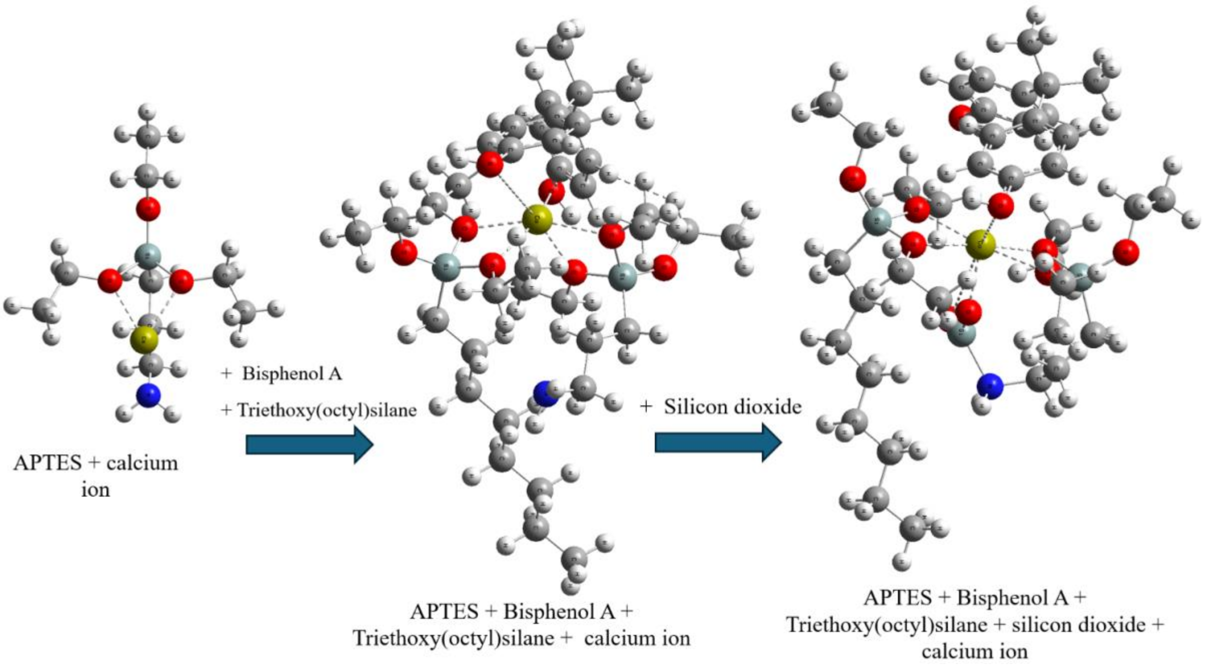

Figure 2. Optimized structures of APTES + calcium ion, APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion, APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion systems. Grey - carbon, white - hydrogen, red - oxygen, blue - nitrogen, teal - silicon, yellow - calcium.

Molecular electrostatic potential maps

Figure 3 shows the molecular electrostatic potential (MEP) maps for the optimized complexes, which illustrate the charge distribution and possible points of interaction for the APTES-based systems. The MEP ranges from -0.53 (red) to +0.53 (blue) and corresponds to electron-rich (nucleophilic) and electron-deficient (electrophilic) regions, respectively.

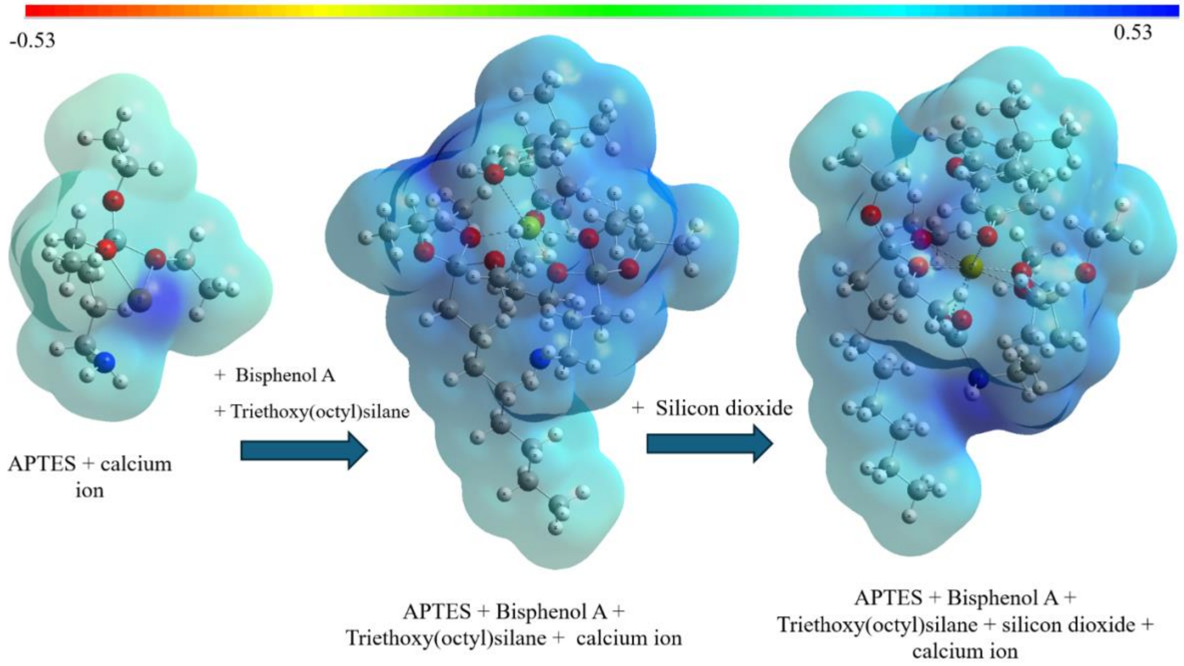

Figure 3. MEPs of optimized systems.

In the second structure, after the addition of Bisphenol A and triethoxy(octyl)silane, it can be seen that the MEP map has expanded regions of electron-poor environments. The addition of the phenolic hydroxyl groups from Bisphenol A and the additional ethoxy groups from triethoxy(octyl)silane contributes to the increased regions of electron-deficient environments, which can be considered to be a more complex environment for connections with SiO_2.

In the final structure with silicon dioxide incorporated, the MEP surface is more evenly distributed. The incorporation of silica increases the amount of oxygen with lone pairs, thereby increasing the local negative potential of the calcium ion. This shows good ion coordination and immobilization in the silica matrix [6], [12], [24]. The MEP analysis confirms the hypothesis that the binding of calcium increases with the incorporation of each new component [12], [16]. and the dipole moment is reduced in the solvation of water.

Reduced density gradient

The reduced density gradient (RDG) versus sign(λ_2)ρ plots for the three molecular systems are shown in Figure 4. The three molecular systems are (a) APTES + calcium ion, (b) APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion, and (c) APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion. The RDG plots offer insights into non-covalent interactions such as van der Waals forces, hydrogen bonds, and steric repulsion.

As shown in Figure 4a, there are spikes in the low-density region near zero sign(λ_2)ρ values, which indicate weak van der Waals interactions [23]. between APTES-calcium ion interfaces. The negative region (blue) corresponds to attractive interactions such as coordination bonds between the calcium ion and electronegative atoms in a molecule. The positive (red) region corresponds to steric repulsion between adjacent groups in a molecule.

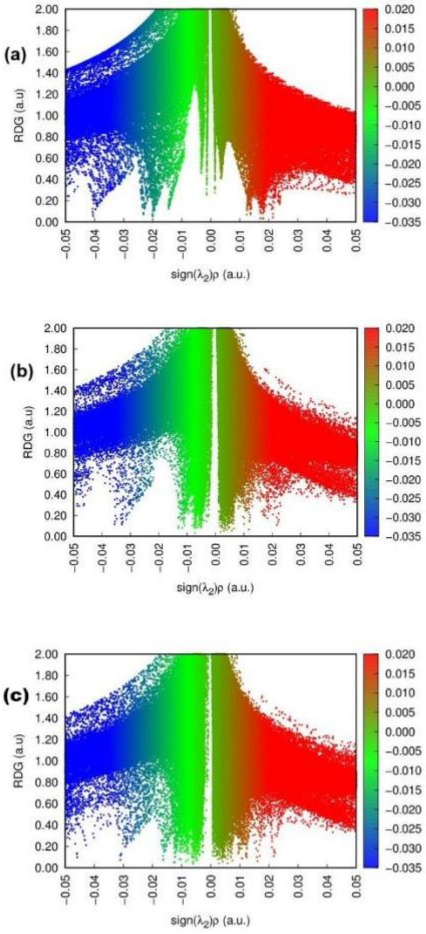

Figure 4. Reduced density gradients of (a) APTES + calcium ion, (b) APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion, (c) APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion.

On the addition of Bisphenol A and triethoxy(octyl)silane (Figure 4b), the RDG profile increases in width and complexity, particularly for the low-gradient region. This is due to the variety of non-covalent interactions such as hydrogen bonding and dispersive interactions from the alkyl groups and aromatic rings. The central peak centered on zero indicates an improvement in van der Waals stabilization and weak hydrogen bonding with the calcium ion [23]. As shown in Figure 4c, the presence of silicon dioxide enhances the complexity of the interaction network. The dark blue areas indicate a greater degree of attractive interaction, and the likely reason for this is the interaction between the calcium ions and the silanol groups of the silica. As shown by the RDG plots, the complexity of the structure and the presence of the silica significantly improve the non-covalent interaction network, thus enhancing the stability of the calcium ions.

Non-covalent interactions

The analysis of the non-covalent interactions (NCIs) gives important insights into the stability and formation of the complex structures presented in Figure 5, especially concerning the role of calcium ions in the concrete industry. From the images, the regions of the attractive (blue), repulsive (red), and weak van der Waals (green) interactions are presented, as they were visualized using reduced density gradient (RDG) isosurfaces.

As for the initial system of APTES + calcium ion, the presence of significant regions of the repulsive interaction, shown as red color, indicates strong steric repulsion, implying a weak interaction or a very localized interaction, which might be unfavorable. However, the presence of some regions of the weak interaction, shown as green, indicates weak van der Waals interactions. When the Bisphenol A and Triethoxy(octyl)silane molecules are added in the compound APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion, a high level of complexity is seen in the NCIs. The appearance of various blue and green regions in the compound indicates the attractive forces, such as hydrogen bonds and van der Waals forces, formed between the molecules and the calcium ion. The decrease in the intensity of the red regions around the calcium ion compared to the initial state indicates that the molecules of Bisphenol A and Triethoxy(octyl)silane provide more attractive forces with the calcium ion.

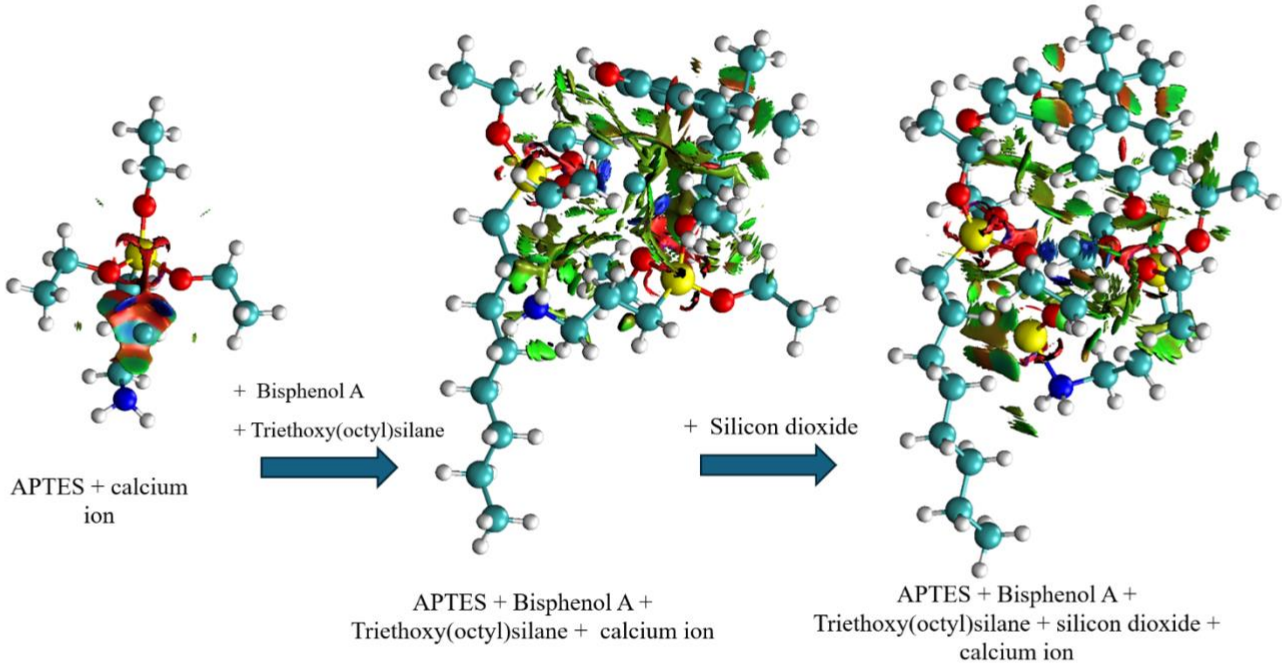

Figure 5: Non-covalent interactions of APTES + calcium ion, APTES + Bisphenol A + Triethoxy(octyl)silane +

calcium ion, APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion.

The inclusion of silicon dioxide in the APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion system modulates the NCI landscape. The large blue regions covering the entire complex, including the silicon dioxide, strongly point to the presence of attractive interactions. This implies that silicon dioxide is playing an important role in stabilizing the entire system [6], [12], [24]. possibly by strong hydrogen bonds and electrostatic interactions with other compounds in the system, including the calcium ion. Furthermore, the large regions of green color that cover the entire system point to the presence of strong van der Waals interactions, as earlier suggested. The decrease in red color in all stages, especially in the final structure, points to a well-integrated system that is not hindered in any way. All these observations point to the crucial role played by the interplay of various non-covalent forces [23]. in determining the integrity and interaction mechanisms of such silica compounds with calcium ions, a factor that is of immense use in concrete environments.

Interaction energies

The interaction energies, as shown in Table 2, offer quantitative insights into the thermodynamic favorability of the interactions between the different components and calcium ions of the silica-based superhydrophobic material systems, which is important for the understanding of their interactions in a concrete environment. When the interaction energy values are negative, it indicates attractive interactions, whereas positive values indicate repulsive interactions.

The interaction energy between APTES and calcium ion for the initial system of APTES + calcium ion is -0.012 kJ/mol, indicating a very weak interaction between the two. However, the interaction energy between the water and calcium ion is much more negative, i.e., -502.77 kJ/mol. This is understandable since calcium ions have a strong interaction with water.

Table 2: Interaction energies of different molecules and water with calcium in different systems.

	Interaction energies (kJ/mol)		
	APTES + calcium ion	APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion	APTES + Bisphenol A + Triethoxy(octyl)silane + silicon dioxide + calcium ion
APTES with calcium ion	-0.012	0.0814	0.026
Bisphenol A with calcium ion	-	20.92	2.663
Triethoxy(octyl)silane with calcium ion	-	-0.008	0.067
Silicon dioxide with calcium ion	-	-	-695.183
Water with calcium ion	-502.77	-667.32	-384.623

On the introduction of Bisphenol A and Triethoxy(octyl)silane into the APTES + Bisphenol A + Triethoxy(octyl)silane + calcium ion system, a significant change in the interaction energy is noted. Here, the interaction between APTES and the calcium ion becomes slightly repulsive, i.e., 0.0814 kJ/mol. This implies that the presence of other molecules may influence the interaction between two molecules. Interestingly, the interaction between Bisphenol A and the calcium ion becomes repulsive, i.e., 20.92 kJ/mol, whereas the interaction between

Triethoxy(octyl)silane and the calcium ion becomes very weak, i.e., -0.008 kJ/mol. However, the interaction energy between water and the calcium ion becomes more negative, i.e., -667.32 kJ/mol. This implies that the interaction between the calcium ion and the water molecule becomes more intense, i.e., the hydration shell of the calcium ion becomes more stable [1], [2], [3]. This may be attributed to the presence of other molecules, which might have affected the electrostatic properties of the calcium ion.The most significant changes are found in the APTES + Bisphenol A + Triethoxy(octyl)silane + Silicon dioxide + Calcium ion system. The interaction between Silicon dioxide and Calcium ion is found to be overwhelmingly attractive, with an energy value of -695.183 kJ/mol. Similar situation is visible in water with calcium ion, resulting in -667.32 kJ/mol. The high negative value indicates the high binding affinity between the calcium ion and Silicon dioxide, an important property in the application in concrete, and initial binding of Ca^{2+} ions with water. The interaction between APTES and calcium ion is found to be slightly repulsive, with an energy value of 0.026 kJ/mol. The interaction between Bisphenol A and calcium ion is found to be reduced and repulsive, with an energy value of 2.663 kJ/mol. The interaction between Triethoxy(octyl)silane and calcium ion becomes slightly repulsive, with an energy value of 0.067 kJ/mol. Most importantly, the attractive interaction of water and calcium ions is seen to significantly reduce in the last system to -384.623 kJ/mol. The decrease in the attractive interaction of water and calcium ions, in combination with the high attractive interaction of silicon dioxide and calcium ions, suggests that the silicon dioxide surface competes with the water in the adsorption of the calcium ions [6], [9], [24]. Such an interaction is desirable in the manipulation of the behavior of calcium ions in concrete materials.

4 Conclusion

This study offers an atomistic insight into the interaction between calcium ions and silica-based hybrid superhydrophobic systems, which are relevant to the protection of concrete structures. Density Functional Theory calculations demonstrated the structural evolution of the complexes under study, showing that the addition of new functional units, such as silicon dioxide, improves the stabilization of the calcium ion in the hybrid matrix. The optimized structures, Molecular Electrostatic Potential calculations, Reduced Density Gradient analysis, and Non-Covalent Interaction visualization confirm that the more complex the structure, the stronger the attractive forces surrounding the calcium ion.

The results also demonstrate that APTES, Bisphenol A, and triethoxy(octyl)silane contribute in different ways to the local coordination environment of Ca^{2+}, and that silicon dioxide plays the key role in facilitating strong calcium binding. In particular, the interaction energy analysis indicates that the system containing SiO_2 has the best interaction with Ca^{2+}, implying that the inorganic part of the system, i.e., the silicon dioxide, is the main active site for calcium binding. On the other hand, the high interaction between Ca^{2+} and water indicates the competitive effect of hydration, which should be taken into account in designing protective coatings for cementitious environments.

The results indicate that the type of hybrid silica-based system studied is able to create a conducive environment for the binding of calcium ions and may play a role in the improved interfacial stability and durability. These studies have provided valuable molecular-level information that may be useful for the design of advanced hydrophobic coatings and silica-based protection technologies. Future studies should attempt to expand this type of simulation to more realistic surfaces and concrete pore solution conditions to try to bridge the gap from the atomic level to the macroscopic level.

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Competing interest: The authors declare no conflict of interest.

Availability of data and material: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

AI Use Disclosure: The authors confirm that No AI tools were used to generate scientific results, data, figures, or interpretations. All analyses, conclusions, and scientific content were developed by the authors.

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