## Supplementary Information

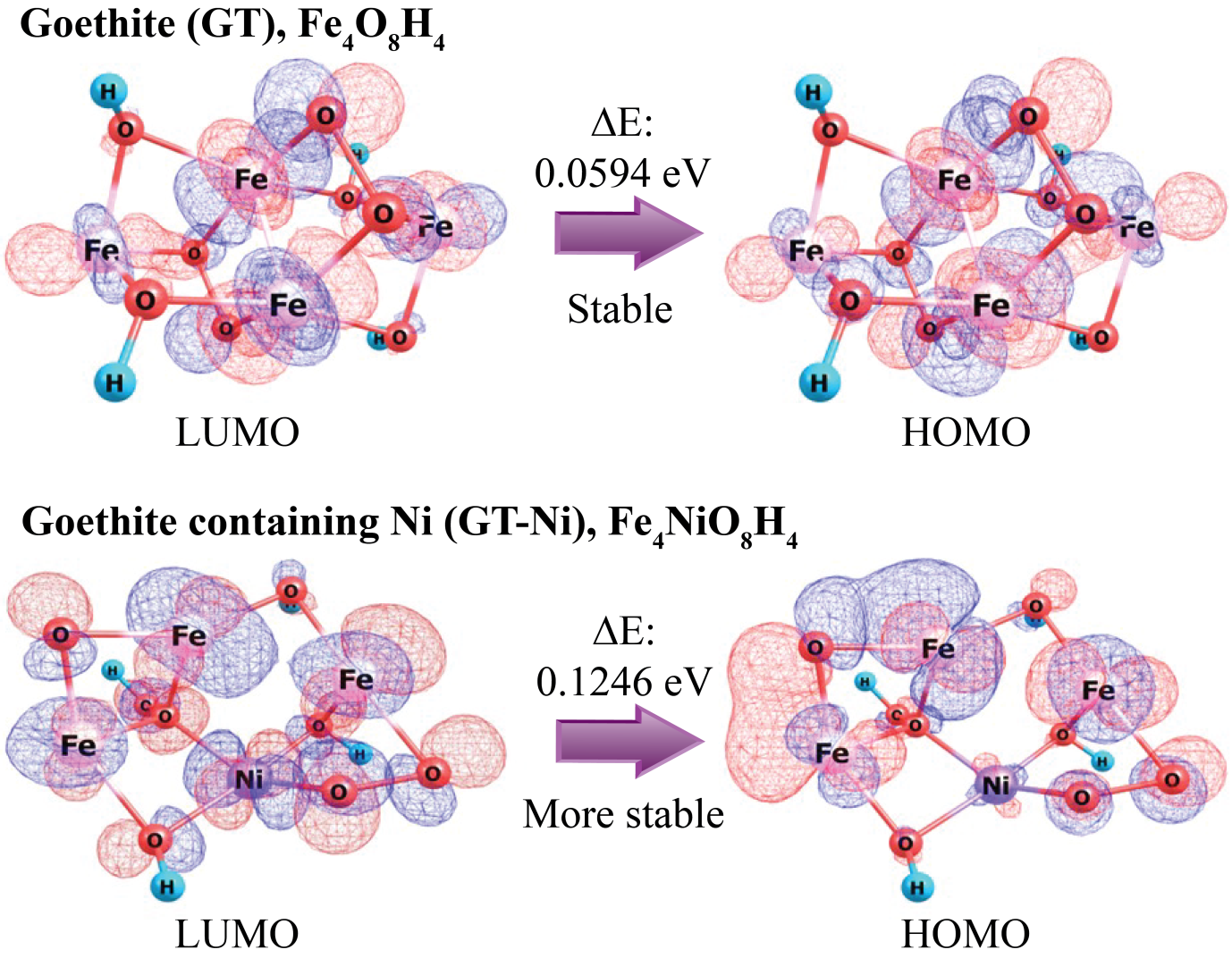
Insights into the changes in the surface properties of goethite with Ni in the lattice in the presence of salicylhydroxamic acid: Experimental and density functional theory studies

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## HOMO–LUMO analysis of the structures

The highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) are vital parameters in the calculation of kinetics and chemical stability. This implies that HOMO and LUMO can further help in determining the electronegativity, global electrophilicity index, chemical hardness, and softness. **Table S1** summarizes the HOMO–LUMO energies of the complexes under consideration**. Figure S1** shows the frontier molecular orbitals of goethite and goethite with Ni. Parr and Zhou [1] reported that the LUMO energy is proportional to the electronic affinity, while that of the HOMO is proportional to the ionization potential. The energy gap determines the chemical stability of the complex. That is, the higher the energy gap, the more stable the complex compared to the rest. For example, the recorded energy gap for goethite was 0.0594 eV, while that of goethite with Niwas 0.1246 eV, indicating that goethite-Ni structure is more stable than goethite without Ni (see **Figure S1**). In agreement with Maslov et al. [2], an increase in the bandgap also implies an increase in the magnetic field. Other important parameters were calculated, as presented in **Table S1.** The chemical hardness of goethite with Ni and goethite was 0.0623 eV and 0.0297 eV, respectively. Moreover, the softness of goethite with Ni and goethite was 8.0257 eV−1 and 16.8350 eV−1, respectively. This implies that stronger bonds are formed upon Ni substitution for Fe, promoting the hardness of goethite with Ni compared to goethite alone. Moreover, a higher bandgap in goethite with Ni than that in goethite alone indicates that the former possesses a higher conductivity.



**Figure S1.** Frontier molecular orbitals (generated by using ChemCraft) and gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)for goethite and goethite with Ni calculated at the PBE0/6-31g(d,p) level of theory. The blue and red colors represent the positive and negative regions, respectively.

**Table S1.** Energies of highest occupied molecular orbitals (*E*HOMO) and lowest unoccupied molecular orbitals (*E*LUMO), HOMO–LUMO energy gap (Δ*E*), and different global reactivity descriptors for monomers and the dimer calculated at the PBE0/6-31(d,p) level of theory for both goethite and goethite with Ni.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Molecular Properties** | **Fe2OH** | **Ni2OH** | **2FeO4H2** | **Fe4O8H4** | **Fe3NiO8H4** |
| *E*HOMO (eV) | −0.2587 | −0.0198 | −0.0004 | −0.1590 | −0.2018 |
| *E*LUMO (eV) | −0.1135 | −0.1338 | −0.1135 | −0.0996 | −0.0772 |
| Δ*E* (eV) | 0.1452 | −0.1140 | −0.1131 | 0.0594 | 0.1246 |
| Ionization potential, *I* (eV) | 0.2587 | 0.0198 | 0.0004 | 0.1590 | 0.2018 |
| Electron affinity, *A* (eV) | 0.1135 | 0.1338 | 0.1135 | 0.0996 | 0.0772 |
| Electronegativity, *χ* (eV) | 0.1861 | 0.0768 | 0.0569 | 0.1293 | 0.1395 |
| Chemical potential, *µ* (eV) | −0.1861 | −0.0768 | −0.0569 | −0.1293 | −0.1395 |
| Chemical hardness, *ŋ* (eV) | 0.0726 | −0.0570 | −0.0565 | 0.0297 | 0.0623 |
| Chemical softness, *S* (eV−1) | 6.8871 | −8.7719 | −8.8417 | 16.8350 | 8.0257 |
| Global electrophilicity index, *ω* (eV) | 0.2385 | −0.0517 | −0.0287 | 0.2815 | 0.0149 |

In summary**,** it can be observed that both the minimum and maximum electrostatic potentials of goethite with Ni were far much lower than that for goethite calculated at the PBE0/def2-svp level of theory. Therefore, cationic collectors are likely to adsorb on the minimum potential sites, while anionic collectors are expected to adsorb on the maximum potential sites. However, since goethite with Ni occurs with other gangue minerals, namely, quartz, the utilization of anionic collectors is common because these collectors are more selective with regard to quartz compared to cationic ones.

## Nature of interactions in goethite and goethite containing Ni in lattice

**Table S2.** Electron density (*ρ*), Laplacian of electron density (2*ρ*), potential energy density (*V*), kinetic energy density (*G*), total energy density (*H* = *V* + *G*), |*V*|/*G* ratio, and the ratio of first and third eigenvalues of the Hessian matrix of electron density (|*λ*1|/*λ*3) for intermolecular interactions occurring in Fe4O8H4(goethite) under investigations calculated at the PBE0/6-31g(d,p) level of theory. All quantities are expressed in atomic units (a.u.). Refer to Figure 6 (a) for the labeling of intermolecular bonding and bond critical points (BCP).

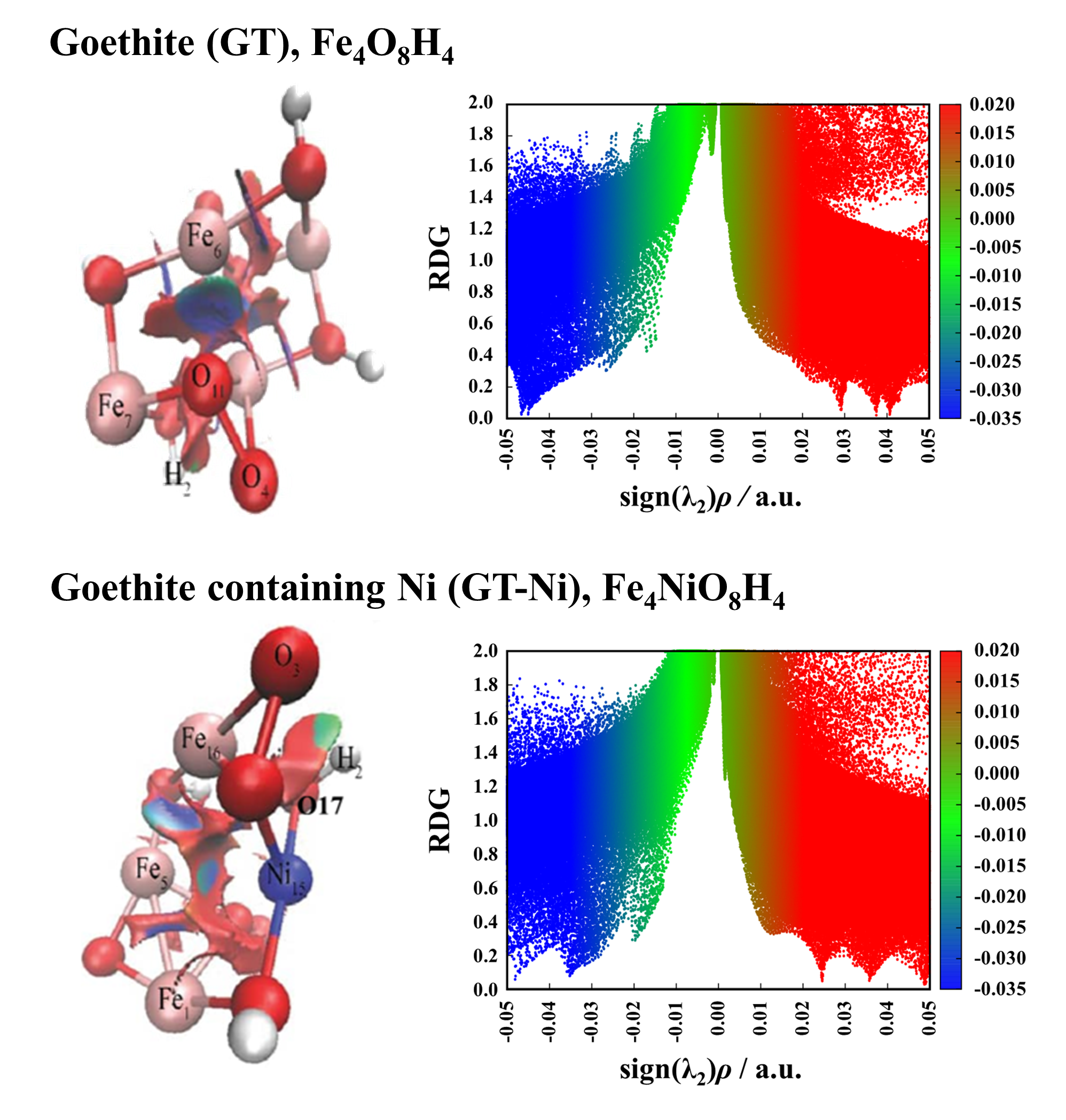
|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Intermolecular bonding | BCP | *ρ* | 2*ρ* | *H* | |*V*|/*G* | |*λ*1|/*λ*3 |
| O15∙∙∙Fe6∙∙∙O3 | Fe6∙∙∙O3 | 0.0717 | 0.5109 | 0.0007 | 0.9943 | 2.1264 |
| H2∙∙∙O4 | H2∙∙∙O4 | 0.3626 | −2.0093 | −0.5864 | 7.9787 | 1.0025 |
| Fe6∙∙∙Fe5 | Fe6∙∙∙Fe5 | 0.0451 | 0.0946 | −0.0179 | 1.4306 | 1.0640 |
| O15∙∙∙Fe6∙∙∙O11 | Fe6∙∙∙O11 | 0.0825 | 0.5472 | −0.0044 | 1.0315 | 1.4423 |
| O13∙∙∙Fe1∙∙∙O15 | Fe1∙∙∙O15 | 0.1101 | 0.7780 | −0.0063 | 1.0312 | 1.5982 |
| O11∙∙∙Fe6∙∙∙O4 | Fe6∙∙∙O4 | 0.1129 | 0.6895 | −0.0134 | 1.0720 | 1.6561 |
| O11∙∙∙Fe7∙∙∙O3 | Fe7∙∙∙O3 | 0.1128 | 0.7749 | −0.0092 | 1.0453 | 1.3355 |
| O3∙∙∙Fe7∙∙∙O11 | Fe7∙∙∙O11 | 0.1291 | 0.9302 | −0.0145 | 1.0586 | 1.1051 |
| O3∙∙∙Fe7∙∙∙O14 | Fe7∙∙∙O14 | 0.1101 | 0.778 | −0.0063 | 1.0311 | 1.5982 |
| O16∙∙∙Fe5∙∙∙O14 | Fe5∙∙∙O14 | 0.0907 | 0.5608 | −0.0054 | 1.0373 | 1.8796 |
| O4∙∙∙Fe6∙∙∙O15 | Fe6∙∙∙O15 | 0.0907 | 0.5608 | −0.0054 | 1.0373 | 1.8796 |
| O12∙∙∙Fe1∙∙∙O13 | Fe1∙∙∙O13 | 0.1128 | 0.7749 | −0.0092 | 1.0453 | 1.3355 |
| O16∙∙∙Fe5∙∙∙O13 | Fe5∙∙∙O13 | 0.0717 | 0.5109 | 0.0007 | 0.9943 | 2.1264 |
| O4∙∙∙O11 | O4∙∙∙O11 | 0.2727 | 0.0460 | −0.2138 | 1.9490 | 1.0126 |
| O14∙∙∙Fe5∙∙∙O11 | Fe5∙∙∙O11 | 0.0467 | 0.1881 | −0.0080 | 1.1452 | 2.2149 |
| O14∙∙∙Fe5∙∙∙O12 | Fe5∙∙∙O12 | 0.0825 | 0.5472 | −0.0044 | 1.0315 | 1.4423 |
| O13∙∙∙Fe1∙∙∙O12 | Fe1∙∙∙O12 | 0.1291 | 0.9301 | −0.0145 | 1.0586 | 1.1051 |
| O4∙∙∙Fe6∙∙∙O12 | Fe6∙∙∙O12 | 0.0467 | 0.1881 | −0.0080 | 1.1452 | 2.2149 |
| O14∙∙∙Fe5∙∙∙O16 | Fe5∙∙∙O16 | 0.1129 | 0.6895 | −0.0134 | 1.0720 | 1.6561 |
| H10∙∙∙O13 | H10∙∙∙O13 | 0.3626 | −2.0093 | −0.5864 | 7.9787 | 1.0026 |
| H8∙∙∙O14 | H8∙∙∙O14 | 0.3631 | −2.0852 | −0.5996 | 8.6565 | 1.0059 |
| H9∙∙∙O15 | H9∙∙∙O15 | 0.3631 | −2.0852 | −0.5996 | 8.6565 | 1.0059 |
| O12∙∙∙O16 | O12∙∙∙O16 | 0.2727 | 0.0460 | −0.2138 | 1.9490 | 1.0126 |

**Table S3.** Electron density (*ρ*), Laplacian of electron density (2*ρ*), potential energy density (*V*), kinetic energy density (*G*), total energy density (*H* = *V* + *G*), |*V*|/*G* ratio, and the ratio of the first and third eigenvalues of the Hessian matrix of electron density (|*λ*1|/*λ*3) for intermolecular interactions occurring in Fe3NiO8H4(goethite with Ni) under investigation calculated at the PBE0/6-31g(d,p) level of theory. All quantities are expressed in atomic units (a.u.). Refer to **Figure 6(b)** for the labeling of intermolecular bonding and bond critical points (BCP).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Intermolecular bonding | BCP | *ρ* | 2*ρ* | *H* | |*V*|/*G* | |*λ*1|/*λ*3 |
| O9∙∙∙Ni15∙∙∙O10 | Ni15∙∙∙O10 | 0.0949 | 0.5132 | −0.0229 | 1.1515 | 1.2810 |
| O13∙∙∙Ni15∙∙∙O3 | Ni15∙∙∙O3 | 0.1122 | 0.7083 | −0.0186 | 1.0953 | 1.1229 |
| H2∙∙∙O3 | H2∙∙∙O3 | 0.3589 | −2.0459 | −0.5897 | 8.5352 | 1.0007 |
| O10∙∙∙Fe1∙∙∙O11 | Fe1∙∙∙O11 | 0.1771 | 0.9852 | −0.054 | 1.1799 | 1.4641 |
| O12∙∙∙Fe16∙∙∙O3 | Fe16∙∙∙O3 | 0.1021 | 0.7295 | −0.004 | 1.0213 | 1.1798 |
| O4∙∙∙Fe16∙∙∙O9 | Fe16∙∙∙O9 | 0.1018 | 0.6692 | −0.0076 | 1.0434 | 1.3173 |
| O11∙∙∙Fe5∙∙∙O12 | Fe5∙∙∙O12 | 0.1104 | 0.6800 | −0.0108 | 1.0560 | 1.6032 |
| O10∙∙∙Fe1∙∙∙O13 | Fe1∙∙∙O13 | 0.1096 | 0.7375 | −0.0072 | 1.0374 | 1.7401 |
| O13∙∙∙Ni15∙∙∙O9 | Ni15∙∙∙O9 | 0.1206 | 0.6806 | −0.0268 | 1.1361 | 1.1033 |
| O12∙∙∙Fe5∙∙∙O10 | Fe5∙∙∙O10 | 0.0903 | 0.6065 | −0.0035 | 1.0225 | 1.6720 |
| O11∙∙∙Fe1∙∙∙O10 | Fe1∙∙∙O10 | 0.1055 | 0.7665 | −0.0049 | 1.0252 | 1.2767 |
| Ni15∙∙∙O9∙∙∙O4 | O4∙∙∙O9 | 0.3065 | −0.0423 | −0.2675 | 2.0412 | 1.0242 |
| O10∙∙∙O14 | O10∙∙∙O14 | 0.2718 | 0.0076 | −0.2085 | 1.9909 | 1.0660 |
| H8∙∙∙O14 | H8∙∙∙O14 | 0.3668 | −2.1451 | −0.6096 | 9.3158 | 1.0451 |
| O12∙∙∙Fe5∙∙∙O11 | Fe5∙∙∙O11 | 0.1487 | 0.8705 | −0.0325 | 1.1301 | 1.5969 |
| H6∙∙∙O12 | H6∙∙∙O12 | 0.3591 | −2.0578 | −0.5919 | 8.6434 | 1.0034 |
| H7∙∙∙O13 | H7∙∙∙O13 | 0.3639 | −2.1179 | −0.6060 | 8.9206 | 1.0057 |
| O3∙∙∙Ni15∙∙∙O13 | Ni15∙∙∙O13 | 0.1034 | 0.6872 | −0.0137 | 1.0738 | 1.0678 |
| O12∙∙∙Fe16∙∙∙O4 | Fe16∙∙∙O4 | 0.1220 | 0.7678 | −0.0162 | 1.0776 | 1.5509 |
| O9∙∙∙Fe16∙∙∙O12 | Fe16∙∙∙O12 | 0.1042 | 0.6177 | −0.0095 | 1.0577 | 2.0606 |

## Non-covalent analysis

To further understand the weaker interactions and the present steric repulsions that were not spotted by QTAIM, NCI investigations were conducted, as proposed by Johnson et al. [3], in conjunction with the multiwfn code [4] and VMD application [5]. **Figure S2** shows the results of the NCI investigations. Strong interactions (blue color) were observed in both structures, and the steric repulsions indicated in red were also noted in both structures (see **Figure S2**). A weak interaction, O17∙∙∙H2∙∙∙O3, was also noticed in goethite with Ni (see **Figure S2**). This interaction was not observed using QTAIM. Moreover, the interactions between O7∙∙∙Ni15∙∙∙Fe5, O3∙∙∙Fe16∙∙∙Fe5, and O4∙∙∙Fe1∙∙∙Fe5 were also confirmed to be very strong using NCI.



**Figure S2.** 2D iso-surface plots for reduced density gradient and scatterplots between and sign(*λ*2)ρ for Fe4O8H4 (goethite) and Fe3NiO8H4 (goethite with Ni) complexes. All quantities plotted are in atomic units (a.u.). The green, blue, and red colors denote van der Waals attraction/weak hydrogen bonding, strong hydrogen bonding, and steric repulsions, respectively.

## NBO analysis

To further understand the nature of bonding promoted by the donor and acceptor atoms in the system, the NBO analysis was conducted. **Tables S4 and S5** present the results. Since the second-order perturbation energy also involves the sharing of electrons, NBO can also be used to confirm the strength of the bonds in a complex. The second-order perturbation for the orbital interactions in goethite was between 2.09 and 15.06 kJ∙mol-1, suggesting the presence of bonding in the Fe4O8H4 complex (see **Table S4**). Furthermore, the second-order perturbation energy in the Fe3NiO8H4 complex indicated the energies ranging between 3.47 and 25.10 kJ∙mol-1 **(**see **Table S5),** further concretizing that goethite with Ni is more stable than goethite without Ni. This is also in agreement with the QTAIM results presented in **Tables S1** and **S2.**

**Table S4.** Second-order perturbation energy (*E*(2)) (donor→acceptor) (in kJ∙mol-1) for intermolecular interactions within goethite without Ni, involving nonbonding orbital of donor (LP(O))and antibonding orbital of acceptor (*σ*\*(O∙∙∙X), where X is Fe, Ni, and H, respectively) in the Fe4O8H4(goethite without Ni) complex. Refer to **Figure 6(a)** for labeling.

|  |  |  |  |
| --- | --- | --- | --- |
| **Intermolecular bonding** | **Donor (LP (O))** | **Acceptor(*σ*\*(O**∙∙∙**X))** | ***E*(2) (kJ**∙**mol-1)** |
| O15∙∙∙Fe6∙∙∙O3 | LP(O3) | σ\* (O15∙∙∙Fe6) | 7.15 |
| H2∙∙∙O4 | LP(O4) | σ\* (H2) | 3.93 |
| Fe6∙∙∙Fe5 | LP(Fe5) | σ\* (Fe6) | 2.80 |
| O15∙∙∙Fe6∙∙∙O11 | LP(O11) | σ\* O15∙∙∙Fe6) | 4.90 |
| O13∙∙∙Fe1∙∙∙O15 | LP(O15) | σ\* (O13∙∙∙Fe1) | 2.18 |
| O11∙∙∙Fe6∙∙∙O4 | LP(O4) | σ\* (O11∙∙∙Fe6) | 5.77 |
| O11∙∙∙Fe7∙∙∙O3 | LP(O3) | σ\* (O11∙∙∙Fe7) | 7.15 |
| O3∙∙∙Fe7∙∙∙O11 | LP(O11) | σ\*(O3∙∙∙Fe7) | 9.20 |
| O3∙∙∙Fe7∙∙∙O14 | LP(O14) | σ\* (O3∙∙∙Fe7) | 10.42 |
| O16-Fe5∙∙∙O14 | LP(O14) | σ\* (O16∙∙∙Fe5) | 6.36 |
| O4-Fe6∙∙∙O15 | LP(O15) | σ\* (O4∙∙∙Fe6) | 6.36 |
| O12-Fe1∙∙∙O13 | LP(O13) | σ\* (O12∙∙∙Fe1) | 5.40 |
| O16-Fe5∙∙∙O13 | LP(O13) | σ\* (O16∙∙∙Fe5) | 10.42 |
| O4∙∙∙O11 | LP(O11) | σ\* (O23∙∙∙Cu25) | 4.90 |
| O14∙∙∙Fe5∙∙∙O11 | LP(O11) | σ\* (O4) | 14.85 |
| O14∙∙∙Fe5∙∙∙O12 | LP(O12) | σ\* (O14∙∙∙Fe5) | 7.74 |
| O13∙∙∙Fe1∙∙∙O12 | LP(O12) | σ\* (O13∙∙∙Fe1) | 9.20 |
| O4∙∙∙Fe6∙∙∙O12 | LP(O12) | σ\* (O4∙∙∙Fe6) | 7.74 |
| O14∙∙∙Fe5∙∙∙O16 | LP(O16) | σ\* (O14∙∙∙Fe5) | 12.18 |
| H10∙∙∙O13 | LP(O13) | σ\* (H10∙∙∙O13) | 3.97 |
| H8∙∙∙O14 | LP(O14) | σ\* (H8) | 3.43 |
| H9∙∙∙O15 | LP(O15) | σ\* (H9) | 3.26 |
| O12∙∙∙O16 | LP(O16) | σ\* (O12) | 3.93 |

**Table S5.** Second-order perturbation energy (*E*(2)) (donor→acceptor) (in kJ∙mol-1) for intermolecular interactions within goethite with Ni, involving nonbonding orbital of donor (LP(O))and antibonding orbital of acceptor (*σ*\*(O∙∙∙X), where X is Fe, Ni, and H, respectively) in the Fe3NiO8H4(goethite with Ni) complex. Refer to **Figure 6(b)** for the labeling.

|  |  |  |  |
| --- | --- | --- | --- |
| **Intermolecular bonding** | **Donor (LP (O))** | **Acceptor(*σ*\*(O**∙∙∙**X))** | ***E*(2) (kJ**∙**mol-1)** |
| O9∙∙∙Ni15∙∙∙O10 | LP(O10) | σ\* (O9∙∙∙Ni15) | 3.72 |
| O13∙∙∙Ni15∙∙∙O3 | LP(O3) | σ\* (O13∙∙∙Ni15) | 8.12 |
| H2∙∙∙O3 | LP(O3) | σ\* (H2) | 4.02 |
| O10∙∙∙Fe1∙∙∙O11 | LP(O11) | σ\* (O10∙∙∙Fe1) | 5.10 |
| O12∙∙∙Fe16∙∙∙O3 | LP(O3) | σ\* (O12-Fe161) | 5.02 |
| O4∙∙∙Fe16∙∙∙O9 | LP(O9) | σ\* (O4∙∙∙Fe16) | 7.15 |
| O11∙∙∙Fe5∙∙∙O12 | LP(O12) | σ\* (O11∙∙∙Fe5) | 2.85 |
| O10∙∙∙Fe1∙∙∙O13 | LP(O13) | σ\* (O10∙∙∙Fe1) | 20.42 |
| O13∙∙∙Ni15∙∙∙O9 | LP(O9) | σ\* (O13∙∙∙Ni15) | 10.04 |
| O12∙∙∙Fe5∙∙∙O10 | LP(O10) | σ\* (O12∙∙∙Fe5) | 3.47 |
| O11∙∙∙Fe1∙∙∙O10 | LP(O10) | σ\* (O11∙∙∙Fe1) | 8.12 |
| Ni15∙∙∙O9∙∙∙O4 | LP(O4) | σ\* (Ni15∙∙∙O9) | 5.48 |
| O10∙∙∙O14 | LP(O14) | σ\* (O16∙∙∙Fe5) | 7.28 |
| H8∙∙∙O14 | LP(O14) | σ\* (O10) | 4.02 |
| O12∙∙∙Fe5∙∙∙O11 | LP(O11) | σ\* (O12∙∙∙Fe5) | 29.12 |
| H6∙∙∙O12 | LP(O12) | σ\* (H6) | 3.31 |
| H7∙∙∙O13 | LP(O13) | σ\* (H7) | 3.47 |
| O3∙∙∙Ni15∙∙∙O13 | LP(O13) | σ\* (O3∙∙∙Ni15) | 23.85 |
| O12∙∙∙Fe16∙∙∙O4 | LP(O4) | σ\* (O12∙∙∙Fe16) | 6.23 |
| O9∙∙∙Fe16∙∙∙O12 | LP(O12) | σ\* (O9∙∙∙Fe16) | 4.69 |

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