Computational modelling of adsorption of O_2 and H_2O on nickel-rich {111} pentlandite surface

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Abstract. *Ab-initio* density functional theory was employed to investigate the interaction of oxygen and water on the nickel-rich pentlandite $Fe_4Ni_5S_8$ {111} surface. During the adsorption, we observed that the oxygen-metal interaction showed preferential iron oxidation than nickel on the surface model. Moreover, the iron preferential oxidation is extensively observed when adsorbing on nickel, where the oxygen molecule tend to move from nickel to bond with iron. The oxidation of the iron atom showed the presence of superoxo isomer species on the surface, while the migration of the oxygen molecule from nickel to iron shows a peroxo species. The hydration on iron-nickel surface termination shows a strong interaction of the water molecule with the iron atom.

1. Introduction

Pentlandite $(Co,Fe,Ni)_9S_8$ are important sources of cobalt, iron and nickel in continental deposits, which over the last decade have been found in mounds formed from ultramafic rocks on the ocean floor of the Mid-Atlantic Ridge (MAR) [1]. Previously, pentlandite had only been mentioned without chemical characterization among the sulphide phases of highly altered gabbros from the Carlsberg and Gorda seafloor ridges in the Indian and Pacific oceans, respectively. The crystal structure of Co_9S_8 was found from powder data by Powder Diffraction method [1], [2]. Pentlandite is widely known as the major source of nickel [3] through ore petrography [4]. It is for this reason that the alteration in particular the oxidation [5], hydration and addition of collectors on the mineral, both in ore deposits and during the extraction process, are important with regard to the nickel yield from the ore. This investigation provides information on the chemistry of pentlandite surfaces that may be applicable to the separation of pentlandite. The surface compositions are important in respect to the extraction efficiency and are, therefore, of commercial interest [6].

In this paper, we employ first principles method to investigate the surface properties of nickel-rich pentlandite mineral, starting from the surface orientation and termination to better understand the surface reaction with oxygen and water molecules. Furthermore, the introduction of organic collectors will be investigated to gain knowledge into the reaction chemistry and their influence.

2. Computational methodology

The investigation of the surface reaction of nickel-rich pentlandite is performed by employing *ab initio* quantum-mechanical density functional theory method [7], [8]. We use the plane-wave (PW) pseudo-potential method within the Vienna *ab initio* Simulation Package (VASP) program [9] [10]. The plane-wave pseudopotential method is necessary for performing full geometry optimization of the structures. The Ultrasoft pseudopotentials is used with a plane-wave basis set, truncated at a kinetic energy of 400 eV since this was found to be optimal in studying these surface. A k-points mesh of 5x5x1 is used in order to determine the quality of the calculations with which the Brillouin zone will be sampled. This is chosen according to the scheme proposed by Monkhorst and Pack [11]. The surface is presented by slab composed of seven layers of atoms separated by a vacuum slab of 20 Å in order to mimic the interaction of the adsorbate with the repeating upper slab. Different termination were sampled to find a termination that is less reactive (low surface energy) for {111} surface. The surface stabilities for different termination are determined by their surface energy, calculated using equation 1:

$$E_{surface} = \left(\frac{1}{2A}\right)[E_{slab} - (n_{slab})(E_{bulk})] \qquad (1)$$

where E_{slab} is the total energy of the cell containing the surface slab, n_{slab} is the number of atoms in the slab, E_{bulk} is the total energy per atom of the bulk and A is the surface area. A low positive value of $E_{surface}$ indicates stability of the surface termination in respective surfaces. The strength of interaction of the surface with the adsorbate is shown by the adsorption energy, calculated by equation 2:

$$E_{adsorption} = E_{slab} - \left(E_{system} + nE_{adsorbate}\right)/n \qquad (2)$$

where E_{system} is the energy of the surface slab with adsorbate, E_{slab} is the energy of the surface slab as above, n is the number of adsorbate adsorbed on the surface and $E_{adsorbate}$ is the energy of the free adsorbate molecule. A negative value shows a strong interaction between the adsorbate and the surface, whereas a positive value reveals the opposite.

3. Results and discussion

Figure 1 show the low index surface {111} of nickel-rich pentlandite ($Fe_4Ni_5S_8$) mineral, and the designated atoms as indicated. The surface was cleaved from the optimise bulk pentlandite structure with space group of *Fm-3m* (225) [12]. Their calculated surface and adsorption energies are given in table 1.

Table 1. Calculated surface energy (eV/Å^2) and adsorption energies (eV) of oxygen and water molecule adsorbed on {111} nickel-rich pentlandite mineral surface metals.

	Surface energy	Adsorption energies			
Surface	$E_{(surface)}$	Oxidation		Hydration	
{111}	0.064	Ni	Fe	Fe	Ni
		-1.385	-1.175	-0.213	-0.211

(a) (b)

Figure 1: The {111} surface (a) un-relaxed and (b) relaxed stable termination surface.

Firstly, we consider the adsorption of oxygen on the surface. We observed a preferential oxidation of iron when oxygen molecule (O_2) is adsorbed or positioned on iron atom. Furthermore, the oxygen molecule bends and forms an orientation of anion superoxo isomer species (Fe-O-O^-). This observation is in agreement to the previous studies of iron interaction with oxygen by Gutsev *et al*. [13]. The excess electron on the oxygen is due to the charge transfer from the 3d orbitals of iron to the π_g* anti-bonding molecular orbitals of oxygen [14]. However, when oxygen molecule (O_2) is adsorbed on nickel atom, we observe that the oxygen molecule migrate from the nickel atom to form a bond with the nearest iron atom. This behavior had shown formation of anion peroxo species isomer (O-Fe-O^-). This observation is also in agreement to the previous studies of iron interaction with oxygen by Gutsev *et al*. [13]. Similarly, the excess electron on the oxygen is due to the charge transfer from the 3d orbitals of iron to the π_g* anti-bonding molecular orbitals of oxygen [14]. The bond length between the iron and the two oxygen atoms (O1 and O2) are different. This gives rise to adsorption energy that is more stable on the peroxo as compared to superoxo isomer species. As a results, this suggests that a mononuclear bonding (peroxo) to iron is more stable.

Secondly, considering the adsorption of water molecule, we note that the iron atoms are more hydrophilic than nickel. We observed that when the water molecule is adsorbed on nickel atom, the water molecule migrates from the nickel atom to bond with the nearest iron atom. This behaviour suggests that the nickel atoms on this surface do not react with water. On the other hand, when the water molecule is adsorbed on iron atom, the hydrogen atoms take or prefer side–way orientation. These suggest that the nickel atoms can easily bond and possible mineral extraction could be achieved on this surface. Moreover, hydration on the nickel atoms on this surface requires less energy since the adsorption energy is favourable.

Table 2. The relaxed bond lengths (*R*, in Å), bond angles (θ, in deg.). The theoretical/ experimental values are shown in parenthesis for comparison.

	{111}	
	Oxidation	
Bonds	Ni	Fe
R(O-O)	1.364 (1.488)	1.293 (1.355) [13]
R(Fe-O)	1.752 (1) and 2.068 (2) (1.884) [13]	1.716 (1.767) [13]
θ(O-Fe-O^{-})	40.81 (46.50) [13]	
θ(Fe-O-O^{-})		136.47 (129.60) [13]
	Hydration	
Bonds	Ni	Fe
R(O-H)	0.976 and 0.979	0.977 and 0.975
R(Fe-O)	2.092	2.093
θ(H-O-H)	105.89	105.90

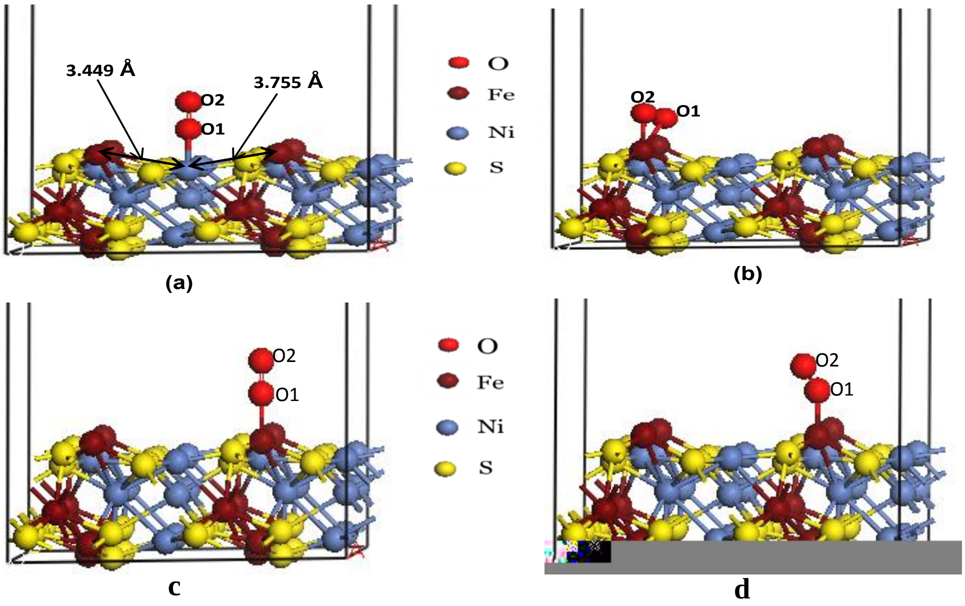
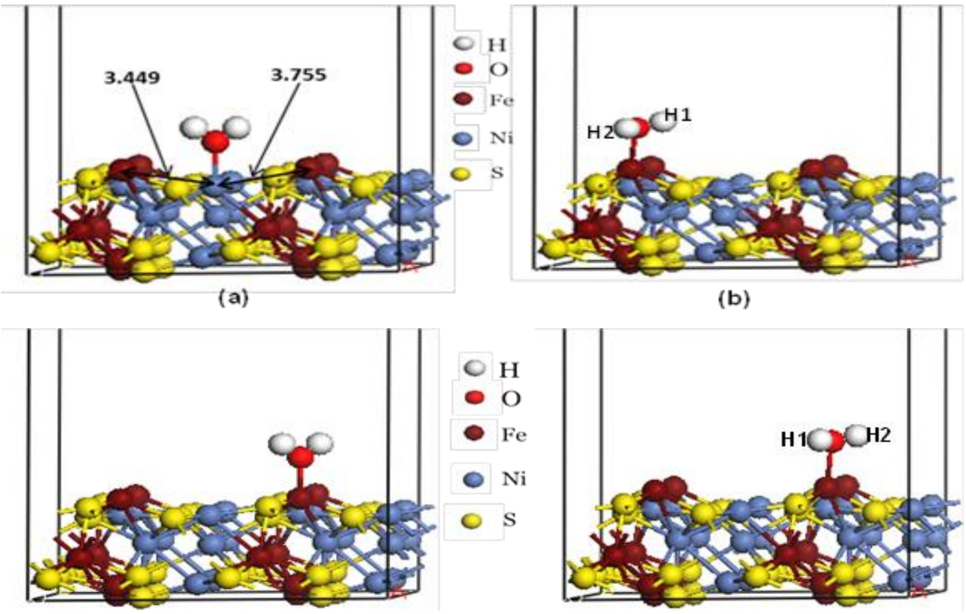


Figure 2: The {111} $Fe_4Ni_5S_8$ surface with oxygen molecule, before relaxation and after relaxation, respectively (a-b) adsorption on nickel and (c-d) adsorption ion iron.



c d

Figure 3: the {111} $Fe_4Ni_5S_8$ surface with water molecule, before relaxation and after relaxation, respectively (a-b) adsorption on nickel and (c-d) adsorption on iron.

4. Conclusions

The adsorption of oxygen and water molecule on the {111} surface for flotation purpose was successfully investigated using DFT method. We observed that the oxidation favoured the formation of anion superoxo and peroxo species on the iron atoms. The oxidation is found to be in agreement to the study by Gutsev *et al*. While the hydration favoured adsorption on iron atom and suggests that the iron atoms are more hydrophilic than nickel. This study had revealed how oxygen and water reacts with iron/nickel in pentlandite naturally and during flotation which are an important aspect that is useful in the floatation of pentlandite.

Acknowledgements

The computations were performed at the Materials Modelling Centre (MMC), University of Limpopo. We also acknowledge South African Mineral to Metals Research Institute (SAMMRI) for financial support.

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