Oxidation/alteration of pentlandite and pyrrhotite surfaces at pH 9.3: Part 1. Assignment of XPS spectra and chemical trends

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ABSTRACT

Using X-ray photoelectron spectroscopy, the oxidation/alteration of massive coexisting pentlandite [(Fe,Ni)9S8] and pyrrhotite (Fe1−xS) from Voiseys Bay has been studied in aqueous solution at pH 9.3. The Fe 2p, Ni 2p, S 2p, and O 1s spectra were obtained for each mineral from polished surfaces, and from surfaces reacted with the solutions for up to 180 minutes. Both minerals oxidize rapidly to give mostly a relatively thin layer (tens of angstroms) of Fe(III) oxyhydroxide (probably FeOOH). In addition, violarite (FeNi2S4), Ni(OH)2, and NiSO4 are found in the pentlandite oxidized overlayer, and Fe(III)-S and polysulﬁde species are found in the overlayers of both minerals. A protocol was developed to fit quantitatively all spectra in a consistent fashion. Fe 2p\(^{2}\) spectra were ﬁtted with two Fe(II)-S peaks depending upon Fe coordination (four and six) in pentlandite, pyrrhotite, and violarite. An Fe(III)-S multiplet, an Fe(III) oxyhydroxide multiplet, as well as Ni Auger peaks, were also required to ﬁt the Fe 2p spectra. The Ni 2p\(^{2}\) spectra for pentlandite were ﬁtted with two Ni(II)-S peaks from the original pentlandite or violarite (four and six coordination), as well as Ni(OH)\(_2\) and NiSO\(_4\) peaks. The S 2p spectra for both minerals were ﬁtted with four and five coordinate S peaks from the original minerals and violarite, as well as polysulﬁdes and sulfate. Finally, the O 1s spectra of both minerals were ﬁtted with peaks from oxide, hydroxide, and adsorbed water.

The pyrrhotite surface oxidizes more rapidly than the pentlandite surface. For example, after ﬁve minutes of reaction the extent of oxidation of pyrrhotite to give an FeOOH overlayer is similar to that of pentlandite after thirty minutes of reaction. In both minerals, iron diffuses from the bulk to the surface and is oxidized. Pentlandite shows small amounts of Ni(OH)\(_2\) and NiSO\(_4\) in the Fe(III) oxyhydroxide-dominated overlayer even after 180 minutes of reaction. These observations of the oxidation and alteration of the pentlandite surface are entirely consistent with thermodynamic calculations of the relative stabilities of pentlandite, violarite, Ni(OH)\(_2\), NiSO\(_4\), and FeOOH. The ﬁrst stage of reaction is characterized by formation of violarite and FeOOH on pentlandite. With continued oxidation, this assemblage yields NiSO\(_4\) plus FeOOH plus violarite, which is eventually converted to Ni(OH)\(_2\) plus violarite plus FeOOH. Finally, after the violarite is consumed, the NiSO\(_4\) plus FeOOH combination occurs as the thermodynamically stable assemblage.

INTRODUCTION

Pentlandite, (Fe, Ni)\(_9\)S\(_8\), (Pn) is the chief source of nickel worldwide, and is most often associated with pyrrhotite (Po), Fe\(_{1-x}\)S, where 0 < x < 0.2 (Klein and Hurlbut 1993). Pentlandite is usually separated from the gangue by flotation. Under typical plant operating conditions, the separation of pentlandite from pyrrhotite is somewhat ineﬃcient, resulting in signiﬁcant amounts of pyrrhotite reporting to the concentrate. Flotation of pentlandite/pyrrhotite ores is usually carried out at a pH of around 9 to 9.5. Since ﬂotation relies on the surface properties of these minerals, surface properties should be understood at these pH values if ﬂotation separation is to become more eﬃcient.

Surface analytical techniques have been used to successfully study the outermost layers of sulfide minerals and the adsorbed collector molecules from a ﬂotation viewpoint (e.g., Cecile et al. 1985; Persson 1994; Buckley 1994; Szargan et al. 1997; Buckley et al. 2003; Shackleton et al. 2003). For example, Fourier transform infrared-attenuated total reﬂectance (FTIR-ATR) has provided much information on adsorption mechanisms of collectors [e.g., potassium amyl xanthate (KAX)] onto sulﬁdes (Bozkurt et al. 1998). Bozkurt et al. (1998) have studied the relative amount of adsorption of KAX onto pentlandite and pyrrhotite, both in contact and separately. They concluded that dixanthogen was the main adsorption product on Pn and that with coexisting Po the dixanthogen adsorption was increased relative to Po alone. This same technique was also used in the study of nickel-DETA complexes (Vreughenhil et al. 1997), as well as in the investigation of the role of DETA in pentlandite-pyrrhotite separation (Xu et al. 1997).

X-ray photoelectron spectroscopy (XPS) normally analyzes the ﬁrst 20–50 Å of a surface (Tanuma et al. 1991) and provides excellent chemical information (both qualitative and quantitative) for elements such as Fe, Ni, S, and O, and thus XPS is useful for...