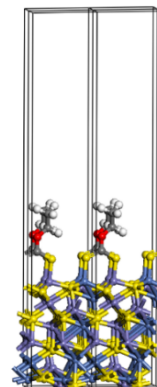


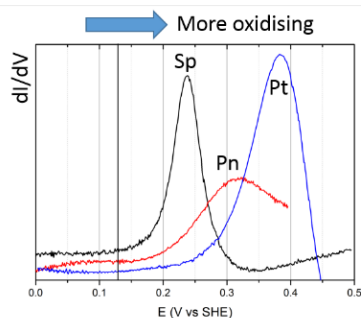
A first principles Study on Ligand Binding and Positional Disorder in Pentlandite

Computational and experimental investigation of ligand binding to mineral surfaces

Modelling dithiolate ligands binding to mineral surfaces (and proving experimentally that it makes sense) slurry in a series of agitated tanks. Selective ligands (typically small organic anion surfactants, see Figure right), are added to bind to the target mineral surface. The hydrocarbon tail renders the surface hydrophobic, facilitating bubble attachment. In this way mineral particles rise up the tank to form a froth, which is mechanically separated for further processing.

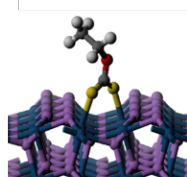


The primary mined source for nickel recovery is pentlandite $(\text{Fe,Ni})_9\text{S}_8$ (Pn). A single unit cell of Pn contains 36 metal sites which can be assigned to either Fe or Ni (see Figure left, metal sites coloured blue and silver), such that the number of possible ordered models runs to many thousands. To identify the nature of the closest metal...metal contacts that act to minimise the bulk energy, we trained a cluster expansion Hamiltonian to a set of randomly, explicitly defined models of Pn using DFT. The resulting Hamiltonian identified that lower energy bulk structures were obtained when nearest neighbour metal contacts were of type Fe...Ni, rather than Fe...Fe or Ni...Ni. The trained Hamiltonian was then used in a Monte Carlo simulation to search for the lowest energy local order model, which was subsequently confirmed to be the most stable arrangement by DFT, and which matched the Ni octahedral and tetrahedral site occupancies reported in a powder neutron diffraction study. The picture that emerges is that, while Pn exhibits long range disorder with respect to Fe,Ni occupancy, some degree of short range order does exist.

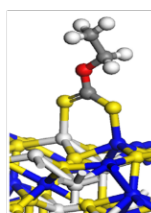


Normalised differentiated anodic currents for ethyl xanthate on three different mineral/metal electrodes.

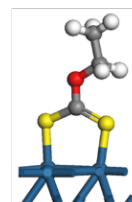
Calculated binding energies for ethyl xanthate on mineral and metal surfaces



Sp (PtAs_2)
-408 kJ mol^{-1}



Pn [$(\text{Fe,Ni})_9\text{S}_8$]
(all Ni surface) -450 kJ mol^{-1}
(all Fe surface) -555 kJ mol^{-1}



Pt
-620 kJ mol^{-1}

Modelling mineral collector ligands bound to surface models under periodic boundary conditions presented a technical problem. The ligands are typically anions, and charged periodic boundary models lack a well-defined energy. To negate this problem we proposed a correction scheme derived from the surface work function correction to remove the additional charge introduced by the ligand. The resulting modelling scheme was then applied to a range of minerals commonly floated together to identify a hierarchy of ligand binding energies to different mineral surfaces. As the minerals investigated are metallic, it is possible to study ligand adsorption in an electrochemical cell. Under oxidising conditions the chemisorbed dithiolate ligands dimerise, reorganise on the surface to be physisorbed, and release two electrons. By varying the oxidising potential of the cell, a spike in the current

associated with the breaking of the mineral–ligand chemical bonds is observed (see Figure below). The greater the oxidising potential, the more strongly the dithiolate ligand is chemisorbed to the mineral surface. From the plot shown the current peak is observed first for sperrylite (a platinum arsenide mineral), then pentlandite, followed by a pure platinum wire electrode. This implies that ethyl xanthate should bind most weakly to the surface of sperrylite, and most strongly to platinum, which matches the binding hierarchy identified in the modelling work.

References: [1]C. N. Waterson, J. O. Sindt, J. Cheng, P. A. Tasker and C. A. Morrison, *J. Phys. Chem. C*, 2015, **119**, 25457.[2]C. N. Waterson, R. Farinato, D.R. Nagaraj, V. Griffin and C. A. Morrison, manuscript in preparation.

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