

Computational modelling studies of pentlandite ($\text{Fe}_4\text{Ni}_5\text{S}_8$) (111) surface: Oxidation and hydration

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Abstract. Minerals are exposed to atmospheric oxidation and hydration during ore grinding, as such the interaction of oxygen and water on mineral surface aid as a tool to determine the oxidation behaviour and wettability. In this study we employed the computational density functional theory (DFT) to investigate the adsorption of oxygen molecule and water molecule on the nickel-rich pentlandite ($\text{Fe}_4\text{Ni}_5\text{S}_8$) (111) surface. The oxidation preferred the bridging on Fe and Ni atoms (Fe-O₂-Ni) with exothermic adsorption energy of $-262 \text{ kJ}\cdot\text{mol}^{-1}$, which resulted from the initial Ni-peroxide adsorption. The hydration showed a strong exothermic interaction of H₂O with Fe than Ni and suggested that water adsorb on the pentlandite surface through the Fe atoms. This study predicts the oxidation and hydration behaviour of pentlandite mineral and suggested that the oxidation weathering of pentlandite will occur preferentially on the Fe atoms sites.

1. Introduction

Pentlandite ($\text{Fe,Ni}_9\text{S}_8$) is an iron-nickel sulphide with Ni:Fe ratio of close to 1:1 [1], and is regarded as a principal source of nickel [2]. Minerals are susceptible to oxidation and weathering overtime and thus investigation of oxidation behaviour is of paramount. Naturally, atmospheric oxidation of minerals results in oxide formation. There is still a lack in oxidation behaviour of pentlandite from computational aspects, in particular investigation of different oxidation mechanisms.

Xiong *et al.* [3] recently investigated the oxidation behaviour of (010) and (001) surfaces of pentlandite and it was reported that the Fe atoms in pentlandite migrated to the surface and were preferentially oxidized to form a thin layer of Fe_2O_3 . Similar prediction was made by Mkhonto *et al.* on pentlandite (110) surface [4]. An interesting phenomenon was observed by Xiong *et al.* where the oxygen molecule adsorptions preferred the bridging sites (Fe-Ni and Fe-Fe) on the surfaces and were the most favourable adsorption sites [3]. It appears that oxidation products are unconventional of the pentlandite composition, where both Iron-rich and Nickel-rich pentlandite give out almost the same products [5].

The hydration of minerals plays a crucial role in understanding the hydrophilicity and hydrophobicity of minerals. In particular during wet grinding, minerals tend to break differently compared to dry grinding. Furthermore, the oxidation of minerals involves water where dissociation

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occurs resulting in formation of Fe–OOH on the mineral surface [6]. Waterson *et al.* has previously reported a strong interaction of water with Fe atoms than Ni atoms [7].

In this paper, we investigated the effects of oxidation and hydration adsorption on the nickel-rich pentlandite (Fe₄Ni₅S₈) (111) surface using the density functional theory (DFT) calculations.

1.1. Bulk pentlandite(Fe₄Ni₅S₈) properties

The pentlandite structure is defined by a space group of *Fm-3m* (225) [8]. An important aspect of the pentlandite structure is the presence of three metal-metal bond extending from each tetrahedral cation to form essential isolated cube cluster of tetrahedral cation, Rajamani and Prewitt [9] and Vaughan and Craig [10]. The conventional unit cell of the pentlandite structure has a cubic close-packed arrangement of sulphide ions include 36 tetrahedral holes and 32 octahedral holes and has 68 atoms. In the nickel-rich pentlandite (Fe₄Ni₅S₈) the octahedral sites are occupied by Ni atoms, while the tetrahedral sites are evenly distributed by Fe and Ni atoms. We have found that the (Fe₄Ni₅S₈) pentlandite structure relaxed to lattice parameters of 9.947 Å. Our model is based on previously determined pentlandite bulk structure by Lu and Yu [11]; where the Fe and Ni distributes in heterogeneous (Fe–Ni) bonding as shown in figure 1a.

2. Computational methodology

The *ab-initio* density functional theory (DFT) [12, 13] method was employed to explore the interaction of oxygen molecule and water molecule onto nickel-rich pentlandite (111) surface. The plane-wave (PW) pseudopotential method with generalized gradient approximation of Perdew-Burke-Ernzerhof (GGA-PBE) within the CASTEP (Cambridge Serial Total Energy Package) [14] code were adopted for all calculations. A plane wave energy cut-off of 400 eV was used with k-points of 5×5×5 for the bulk and 5×5×1 for the surface as proposed by Monkhorst-Pack [15]. The (111) surface was used in this study and previously similar surface was investigated by Waterson *et al.* [7]. The surface energies are calculated using equation (1):

$$E_{surface} = \frac{E_{slab} - (n_{slab})(E_{bulk})}{2A} \quad (1)$$

where the surface slab area is A , E_{slab} is the total slab energy, n is the number of atoms in the slab, and E_{bulk} is the total bulk energy per atom. The lowest positive surface energy indicates a stable surface.

The strength of surface interaction with adsorbates (O₂ and H₂O) was calculated from equation (2):

$$E_{adsorption} = E_{system} - (E_{adsorbate} + E_{surface}) \quad (2)$$

where the energy of the surface slab and the adsorbate is E_{system} , the energy of the clean surface slab is $E_{surface}$, and the isolated adsorbates energy is $E_{adsorbate}$. The positive energy of adsorption corresponds to the endothermic process. The negative energy of adsorption corresponds to the process of exothermic adsorption and indicates a strong interaction between the adsorbate and the surface.

Now, in order to calculate the adsorption energies, the energy of the free O₂ and H₂O molecules were relaxed in a cubic box of 10 Å with similar oxygen ultrasoft pseudopotential, cut-off energy, at gamma point k-points and other equivalent precision parameters as in the surface calculations.

3. Results and discussion

3.1. Structural relaxation of pentlandite (Fe₄Ni₅S₈) (111) surface

The (111) surface was cleaved from the relaxed bulk pentlandite structure and the calculated surface energy is given in table 1. The (111) surface is composed of two slabs of repeating bulk thickness, with each slab containing seven layers (figure 1b). The slab thickness of pentlandite was previously investigated and reported that the 14 layers was sufficient for adsorption [7]. The supercell (111)

surface of 2×2 was adopted. The surface was fully relaxed before adsorption allowing only the atomic position to relax. After surface relaxation, we noted a slight change on the surface, where the Ni atoms relaxed inwards, while the Fe atoms relaxed outwards. Mkhonto *et al.* and Xiong *et al.* [4, 3] previously reported this behaviour.

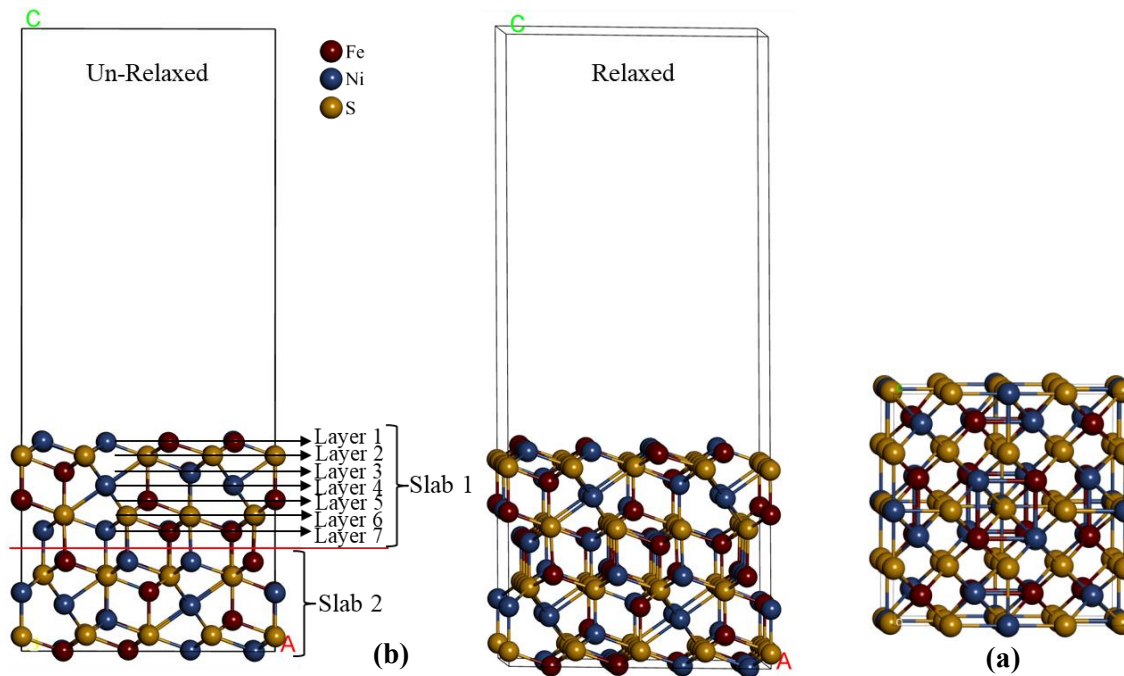


Figure 1: Crystal structures: (a) bulk nickel-rich ($\text{Fe}_4\text{Ni}_5\text{S}_8$) pentlandite and (b) side view of the un-relaxed and relaxed (111) $\text{Fe}_4\text{Ni}_5\text{S}_8$ surface.

3.2. $\text{Fe}_4\text{Ni}_5\text{S}_8$ (111) surface oxidation

The oxygen molecule adsorption on the $\text{Fe}_4\text{Ni}_5\text{S}_8$ (111) surface was performed on different adsorption sites namely: Ni-peroxide (Ni-O_2), Fe-peroxide (Fe-O_2), Ni-superoxide (Ni-O_2^-), Fe-superoxide (Fe-O_2^-) and Ni-bridge ($\text{Ni-O}_2\text{-Ni}$). Each O_2 adsorption mode was allowed to relax to its preferential bonding site and we observed different behaviour of the oxygen molecule on the surface. The most exothermic adsorption was Ni-peroxide with adsorption energy of -262 kJ.mol^{-1} as shown in table 1. We presented the un-relaxed and relaxed structures to identify the changes after relaxation.

Table 1: Calculated surface energy of $\text{Fe}_4\text{Ni}_5\text{S}_8$ (111) surface and adsorption energies of oxygen and water molecules

Surface	$\text{Fe}_4\text{Ni}_5\text{S}_8$ Surface energy (J.m^{-2})		
(111)	0.92		
	Oxidation	Hydration	
Adsorption modes	$E_{\text{adsorption}}$ (kJ.mol^{-1})	Adsorption modes	$E_{\text{adsorption}}$ (kJ.mol^{-1})
Fe-Peroxide	-188	Fe-Top	-53
Ni-Peroxide	-262	Ni-Top	-22
Ni-Superoxide	-253		
Fe-Superoxide	-168		
Ni-Ni-Bridge	-122		

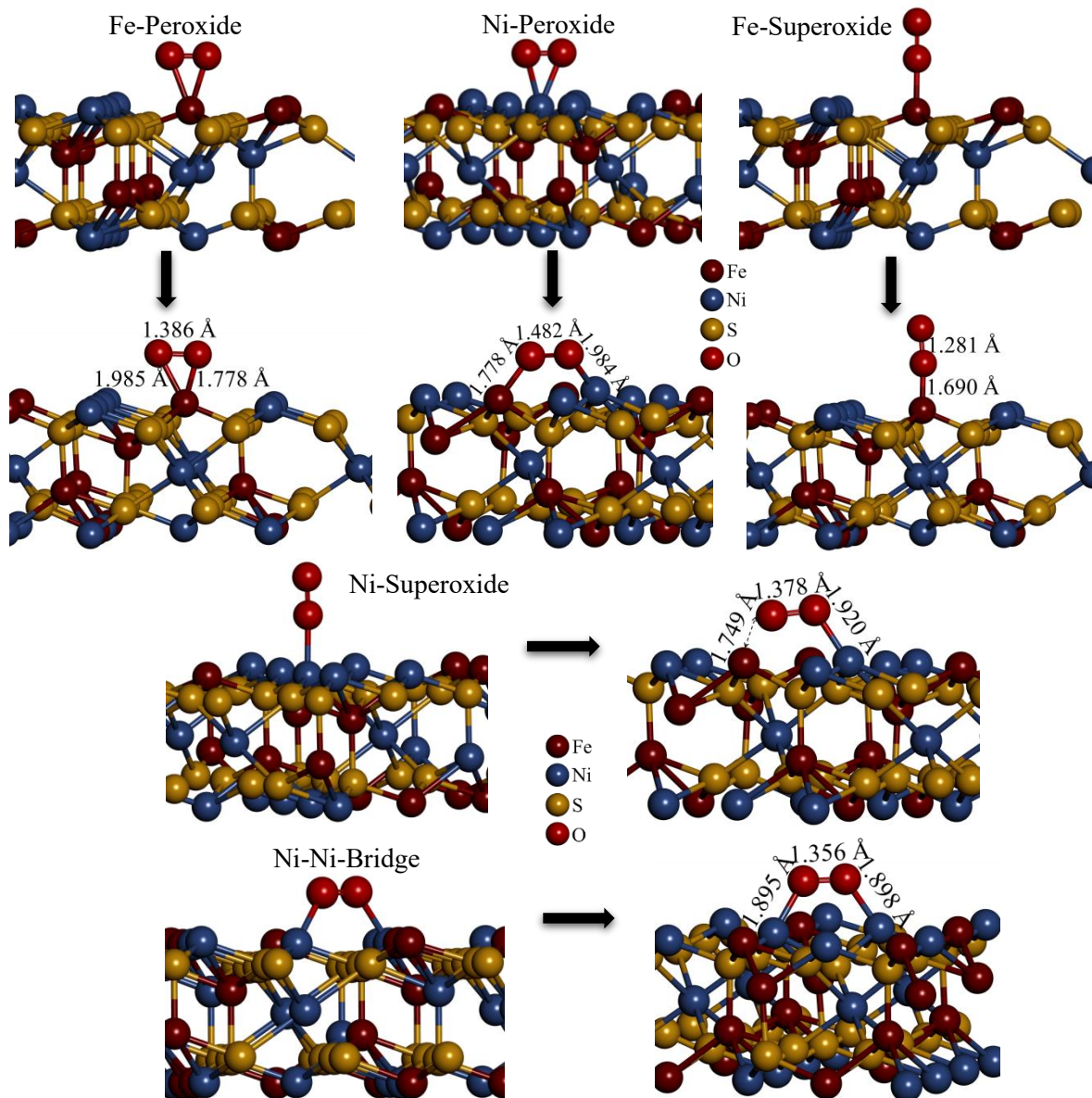


Figure 2: Adsorption sites of Oxygen molecule on the $\text{Fe}_4\text{Ni}_5\text{S}_8$ (111) surface.

The adsorption of O_2 in figure 2 (Ni-peroxide) showed that, the O_2 molecule moves and a bridge bond on Fe and Ni atoms ($\text{Fe}-\text{O}_2-\text{Ni}$), which suggested the preferential oxidation of Fe atom. The adsorption on Fe-peroxide and Fe-superoxide did not change the bonding mode. It is noted that Ni-superoxide resulted in oxygen molecule bending towards Fe atoms giving a distance of $\text{Fe}-\text{O} = 1.749$ Å, although the bond was not created. This resulted in adsorption energy close to that of Ni-peroxide (leading to $\text{Fe}-\text{O}_2-\text{Ni}$). It was found that the $\text{Ni}-\text{O}_2-\text{Ni}$ bridge was weaker amongst the adsorption sites ($-122 \text{ kJ}\cdot\text{mol}^{-1}$). In all adsorptions, except for Fe-superoxide the oxygen molecule ($\text{O}-\text{O}$) bond length stretched to over 1.300 Å, which indicated a weakened bond due to electron transfer from the d-orbital to the unoccupied orbital of oxygen molecules.

3.3. $\text{Fe}_4\text{Ni}_5\text{S}_8$ (111) surface hydration

The interaction of water (H_2O) with nickel-rich (111) pentlandite surface was tested on Fe-top ($\text{Fe}-\text{OH}_2$) and Ni-top ($\text{Ni}-\text{OH}_2$). Table 1 shows that the Fe atom gave the most exothermic adsorption energy than Ni atom, suggesting that the Ni-rich pentlandite is more hydrophilic on Fe atoms and thus,

the most preferred adsorption site for H₂O on the (111) surface. This is in line with previous report of water interaction with Ni-Pn and Fe-Pn [7]. In order to examine the structural bonding mode of the H₂O on the (111) surface, we present the un-relaxed and relaxed structures.

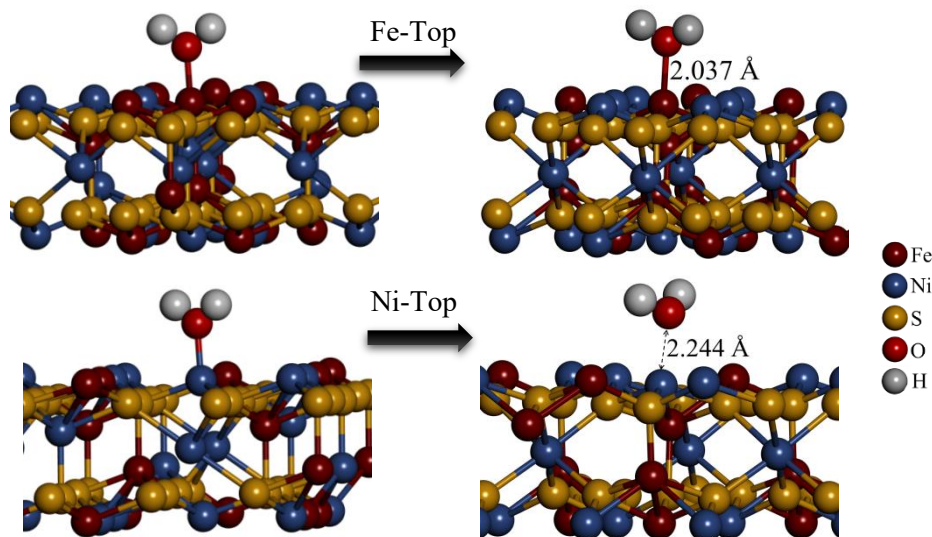


Figure 3: Adsorption sites of water molecule on the Fe₄Ni₅S₈ (111) surface.

We observed that figure 3, indicates the adsorption of water on Fe-top did not change the orientation. The adsorption of H₂O on Ni-top resulted in water relaxing upwards leaving a distance of Ni---OH₂ = 2.244 Å. In addition, we found that the Fe---OH₂ (2.037 Å) bond length was shorter than for Ni---OH₂ (2.244 Å), indicating the strong interaction between Fe and water molecule. The O---H bond length for Fe-top was approximately equal to that of Ni-top (0.980 Å). The water molecules resulted in bond angles of 107.69° on Fe-top and 106.34° on Ni-top.

4. Conclusion

In this study the oxidation and hydration of Fe₄Ni₅S₈ (111) surface was investigated using the *ab-initio* DFT method. The adsorption of oxygen and water molecule on the (111) surface of nickel-rich pentlandite were tested on different adsorption sites, preferably the Ni and Fe atoms. We found that the oxidation preferred the Ni-peroxide mode, which resulted in bridging on Fe and Ni atoms (Fe---O₂---Ni). This bonding was the most exothermic with adsorption energy of -262 kJ.mol⁻¹ and therefore signifying preferential oxidation of Fe atoms. In the case of hydration of (111) surface, we observed that the water adsorb strongly on iron (-53 kJ.mol⁻¹) as compared to nickel (-22 kJ.mol⁻¹) and complimented by the bond length after surface relaxation. This study demonstrated that the oxidation and hydration behaviour of pentlandite mineral. Moreover, the oxidation by weathering of pentlandite is found to occur spontaneously on the Fe sites.

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