DFT study of the fouling deposition process in the steam generator by simulating the absorption of Fe$^{2+}$ on Fe$_3$O$_4$ (001)

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Abstract: In this paper, the interaction between free Fe$^{2+}$ and Fe$_3$O$_4$ corrosion products on the pipe surface in the secondary circuit of PWR nuclear power plant was studied, and the reason of agglomeration formation was analyzed. The complex physical and chemical interaction was simplified by describing the electron interaction. Based on the first principles, CASTEP was used to simulate seven kinds of highly symmetric adsorption structure models of Fe$_{tet1}$ and Fe$_{oct1}$ on Fe$_3$O$_4$ (001) surface, and their adsorption energies and stable adsorption conformations were calculated. The results show that the most stable adsorption structures of the Fe$^{2+}$/Fe$_3$O$_4$ (001) configurations are Fe$_{oct1}$-b and Fe$_{oct1}$-O$_b$. During the adsorption, the Fe-Fe, Fe-O bond length and Fe-Fe-O bond angle of (001) surface changed, and the atomic positions parallel and perpendicular to (001) surface changed correspondingly, the surface layer changes the most. The results prove that the adsorption has great effect on the physical structure of Fe$^{2+}$ and Fe$_3$O$_4$ (001). The calculation of charge population, the density of states and

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electron local function of Fe$$^{2+}$$/Fe$_3$O$_4$ (001) optimal adsorption configuration also shows that there is electron transfer between Fe$$^{2+}$$ and Fe$_3$O$_4$ (001), and the adsorption type is chemisorption. Among them, Fe (Fe$$^{2+}$$)-Fe (Fe$_3$O$_4$) forms a metal bond, and Fe (Fe$$^{2+}$$)-O (Fe$_3$O$_4$) forms the ionic bond.

**Keywords:** First principle; DFT; Fe$_3$O$_4$ (001) surface; Adsorption energy; Fouling; PWR.

**Declaration**

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**Conflicts of interest**

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

**Availability of data and material**

All data used during the study appear in the submitted article.

**Code availability**

Not applicable.

**Authors’ contributions**

**San chuan Pan:** Conceptualization, Methodology, Resources, Writing – Original draft preparation. **Lu Ren:** Conceptualization, Methodology, Resources, Funding acquisition, Writing – review & editing. **Jian Xu:** Writing – review & editing. **Tetsuo Shoji:** Writing – review & editing. **Ningning Li:** Writing – review & editing. **Tong Zhang:** Writing – review & editing **Hongying Yu:** Writing – review & editing. **Dongbai Sun:** Writing – review & editing.
1 Introduction

The secondary heat exchange surface of steam generator (SG) in pressurized water reactor (PWR) of nuclear power plant (NPP) is easy to fouling, making the wing hole being gradually blocked by corrosion products[1]. The fouling phenomenon in SG secondary circuit was first found in Chalk River[2, 3]. The blocking phenomenon reduces the flow rate of the fluid passing through the supporting plate, and also increases the pressure drop, hinders the liquid passing through the secondary circuit, and reduces the heat exchange efficiency of SG[4]. When the blockage phenomenon becomes serious, the SG heat exchange tube and support plate will have strong vibration, and lead to fatigue fracture of the steam generator pipe. At present, several works proved that the majority of the fouling is in form of magnetite \(\text{Fe}_3\text{O}_4\)[1,5,6]

\(\text{Fe}_3\text{O}_4\) has strong sub-magnetism and high electrical conductivity at room temperature, and widely used as a metal oxide catalyst. The fouling magnetite is composed of particle deposition and soluble ions in the medium. The soluble ions mainly come from the surface of materials dissolved in the secondary circuit. Moreover, the existence of \(\text{Fe}_3\text{O}_4\) on the surface of SG heat exchange tube also has a certain adsorption effect on \(\text{Fe}^{2+}\) in the secondary circuit[7,8].

In order to analyze the interaction between \(\text{Fe}^{2+}\) and \(\text{Fe}_3\text{O}_4\) surface in the agglomeration process, the density functional theory (DFT) was used for theoretical calculation[9-12]. At the same time, some studies involved the corresponding nanoscale model of corrosion fouling were carried out to find the most stable adsorption configuration of corrosion fouling in the protective layer and verified by molecular simulation[13, 14]. \(\text{Fe}_3\text{O}_4\) is a kind of widely used oxide in industry, which has important catalytic performance[15-17]. The related research about the adsorption and dissociation of gas molecules on \(\text{Fe}_3\text{O}_4\) surface provides a reference method for the interaction and agglomeration of \(\text{Fe}_3\text{O}_4\)
surface in the secondary circuit[18-20]. Yang et.al.[21] studied the surface structures of Fe₃O₄ (111), (110) and (001) by DFT method, and reasonably explained the diversity and complexity of the adsorption and catalytic properties of Fe₂O₃. Yin et.al.[22] used DFT method to analyze the behaviour of adding single-walled carbon nanotubes (SWNTs) to Fe₂O₃ nanoparticle electrodes, which can significantly improve the conductivity and performance of lithium-ion batteries. They believe that transition metal (Fe, Ni) atoms or clusters are helpful to form strong chemical bonds between SWNTs and Fe₂O₃ (001) surfaces, which provides a good channel for electrons and improve the conductivity. Xue et.al.[23] studied the adsorption characteristics of CO on the non-defect and defect (oxygen-containing vacancy) B-layer Fe₂O₃ (001) surface (octahedral environment) by using spin polarization DFT and Hubbard u parameter (DFT + U). They confirmed that both two types of B-layer Fe₂O₃ (001) surfaces had great CO oxidation ability. Yu et.al.[24] systematically analyzed the adsorption behaviour of CO on Fe₂O₃ (111), (110) and (001) surfaces, and analyzed the adsorption mechanism according to the projected density of states. Zhou et.al.[25] used DFT method to calculate the oxidation mechanism of Hg0 on Fe₂O₃ (001) surface by heterogeneous H₂O₂. The results show that the oxidation process may go through three different ways at the same time, and the mechanism may become an attractive method for mercury control in the flue gas. Therefore, the adsorption behaviour of particles on Fe₂O₃ (001) surface is affected by many factors, such as the structural electrification and surface integrity. At present, we can only find out that Fe²⁺ released by secondary side surface can adsorb on Fe₂O₃ surface, and lead to the continuous increase of Fe₂O₃ fouling in SG secondary circuit, but the relevant mechanism is still unclear.

In this paper, we simulate the deposition behaviour of Fe²⁺ on different terminals of (001) surface based on the first principles and find out the most stable adsorption configuration. We also analyze the adsorption structure characteristics and physical parameters and the adsorption behaviour characteristic.
The adsorption behaviour can be considered as the basis of the Fe$_3$O$_4$ deposition and agglomeration on the heat exchange tube secondary surface of the steam generator. In addition, by studying the geometry structure and adsorption energy of Fe$^{2+}$ on Fe$_3$O$_4$ (001) surface, we can better understand the active electron properties, track the transfer direction of active electrons, and analyze the charge to describe the electronic properties of the most favourable adsorption configuration of Fe$^{2+}$ on Fe$_3$O$_4$ (001) surface.

2 Computational methods and models

2.1 Methods

All the DFT calculations are performed using the Cambridge sequential total energy program package (CASTEP) module in the Materials Studio software package. The interaction between nucleus and electron is treated by ultra-soft pseudopotential. The generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerh (PBE) is used to describe the exchange correlation energy, and the plane wave basis set is used to expand the wave function[26-28], and the truncation energy is 450eV. In previous work, the magnetic properties of Fe$_3$O$_4$ have been confirmed by vibrating sample magnetometer (VSM), so the magnetic properties and the attached spin polarization of Fe$_3$O$_4$ have been considered in all calculations. To follow the principle of minimum energy, the spin from top to bottom of the unit cell is set as 4 and -4, described as Fe$_{oct}$ and Fe$_{tet}$. The Fermi broadening of 0.1eV is used to accelerate the convergence. During Fe$_3$O$_4$ cell (space group Fd-3m/mmm) relaxing, the k-point in Brillouin zone is produced by Monkhorst-pack method, which is 3 × 3 × 1. In the relaxation process, when the maximum atomic force in any direction converges to 0.05eV/Å, the structural optimization is completed. The convergence criteria of self-consistent allowable error, energy, maximum displacement and maximum stress are set as 2.0×10$^{-6}$eV/atom, 2.0×10$^{-5}$eV/atom, 0.00 Å and 0.1GPa. The lattice
The constant of Fe$_3$O$_4$ crystal cell after optimization is $a = b = c = 8.3942$ Å, $\alpha = \beta = \gamma = 90^\circ$, which is close to the literature value ($a = b = c = 8.394$ Å, $\alpha = \beta = \gamma = 90^\circ$)[20].

The Fe$_3$O$_4$ crystal contains Fe$^{2+}$ and Fe$^{3+}$ and has a trans-spinel structure. The chemical formula can be written as $(\text{Fe}^{3+})_n(\text{Fe}^{3+}\text{Fe}^{2+})_m\text{O}_4$. There are 64 oxygen tetrahedral gaps (A sites) and 32 oxygen octahedral gaps (B sites). Among them, 1/8 A sites are occupied by Fe$^{3+}$, and 1/2 B sites are occupied by Fe$^{2+}$ and Fe$^{3+}$. In Fe$_3$O$_4$, the sublattice containing tetrahedral oxygen gap is A-type sublattice, and the octahedral oxygen gap is B-type. The cell of Fe$_3$O$_4$ is formed by alternating stacking of A and B sublattices[20, 29-31].

In the SG secondary circuit of PWR, fouling deposit Fe$_3$O$_4$ have a low index surface (001) with higher symmetry, which has stable surface free energy in thermodynamics. Six nonequivalent ideal terminals can be obtained by cutting the Fe$_3$O$_4$ (001) stacking sequence. The terminals with fewer dangling bonds have higher stability. Therefore, the Fe$_3$O$_4$ (001) surfaces terminated by fetet1 and feoct1 can be regarded as the most stable terminals. The main content of this experiment is to explore the specific behaviour of fe tet1 and fe oct1 terminal configurations on Fe$_3$O$_4$ (001) surface in the secondary circuit[23].

By cutting (001), there are four terminals of stacking sequence, which are Fe tet1 and Fe tet2 with tetrahedral coordination Fe atoms exposed, Fe oct1 with exposed octahedral coordination Fe atoms and close packing O oct1 layer. The atomic plane stacking sequence perpendicular to (001) direction can be written as Fe oct1-Fe tet1-O oct1-Fe tet2. The (001) surface low index crystal surface of Fe$_3$O$_4$, with low Bragg index and high symmetry. In thermodynamics, the surface free energy of (001) surface is more favourable than that of natural growth surface (111), and its catalytic activity is consistent with (111)[32]. There will be different terminal faces after cleaving (001) surface, and the terminal surfaces with fewer dangling
bonds are relatively stable. That is, the Fe_{oct1} and Fe_{oct1}-terminal surface with the least dangling bonds are stable. Fe_{oct1}-terminal surface has one exposed tetrahedral Fe atom, and Fe_{oct1}-terminal surface two exposed octahedral Fe atoms and four exposed O atoms. Among these two kinds of terminal surfaces, the Fe_{oct1}-terminal surface is more likely to be the most active surface, because the exposed octahedral Fe atoms on this terminal surface have two valence states, which electrons can transition between them[21].

To analyze the stability of different adsorption configurations, we use the adsorption energy $E_{ad}$ to compare the energy difference before and after adsorption. The formula is as follows:

$$E_{ad} = E_{Fe^{2+}/Fe_3O_4} - E_{Fe_3O_4} - E_{Fe^{2+}}$$

(1)

where $E_{Fe^{2+}/Fe_3O_4}$ is the total energy of adsorbate and surface, $E_{Fe_3O_4}$ is the total energy of Fe$_3$O$_4$ (001) surface, and $E_{Fe^{2+}}$ is the total energy of isolated Fe$^{2+}$. When the adsorption energy is negative, it can be adsorbed, and the greater the absolute value, the easier the adsorption.

2.2 Models

Although Fe_{tet1}, O_{oct1}, Fe_{oct1}, and Fe_{tet2} can obtain nonequivalent ideal body termination by cutting Fe$_3$O$_4$ (001) stacking sequence, Fe_{tet1} and Fe_{oct1} terminals (as shown in Fig. 1) have only 6 bond breaks, and other terminations are more than this, so Fe_{tet1} and Fe_{oct1} terminals are stable. The Fe_{oct1}-terminal surface with exposed octahedral Fe atoms, as shown in Fig. 2, is selected as the model to study the secondary circuit reaction. Choosing the atomic model as the research object can achieve a good balance in precision and calculation time. The thickness of the vacuum layer is set at 15 Å to eliminate the periodic interaction. In the calculation process, the atoms at the bottom are fixed, and the atoms at the top two layers and adsorbate are allowed to relax.
After geometry optimization, the partial density of states (PDOS) and energy band of Fe\textsubscript{tet1} and Fe\textsubscript{oct1} termination surfaces can be calculated, as shown in Fig. 2. The curves of PDOS show a similar trend, indicating that the two terminal surfaces have similar surface properties.

The local density of states of bulk structure includes the density of states of the nonequivalent atoms
Fe\textsubscript{tet}, Fe\textsubscript{oct} and O. the Fermi surface is represented by a straight line with zero energy. It can be seen from the TODS diagram of the bulk structure that the spin up and spin down subbands are divided into several parts, and there is no obvious band gap near the Fermi plane.

Through the calculation of the surface electronic structure of Fe\textsubscript{3}O\textsubscript{4} (001), the DOS and energy band of Fe\textsubscript{tet1} and Fe\textsubscript{oct1} are given. POS includes TDOS, LPOS and PDOS, LDOS includes the density of states of Fe\textsubscript{tet} and Fe\textsubscript{oct} atoms, and PDOS includes the density of states of 3d orbital of Fe\textsubscript{tet} and Fe\textsubscript{oct} atoms. It can be found in TDOS that both spin-up and spin-down filled with electrons, which destroys the semi-metallicity. Similarly, the spin-up and spin-down sub-bands are divided into several parts, and no obvious band gap near the Fermi plane. Comparing the local density of states and the partial density of States, the spin-up electrons mainly occupy the 3d orbital of the surface Fe\textsubscript{tet} atom and are highly localized near the Fermi plane, while the spin-down electrons occupy the d orbital near Fermi level. Both spin-up and spin-down are doped with a part of p orbitals of O atoms, and the density of states are also highly localized. The decrease of the coordination number of surface Fe ions may be the reason, and also lead to a decrease of sub-band gap and the instability of semi-metallicity.

In previous research, it had been concluded that the spin-down Fermi surface in PDOS diagram is mainly occupied by the electrons of Fe\textsubscript{oct} atom and has a certain bandwidth, which leads to the semi-metallicity of Fe\textsubscript{3}O\textsubscript{4} bulk structure [33, 34]. In the energy band diagram of Fe\textsubscript{oct1}, we can find the 0.11eV spin-down bandgap, but no bandgap in the total density of states diagram. The bandgap indicates that the semi-metallicity of Fe\textsubscript{oct} surface exists, but it is not as strong as the original structure.

The high symmetry adsorptions sites are top (t), bridge (b) and hollow (h). According to the possible position of the highest adsorption energy and the high symmetry of Fe\textsubscript{3}O\textsubscript{4} (001) surface, the following seven optimal adsorption points are listed: Fe\textsubscript{3}O\textsubscript{oct}\textsubscript{(001)}-t (Fe\textsuperscript{2+} above Fe\textsubscript{oct}), Fe\textsubscript{3}O\textsubscript{oct}\textsubscript{(001)}-b (Fe\textsuperscript{2+} above Fe-O
bond), Fe$_3$O$_{4\text{oct}}$-h (Fe$^{2+}$ above Fe-O bond), Fe$_3$O$_{4\text{oct}}$-t (Fe$^{2+}$ above Fe$_{\text{oct}}$), Fe$_3$O$_{4\text{tet}}$-b site (Fe$^{2+}$ above Fe-O bond), Fe$_3$O$_{4\text{tet}}$-O$_h$ (Fe$^{2+}$ above the hollow formed by O atoms) and Fe$_3$O$_{4\text{tet}}$-h (Fe$^{2+}$ above the void formed by Fe and O). Figure 3 shows the front and top views of the corresponding configurations.

Fig. 3 Front view and top view of Fe$^{2+}$ adsorption sites on Fe$_3$O$_4$ (001) surface

(a) Fe$_3$O$_{4\text{oct}}$-t (b) Fe$_3$O$_{4\text{tet}}$-b (c) Fe$_3$O$_{4\text{oct}}$-h (d) Fe$_3$O$_{4\text{oct}}$-t (e) Fe$_3$O$_{4\text{tet}}$-b (f) Fe$_3$O$_{4\text{tet}}$-h (g) Fe$_3$O$_{4\text{tet}}$-O$_h$

3 Results and discussion

3.1 Adsorption structures and energy

The possible stable adsorption configuration of Fe$^{2+}$ on Fe$_3$O$_4$(001) surface is shown in Fig. 4. The corresponding geometric structure parameters and adsorption energy can be seen in Table 1. The structure of Fe$_3$O$_4$(001) outmost surface may be affected by the adsorption behaviour of Fe$^{2+}$. The adsorption energy and the stable conformation of the system indicate that the most stable adsorption structure of Fe$^{2+}$/Fe$_3$O$_4$(001) surface are Fe$_3$O$_{4\text{oct}}$-b and Fe$_3$O$_{4\text{tet}}$-O$_h$ site. After adsorption, Fe$_{\text{oct1}}$-O$_{\text{oct1}}$, Fe$_{\text{tet1}}$-O$_{\text{oct1}}$ bond length and Fe$_{\text{oct1}}$-O$_{\text{oct1}}$-Fe$_{\text{tet1}}$, O$_{\text{oct1}}$-Fe$_{\text{tet1}}$-O$_{\text{oct1}}$ bond angle change, varies from adsorption
configuration. \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-b} \) and \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-h} \) change the most. In \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-b} \) configuration, Fe2+ bonds with both Fe atom and O atom of Fe\text{oct1} termination surface, and have different bond length: Fe\text{2+}-Fe(Fe\text{oct1}) is 2.170 Å, Fe\text{2+}-Fe(Fe\text{tet1}) is 2.425 Å, and Fe\text{2+}-Fe(O\text{oct1}) is 2.526 Å. Should be noted that three Fe-Fe bonds have different electronic configurations, and will be further discussed later. Fe\text{2+} bond with outmost Fe atom of Fe\text{oct1}, such abehavior happen in all \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}} \) configuration, meaning that Fe\text{2+} affects the Oct1 surface of \( \text{Fe}_3\text{O}_4 (001) \), and enables to bond with the nearest Fe atom. Similarly, the O atoms on Fe\text{oct1} is also affected, and all of the \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}} \) configuration have Fe\text{2+}-O(Fe\text{oct1}). In \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}} \) configuration, \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-t} \) and \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-h} \) have only one Fe\text{2+}-Fe bond, but bonding Fe atoms have a different environment. \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-t} \) one come from the outermost Fe\text{oct1} layer, while \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-h} \) one comes from the inner O\text{oct1} layer. This result may be related to the distance between Fe\text{2+} and different Fe atoms before the adsorption. From Table 1, we can know that \( \text{Fe}_3\text{O}_4 \text{o}_{\text{oct}-b} \) is the largest adsorption energy site in \( \text{Fe}_3\text{O}_4 \text{o}_{\text{oct}} \) configuration, about -5.399eV the adsorption energy, while \( \text{Fe}_3\text{O}_4 \text{o}_{\text{oct}-h} \) is the largest adsorption energy site in \( \text{Fe}_3\text{O}_4 \text{o}_{\text{tet}} \) configuration, about -4.599eV the adsorption energy. Compared the bonding conditions of the two configurations, it can be concluded that the more bonding one has the bigger adsorption energy, and the adsorption of Fe\text{2+} on the surface of the Fe-O bond is more significant.

| Substrate | terminal | Adsorption sites | \( E_{\text{ad}}/\text{eV} \) | \( d_{\text{Fe-O}}/\text{Å} \) | \( d_{\text{Fe-Fe}}/\text{Å} \) | bond angle/° |
|-----------|----------|-----------------|----------------|----------------|----------------|-------------|
| \( \text{Fe}_3\text{O}_4 \text{(0 0 1)} \) | \( \text{Fe}_{\text{oct1}} \) | \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-t} \) | -1.799 | 2.238 | 2.095 | 51.700 |
| | | \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-b} \) | -5.399 | 1.802;1.736 | 2.170;2.245;2.526 | 49.402;94.737 |
| | | \( \text{Fe}_3\text{O}_4 \text{a}_{\text{oct}-h} \) | -3.899 | 1.783;1.777 | 2.399;2.384 | 58.297;58.268 |
| | | \( \text{Fe}_3\text{O}_4 \text{a}_{\text{tet}-t} \) | -2.599 | --- | 2.015 | 87.641 |
| \( \text{Fe}_{\text{tet1}} \) | | \( \text{Fe}_3\text{O}_4 \text{a}_{\text{tet}-O} \) | -3.099 | 1.865 | 2.041 | 57.188 |
| | | \( \text{Fe}_3\text{O}_4 \text{h}_{\text{tet}-O} \) | -4.599 | 1.790;1.784 | 2.218;2.409 | 50.090;52.237 |
Fig. 4 Simulation results of Fe$^{2+}$ adsorption on Fe$\text{tet}^{1}$ and Fe$\text{oct}^{1}$ terminated surfaces (a) Fe$\text{O}_4^{(001)}$

Fig. 5 shows the trajectories of Fe$\text{O}_4^{(001)}$-b adsorption. Before adsorption, the Fe atom distances between Fe$^{2+}$ and Fe$\text{oct}^{1}$, Fe$\text{tet}^{1}$ and O$\text{oct}^{1}$ are 3.204 Å, 5.165 Å and 5.252 Å, respectively. After 8ps relaxation, Fe$^{2+}$ firstly forms a bond with Fe$\text{oct}^{1}$, and then desorb at 10ps due to the movement of the Fe atom. After 12ps of relaxation, Fe$^{2+}$ reabsorbs and form a bond with 2.818 Å. At 54ps, a new Fe-Fe$\text{tet}^{1}$ bond is formed due to the effect of Fe atoms in the Fe$\text{oct}^{1}$ layer. In this process, the bond length of Fe-Fe$\text{oct}^{1}$ is shortened to 2.120 Å. At 60ps, Fe$^{2+}$ interacts with the Fe atom of O$\text{oct}^{1}$ and bonds with it, the bond length is 2.883 Å, while Fe-Fe$\text{oct}^{1}$ is shortened to 2.341 Å, Fe-Fe$\text{oct}^{1}$ is elongated to 2.206 Å. The stretching of the Fe-Fe$\text{oct}^{1}$ bond indicates that the new chemisorption bond is formed during the relaxation process, while the Fe-Fe$\text{oct}^{1}$ is weakened, part of the electrons is transferred to the Fe-O$\text{oct}^{1}$ bond. The
difference of Fe-Fe_{oct1}, Fe-Fe_{tet1} and Fe-O_{oct1} needs further analysis.

Fig. 5 Simulation outcome of Fe_{3}O_{4}^{\text{oct}}-b (a) 1ps (b) 8ps (c) 10ps (d) 12ps (e) 24ps (f) 51ps (g) 54ps (h) 60ps (i) 75ps

Fig. 6 Simulation outcome of Fe_{3}O_{4}^{\text{tet}}-O_{h} (a) 1ps (b) 16ps (c) 33ps (d) 37ps (e) 50ps

Fig. 6 shows the trajectory of Fe_{3}O_{4}^{\text{tet}}-O_{h} adsorption. Before adsorption, the distances between Fe^{2+} and the Fe atom of Fe_{tet1} and Fe_{tet2} layers are 3.391 Å and 5.408 Å, respectively. After 16ps, Fe^{2+} is influenced by the outermost Fe atom in the Fe_{tet1} layer and bonding with each other. The bond length is gradually shortened and the electronic interaction is enhanced during relaxation. At 33ps, the Fe atoms in the Fe_{tet2} layer interact with Fe^{2+} and bonding, then this Fe-Fe_{tet2} bond continues to shorten in the relaxation process, while the Fe-Fe_{tet1} bond becomes lengthen in the relaxation process, meaning the
electronic interaction weakens. After 50ps, the bonding is stable. The bond length of Fe-Fe\textsubscript{tet1} and Fe-Fe\textsubscript{tet2} is 2.202 Å and 2.233 Å, respectively.

In conclusion, Fe\textsubscript{3}O\textsubscript{4}(001)-b is the most stable adsorption site of (001) surface. In the relaxation process, electron interaction can be found between Fe\textsuperscript{2+} and the surface, meaning that Fe\textsuperscript{2+} adsorption is chemisorption. This configuration has the most of chemical bonds and the highest adsorption energy.

3.2 Mulliken population

| Substrate | Terminal | Adsorption sites | \(q_{o1}/\text{eV}\) | \(q_{o2}/\text{eV}\) | \(q_{fe1}/\text{eV}\) | \(q_{fe2}/\text{eV}\) | \(q_{fe2+}/\text{eV}\) |
|-----------|---------|-----------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Fe\textsubscript{oct1} | Fe\textsubscript{3}O\textsubscript{4}(001)-t | 0.14 | 0.11 | 0.18 | --- | 0.43 |
| | Fe\textsubscript{3}O\textsubscript{4}(001)-b | 0.48 | 0.39 | 0.21 | -0.13 | 0.95 |
| | Fe\textsubscript{3}O\textsubscript{4}(001)-h | 0.38 | 0.39 | 0.02 | 0.04 | 0.83 |
| Fe\textsubscript{tet1} | Fe\textsubscript{3}O\textsubscript{4}(001)-t | -0.02 | -0.03 | 0.63 | --- | 0.58 |
| | Fe\textsubscript{3}O\textsubscript{4}(001)-Fe\textsubscript{h} | --- | --- | 0.16 | --- | 0.16 |
| | Fe\textsubscript{3}O\textsubscript{4}(001)-O\textsubscript{h} | 0.34 | 0.32 | 0.13 | 0.12 | 0.91 |
| | Fe\textsubscript{3}O\textsubscript{4}(001)-O\textsubscript{t} | 0.24 | --- | 0.29 | --- | 0.53 |

As shown in Table 2, the maximum Mulliken charge of Fe\textsuperscript{2+} is 0.95eV of Fe\textsubscript{3}O\textsubscript{4}(001)-b and 0.91eV of Fe\textsubscript{3}O\textsubscript{4}(001)-O\textsubscript{h}, both of them are positive, indicating that electrons transfer from Fe\textsubscript{3}O\textsubscript{4} (001) surface to Fe\textsuperscript{2+}. Analyzing the changes of Mulliken charge population and bond population before and after adsorption, the bonding strength between Fe\textsuperscript{2+} and Fe\textsubscript{3}O\textsubscript{4} (001) surface, the electronic configuration, and further the characteristics of electron exchange between Fe\textsuperscript{2+} and Fe\textsubscript{3}O\textsubscript{4} (001) surface can be obtained.

The higher Mulliken charge can be observed on Fe\textsubscript{oct1} terminal surface, which because of the higher prominent molecular polarity on Fe\textsubscript{tet1} terminal surface, making the bonding atoms contribute less charge. Fe\textsubscript{3}O\textsubscript{4}(001)-b configuration has the largest adsorption energy, about -5.399eV, and its Mulliken charge value is also the largest among all configurations. Therefore, the charge distribution of Fe\textsubscript{3}O\textsubscript{4} (001) surface can be understood by analyzing the Mulliken charge value of Fe\textsubscript{3}O\textsubscript{4}(001)-b adsorption site. The above calculation results show that when Fe\textsuperscript{2+} is adsorbed on Fe\textsubscript{3}O4 (001) surface, the adsorbed Fe\textsuperscript{2+} is the
acceptor and absorb electrons from the Fe_{oct1} and Fe_{tet1} terminal surface.

Table 3 Mulliken population of Fe_3O_4\textsuperscript{(001)}

| Species | Spin | Mulliken population (before adsorption)/e | Mulliken population (after adsorption)/e |
|---------|------|------------------------------------------|------------------------------------------|
|         |      | s       p   d  | Charge(e) | Spin(hbar/2) | s       p   d  | Charge(e) | Spin(hbar/2) |
| O1      |      | 0.94    2.41 | -0.64     | 0.94        2.45 | -0.65 |
| O2      |      | 0.93    2.42 | -0.67     | 0.94        2.37 | -0.65 |
| O3      |      | 0.94    2.41 | -0.63     | 0.94        2.49 | -0.67 |
| O4      |      | 0.93    2.42 | -0.67     | 0.93        2.41 | -0.67 |
| O5      |      | 0.94    2.37 | -0.58     | 0.94        2.34 | -0.57 |
| O6      |      | 0.94    2.42 | -0.64     | 0.94        2.43 | -0.64 |
| O7      |      | 0.94    2.41 | -0.63     | 0.93        2.40 | -0.63 |
| O8      |      | 0.94    2.37 | -0.63     | 0.94        2.40 | -0.62 |
| O9      |      | 0.93    2.42 | -0.63     | 0.93        2.342 | -0.66 |
| O10     |      | 0.93    2.42 | -0.67     | 0.93        2.37 | -0.64 |
| O11     |      | 0.93    2.44 | -0.63     | 0.94        2.45 | -0.65 |
| O12     |      | 0.93    2.44 | -0.63     | 0.94        2.44 | -0.63 |
| Fe1     |      | 0.14    0.19 4.27 | 0.77 | 2.09 | 0.26 | 0.22 | 4.65 | 0.82 | 3.07 |
| Fe2     |      | 0.16    0.18 1.87 | 0.82 | -2.69 | 0.15 | 0.25 | 1.89 | 0.74 | -2.70 |
| Fe3     |      | 0.17    0.23 1.77 | 0.68 | -2.92 | 0.13 | 0.23 | 1.79 | 0.80 | -2.88 |
| Fe4     |      | 0.15    0.24 4.30 | 0.63 | 2.06 | 0.18 | 0.26 | 4.68 | 0.66 | 2.90 |
| Fe5     |      | 1.15    0.26 2.21 | 0.15 | 0.28 | 1.80 | 0.15 | 0.28 | 1.80 |
| Fe6     |      | 0.15    0.24 4.31 | 0.99 | 2.04 | 0.17 | 0.23 | 4.38 | 0.63 | 2.19 |
| Fe7     |      | 0.15    0.27 2.25 | 0.16 | 0.26 | 2.17 | 0.15 | 0.26 | 2.17 |
| Fe8     |      | 0.20    0.18 4.38 | 0.92 | 2.51 | 0.19 | 0.25 | 2.50 | 0.57 | -1.54 |
| Fe9     |      | 0.14    0.15 1.95 | 0.19 | 0.24 | 4.05 | 0.14 | 0.15 | 1.95 |
| Fe10    |      | 0.21    0.18 4.42 | 0.92 | 2.53 | 0.18 | 0.18 | 4.55 | 1.00 | 2.81 |
|         |      | 0.15    0.15 1.98 | 0.13 | 0.16 | 1.81 | 0.15 | 0.15 | 1.81 |
|         |      | 0.19    0.19 4.58 | 0.92 | 5.83 | 0.19 | 0.16 | 4.43 | 0.87 | 2.43 |
|         |      | 0.15    0.17 1.81 | 0.15 | 0.15 | 2.05 | 0.15 | 0.15 | 2.05 |
|         |      | 0.19    0.18 4.58 | 0.92 | 2.82 | 0.19 | 0.19 | 4.69 | 0.97 | 3.12 |
|         |      | 0.15    0.16 1.81 | 0.15 | 0.17 | 1.63 | 0.15 | 0.17 | 1.63 |
|         |      | 0.24    0.11 2.30 | 0.61 | -2.10 |
|         |      | 0.29    0.10 4.35 |

Table 3 shows the Mulliken charge population of Fe_3O_4\textsuperscript{(001)}-b site before and after adsorption.

Compared the values before and after adsorption, the charge population of each atom in the matrix.
changes stably. Fe$^{2+}$ mainly obtains the surface electrons of Fe$_3$O$_4$ (001) through 3d orbitals, 2.30e in spin-up and 4.35e in spin-down. Fe2, Fe4 and Fe6 atoms which bonded with Fe$^{2+}$ show the electron numbers change in p and d orbitals. The spin-up electrons of Fe2 and Fe4 decrease, and spin-down electrons increase. In Fe6, however, have reverse phenomenon, which spin-up electrons increase and spin-down electrons decrease. These results show that the bonding mechanism of Fe2, Fe4 and Fe6 with Fe$^{2+}$ is different, and may make a different influence on the electronic configuration of the adsorbed surface. The change of the electrons number indicates that there is electron transition between Fe$^{2+}$ and Fe$_3$O$_4$ (001) surface, and further proves that the interaction between Fe$^{2+}$ and atoms on Fe$_3$O$_4$ (001) surface include electron transfer and chemical bond formation when Fe$^{2+}$ is adsorbed on Fe$_3$O$_4$ (001) oct-b site.

Table 4 shows the changes of bond population and bond length after adsorption on Fe$_3$O$_4$ (001) oct-b site. It can be seen from Table 4 that the newly formed bond O2-Fe10 population is 0.39e and the bond length is 1.801 Å; bond O8-Fe10 population number is 0.48e and the bond length is 1.736 Å. The Fe-O bond length of the matrix is between 1.577 μ and 2.268 μ, which indicates that the newly formed Fe-O bond can be regarded as the extension of the matrix, and O2 and O8 atoms make a great effect to Fe$^{2+}$, which can be regarded as the existence of electric field effect, meaning the new Fe-O bond is an ionic bond. Besides, the populations of Fe2-Fe10, Fe4-Fe10 and Fe6-Fe10 formed after adsorption are 0.05, 0.21 and -0.13, respectively, and the bond lengths are 2.242 Å, 2.525 Å and 2.170 Å, respectively, meaning that the interaction between Fe4 and Fe$^{2+}$ is strong, while the influence of Fe2 and Fe6 is weak. The negative population indicates that the electron is transferred from Fe$^{2+}$ to Fe10 on Fe6-Fe10, so the bonding behaviour of Fe$^{2+}$ is much more complex.
Table 4 Population and length of chemical bond of Fe$_3$O$_4$ (001) - b site

| Bond | Population/e | Spin | Length/Å | Bond | Population/e | Spin | Length/Å |
|------|--------------|------|----------|------|--------------|------|----------|
| O8-Fe10 | 0.48 | 0.04 | 1.7362 | O4-Fe8 | 0.34 | -0.03 | 1.884 |
| O5-Fe6 | 0.51 | 0.04 | 1.7852 | O4-Fe9 | 0.36 | -0.04 | 1.885 |
| O4-Fe3 | 0.49 | 0.06 | 1.7907 | O9-Fe9 | 0.35 | -0.04 | 1.887 |
| O10-Fe6 | 0.43 | 0.02 | 1.8002 | O11-Fe2 | 0.37 | 0.05 | 1.888 |
| O2-Fe10 | 0.39 | 0.01 | 1.8018 | O12-Fe5 | 0.33 | -0.02 | 1.890 |
| O9-Fe3 | 0.5 | 0.06 | 1.812 | O7-Fe3 | 0.35 | 0.04 | 1.902 |
| O12-Fe2 | 0.44 | 0.06 | 1.824 | O5-Fe7 | 0.32 | -0.03 | 1.914 |
| O3-Fe1 | 0.43 | -0.02 | 1.830 | O3-Fe8 | 0.32 | -0.01 | 1.934 |
| O5-Fe5 | 0.4 | -0.02 | 1.830 | O1-Fe8 | 0.29 | -0.01 | 1.937 |
| O6-Fe3 | 0.45 | 0.07 | 1.834 | O7-Fe1 | 0.23 | -0.05 | 1.947 |
| O2-Fe7 | 0.38 | -0.04 | 1.8393 | O12-Fe4 | 0.3 | -0.03 | 1.952 |
| O10-Fe7 | 0.38 | -0.05 | 1.842 | O1-Fe5 | 0.28 | 0 | 1.955 |
| O10-Fe2 | 0.4 | 0.04 | 1.843 | O6-Fe1 | 0.19 | -0.05 | 1.964 |
| O2-Fe2 | 0.38 | 0.04 | 1.854 | O11-Fe9 | 0.2 | -0.06 | 1.985 |
| O1-Fe1 | 0.41 | -0.02 | 1.855 | O12-Fe8 | 0.18 | -0.06 | 1.996 |
| O9-Fe8 | 0.35 | -0.03 | 1.873 | O11-Fe5 | 0.25 | -0.03 | 2.001 |
| O8-Fe7 | 0.32 | -0.03 | 1.875 | O11-Fe4 | 0.26 | -0.04 | 2.016 |
| O7-Fe6 | 0.38 | 0.03 | 1.876 | O6-Fe7 | 0.21 | -0.06 | 2.037 |
| O8-Fe4 | 0.41 | -0.03 | 1.882 | O3-Fe9 | 0.27 | -0.02 | 2.039 |

In conclusion, after Fe$^{2+}$ adsorbs on Fe$_3$O$_4$ (001) surface, there is an electron exchange and new chemical bond formation between Fe$^{2+}$ and Fe$_3$O$_4$ (001) surface. Electron exchange between Fe atoms and Fe$^{2+}$ form metal bonds, while electron exchange between O atoms and Fe$^{2+}$ form an ionic bond. According to the analysis of the Mulliken population and bond population, Fe$_3$O$_4$ (001) surface can adsorb Fe$^{2+}$ in PWR nuclear power plant secondary circuit and create new chemical bonds, which is also the reason for the continuous deposition of Fe$_3$O$_4$ surface particles. This is also consistent with the conclusion.

3.3 Electronic density of states

To analyze the electronic density of states of different bonding formed at adsorption sites, the PDOS of Fe$_3$O$_4$ (001) - b configuration after adsorption is made, as shown in Fig. 7, so the comprehensive changes of bonding conditions, adsorption energy and electronic density of states can be studied.
Comparing the PDOS diagram of the Fe$_3$O$_4$(001)-b configuration with that of Fe$_{oct}$ termination face before adsorption, it is observed that the charge change mainly occurs in the 3d orbit, and the 3d orbit of Fe$^{3+}$ has a hybrid orbital peak near the Fermi level. The 3d resonance of Fe$^{3+}$ spin-up electrons occurs at Fermi level indicates that the spin-up electrons can only be partially filled and the adsorption is characterized by a covalent bond. However, the 3d resonance of the spin-down electrons mainly occurs below the Fermi level, about -3eV, indicates that Fe$^{3+}$ is mainly affected by negative ions during the adsorption. At the same time, the broadening of spin-up and spin-down p-orbital electrons at 4eV is also increasing, which enhances the p-orbital hybridization. However, there are no s-and p-orbital hybridization characteristics of O atom at this place, meaning that Fe$^{2+}$ has little effect from the O atom of Fe$_3$O$_4$. Therefore, the agglomeration process is mainly affected by the 3d orbital of the Fe atom and has a covalent bond effect. However, a small peak included 3s, 3p and 3d orbitals appear at -20eV in the PDOS diagram of Fe$^{2+}$, while only the 2s orbit of O has a high electron peak here, which means that in Fe$_3$O$_4$(001)-b configuration, the 2s orbital of O atom will participate in the orbital hybridization of Fe$^{2+}$ and affect the bonding, but the effect is not as great as that of 3d orbital of Fe atom.

Fig. 7 PDOS after Fe$^{2+}$ is absorbed at Fe$_3$O$_4$(001)-b site (a) Fe$_3$O$_4$(001)-b (b) Fe$^{2+}$ in Fe$_3$O$_4$(001)-b
configuration (c) O atom in Fe₃O₄\textsuperscript{001} -b configuration

![Energy band diagram of Fe₃O₄\textsuperscript{001} -b configuration](image)

**Fig. 8 Energy band diagram of Fe₃O₄\textsuperscript{001} -b configuration**

The energy band diagram of Fe₃O₄\textsuperscript{001} -b configuration is shown in Fig. 8. Compared with Fig. 8 and Fig. 3c, the fluctuation of Fe\textsuperscript{2+} after adsorption at Fe₃O₄\textsuperscript{001} -b site tends to be gentle, indicates that electron localization is weakened and the surface charge distribution is uniform, which may due to the effect of Fe\textsuperscript{2+} bonding with multiple surface Fe atoms and O atoms. It can be observed that the spin-up and spin-down sub-bands are divided into several parts, and the bandgap near the Fermi plane is small. Comparing the local density of states and the partial density of states, we can found that the electrons near the Fermi surface occupy the 3d orbits of the surface Fe atoms, and the electrons are highly localized near the Fermi surface. When Fe\textsuperscript{2+} relaxes on the Fe₃O₄ (001) surface, the formation of Fe-Fe bond makes the adsorption surface show the characteristics of Fe₃O₄ (001) surface and shows strong metallicity, which is similar to the previous calculation. The active metal bond leads to electrons appear in the forbidden band, and the surface charge is evenly distributed, which makes it easier for Fe\textsuperscript{2+} to become a new part of Fe₃O₄ surface after adsorption, accelerates the agglomeration process and
enhances the matrix effect.

Fig. 9 Differential electron density diagram of Fe$_3$O$_4$ (001)-b configuration (a) differential electron density diagram (b) local electron distribution of Fe$_2$-Fe$^{2+}$-Fe$_6$ (c) local electron distribution of O$_2$-Fe$^{2+}$-O$_8$ (d) local electron distribution of O$_8$-Fe$^{2+}$-Fe$_4$

For further analysis about the electron localized behaviour of Fe$^{2+}$ on the Fe$_3$O$_4$ (001)-b site, as shown in Fig. 9, the differential electron density diagram is used to directly describe the redistribution of surface electrons after relaxation. We definite $\Delta \rho = \rho (\text{Fe}^{2+}/\text{Fe}_3\text{O}_4) - \rho (\text{Fe}^{2+}) - \rho (\text{Fe}_3\text{O}_4)$, varies from $-0.9e^3$ to $1.0e^3$. The red area means electron enrichment and the blue area means electron depletion. It can be seen that on Fe$_3$O$_4$ (001) surface, obvious charge transfer exists between Fe$^{2+}$-Fe. The change of charge density is the largest, leading to new bonding between atoms, and finally, form a stable chemisorption configuration. In the diagram, Fe$^{2+}$ and Fe$_6$ atoms have electron interaction, and the electron density increases, indicating that a great overlap covalent bond exists between them, which can be considered as $\sigma$ bond. At the same time, fig.9c also shows electron interaction between Fe$^{2+}$ and Fe$_2$, but the electron localization is not as large as that of Fe$^{2+}$-Fe$_6$, and the orbital overlap is low, indicates that the covalent
bond formed should be β bond. The d electron localization of Fe\(^{2+}\)-Fe4 is even lower than that of Fe\(^{2+}\)-Fe2, so have a weaker β covalent bond. It can be found through the electronic localization that the density of electron cloud around Fe6 is more negative than that of Fe\(^{2+}\) after Fe6 is bonded with Fe\(^{2+}\), and the bonding condition of Fe6 is different from Fe2 and Fe4. According to the different electronegativity, Fe\(^{2+}\) may form a bond with Fe6 by giving electrons, and after bonding, Fe6 feedback some electrons to Fe\(^{2+}\), which makes the electronic localization of Fe\(^{2+}\)-Fe6 increase. Also, the electron interaction between Fe\(^{2+}\) and the nearby O atoms increases with the decrease of the distance, forming new Fe-O bonds. The charge density of the O atom is high, have maximized electrostatic interaction with Fe\(^{2+}\). The rearrangement of these charges will lead to the activation of the Fe-O bond and become ionic bond structure.

4 Conclusion

Fe\(^{2+}\) adsorption on the surface of the nuclear power plant steam generator secondary circuit heat transfer tube will agglomerate the fouling and accelerate the scaling process through the electron interaction. Through the first-principles calculation, we simulated the changes of Fe\(_3\)O\(_4\) (001) surface before and after adsorption. It is found that all the atom positions of Fe\(_3\)O\(_4\) crystal parallel to and perpendicular to (001) surface change, and the outmost surface layer changes the most, which means that the adsorption has great influence on the physical structure of Fe\(^{2+}\) and Fe\(_3\)O\(_4\) (001) crystals. This article also studies the charge population, density of States and electron local function of Fe\(^{2+}\)/Fe\(_3\)O\(_4\) (001) adsorption system. The calculation shows that there is electron transfer between Fe\(^{2+}\) and Fe\(_3\)O\(_4\) (001) to form a chemical bond. Among them, Fe (Fe\(^{2+}\)) - Fe (Fe\(_3\)O\(_4\)) forms a metal bond, and Fe (Fe\(^{2+}\)) - O (Fe\(_3\)O\(_4\)) forms the ionic bond. The formation of Fe (Fe\(^{2+}\)) - Fe (Fe\(_3\)O\(_4\)) metal bond leads to the electronic state in the forbidden band, which may be the reason why Fe\(^{2+}\) adsorbs on the surface of Fe\(_3\)O\(_4\) (001) and
enhances the matrix effect.

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Declaration of interests

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

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