Study of the role of surface chemical composition of sulfide minerals in flocculation by ESCA

S. Acar and P. Somasundaran

Abstract—Results of selective flocculation of natural ores containing two or more minerals and of synthetic mineral mixtures do not usually agree with what is expected on the basis of the results from single mineral tests (Acar and Somasundaran, 1985). This is mainly due to the ionic species released by the minerals, which act differently under different pH values. The objective of this investigation was to study 1) the surface chemical composition of selected sulfide minerals—natural chalcopyrite and pentlandite and synthetic covellite, millerite, and pyrrhotite—and 2) the changes brought about by the dissolved mineral species. Electron Spectroscopy for Chemical Analysis (ESCA) was used to perform the surface analyses.

Introduction

Electron Spectroscopy for Chemical Analysis (ESCA) is a surface analysis technique that provides a depth of analysis ranging from 10 Å to 50 Å. The method involves irradiation of the solid sample in high vacuum with monoenergetic soft X-rays (Mg Ka or Al Ka X-rays) and sorting the emitted electrons by energy (Perkin Elmer). The spectrum obtained is a plot of the number of emitted electrons per energy interval versus their binding energy. Each element (with the exceptions of hydrogen and helium) has a characteristic set of electron binding energies that can be used to identify the element. Moreover, ESCA can often differentiate between chemical environments or valence states of any given element.

ESCA has been extensively used in the minerals and metals
industry. Manocha and Park (1977) used ESCA to characterize the nature of chemical species on galena (PbS) surfaces exposed to air and aqueous environments and concluded that lead sulfate is the major product of oxidation of PbS in air and aqueous environments. The presence of small amounts of elemental sulfur in the early stages of oxidation suggested that the initial oxidation step differs from the later major oxidation processes.

ESCA has also been used to determine the bonding nature of adsorbed cations.

Koppelman and Dillard (1978) used X-ray photoelectron spectroscopy (XPS) to study the bonding nature of metal ions adsorbed from aqueous solutions by the marine clay minerals kaolinite, illite, and chlorite. Binding energies for the lattice elements Si, Al, O, Mg, K, and Ca were found to be in good agreement with the published values. However, significant differences in bonding energies (1.9 eV) for the Fe 2p3/2 level for iron in chlorite and nontronite were observed. This was attributed to the two different oxidation states of iron, Fe** in chlorite and Fe*** in nontronite. Fe*** adsorbed onto kaolinite had an Fe 2p3/2 level binding energy 1.2 eV lower than lattice Fe**+. This lowering of binding energy was attributed to the negative potential of the electrical double layer at the mineral surface when the cation is adsorbed.

Flotation responses of sulfide minerals and the amount of collector adsorption have been shown to be dependent upon the state of oxidation of the sulfide mineral surface (Clifford and Miller, 1974; Majima, 1970; Plaskin, 1958; Yamaski and Usui, 1965). ESCA has been used to characterize the surfaces of galena, sphalerite, chalcopyrite, chalcocite, covellite, bornite, pyrite, pyrrhotite, molybdenite, and millerite (Clifford, Purdy and Miller, 1975). Surface analyses were made after comminution in air and comminution in a nitrogen atmosphere, and after adsorption of xanthate or dithiophosphate collector. Analyses were also made after treating with modifiers such as Na2Cr2O7, SO2, starch, NaCN, and CuSO4.

In the present study, ESCA was used to investigate the effect of dissolved species from natural and synthetic sulfide minerals on the surface chemical composition in selective flocculation systems.

**Experimental materials and methods**

**Materials**

*Minerals:* Natural chalcopyrite was purchased from Ward's
Natural Sciences Establishment Inc. After crushing and concentrating using an electrostatic separator, the chalcopyrite was ground in a stainless steel ball mill and wet screened at minus 20 μm (625 mesh). It was dried and stored in a Teflon bottle under nitrogen atmosphere to prevent further oxidation. Surface area of the sample as measured by the BET nitrogen gas adsorption method was 1.22 m²/g (406 sq ft per oz).

Flotation concentrate of pentlandite was obtained from Inco Limited and was cleaned to remove the flotation reagent. The cleaned concentrate was screened to minus 20 μm and leached with dilute HCl. Leached material was repeatedly washed with distilled and triple distilled water until natural pH of triple distilled water was obtained. The sample was then freeze dried and stored in a Teflon bottle under nitrogen atmosphere. The surface area of this sample was determined to be 1.43 m²/g (476 sq ft per oz).

Synthetic covellite of surface area 2.74 m²/g (912 sq ft per oz) purchased from Morton Thiokol Inc., Alfa Products was used as received.

Synthetic millerite, also purchased from Morton Thiokol Inc., was ground under nitrogen atmosphere in an agate mortar and stored in a Teflon bottle. The surface area of the sample was determined to be 0.75 m²/g (250 sq ft per oz). Synthetic millerite was stated to be 99.9% pure, and its X-ray diffraction pattern matched ASTM pattern number 2-1280 for nickel-2-sulfide.

Synthetic pyrrhotite was obtained from Fisher Scientific Corp. as minus 2.36-mm (minus 8-mesh) lumps. It was also ground in an agate mortar under nitrogen atmosphere and stored in a Teflon bottle. The surface area of this sample was found to be 0.75 m²/g (250 sq ft per oz).

Inorganic reagents: Fisher certified CuCl₂·2H₂O, NiCl₂·6H₂O, and FeCl₃·4H₂O were used in the experiments as the source of the desired metallic cations. Fisher certified HCl and NaOH (1N, 0.1N, and 0.01N) were used to adjust the pH. Amend Drug and Chemical Co. reagent grade NaCl, which is 99.96% pure, was used to make 3·10⁻² kmol/m³ salt solution for all the experiments.

Water: Triple-distilled water with specific conductivity of about 10⁻⁶ mmhos/cm was collected from a quartz still.

Methods

Experimental procedure for the surface compositional studies began with pretreatment of the mineral surfaces by conditioning them in various inorganic solutions and then analyzing the treated and untreated surfaces using ESCA. 1.5-g (0.05-oz) mineral samples were conditioned in Teflon bottles using a wrist action shaker in 50 ml (1.7 fl oz) of the required solution at the desired pH for three hours. The mineral samples were rinsed several times with triple-distilled water and separated from the solution by filtration followed

![Fig. 3—XPS spectrum of millerite (a, left) and millerite conditioned in 10⁻² kmol/m³ FeCl₃·4H₂O (b, right)
by several washes with triple-distilled water. After drying, solids were removed from the filter paper and kept in glass vials for surface analysis.

XPS spectra were obtained using the Perkin Elmer Physical Electronics Division ESCA/AUGER system model number 548 equipped with a magnesium anode. The samples were loaded by first spreading the powders on a double-stick scotch tape attached to a molybdenum mask. The electrons leaving the sample were detected by an electron spectrometer according to their kinetic energy. Identification of chemical states was made from the positions and separations of the peaks, as well as from certain spectral contours.

Results and discussion

XPS spectrum of natural pentlandite conditioned in 3.10⁻² kmol/m³ NaCl solution at the natural pH of the mineral is shown in Fig. 1a. As can be seen from the figure, the most intense Ni peak [Ni(2p₃)] is located at 855.0 eV along with Ni(2p₁) peak at 877.0 eV binding energies. The spectrum also exhibits Fe(2p₃) peak at 714.0 eV and Fe (auger) peak at 608.0 eV.

On the other hand, when pentlandite is conditioned in chalcopyrite supernatant, Cu(2p₃) and Cu(2p₁) peaks are seen at the binding energies of 933.6 eV and 935.0 eV, respectively (Fig. 1b). Comparison of the two spectra shows that pentlandite surface can have significant amounts of copper species when it is conditioned in chalcopyrite supernatant.

The spectrum obtained for chalcopyrite conditioned in 3.10⁻² kmol/m³ NaCl solution is illustrated in Fig. 2a. This spectrum exhibits copper peaks at 954.0 eV and 934.0 eV of binding energies for Cu(2p₃) and Cu(2p₁). Electron binding energies of Cu(2p₃) for five different chalcopyrite samples are reported to be in the range of 932.16 - 934.61 eV. The S(2p₃) peak is located at 163.6 eV, which corresponds to sulfide (Clifford, Purdy, and Miller, 1975).

While the chalcopyrite spectrum showed no indication of a nickel peak, the spectrum of chalcopyrite conditioned in pentlandite supernatant exhibited a small Ni(2p₃) peak at 854.6 eV electron binding energy (Fig. 2b). This most probably resulted from the adsorption of nickelous ions at this relatively low pH (natural pH of 4.2) on the chalcopyrite surface. The indication of the adsorption of the dissolved species of chalcopyrite and pentlandite was seen from the results of zeta potential measurements of the minerals in the presence and in the absence of supernatant of each other (Acar, 1955).

Based on the results obtained from surface chemical analysis of the natural minerals, a more systematic study employing selected synthetic sulfide minerals was initiated. Chemical equilibria calculations reported earlier for the sulfide mineral systems showed covellite to be more stable, followed by millerite and pyrrhotite, and that surface conversion of the least stable mineral to a more stable mineral can occur under certain conditions (Acar, 1985).

In fact, comparison of supernatant composition of pyrrhotite with that of pyrrhotite in CuCl₂ solution showed that the mineral dissolution was increased significantly by CuCl₂, which itself was completely depleted, suggesting the exchange of iron on the pyrrhotite with copper to form covellite on the surface. Similar results were also obtained for the millerite/CuCl₂ and pyrrhotite/NiCl₂ systems, showing significant surface conversions. The surface conversion and/or adsorption of dissolved species in the selective flocculation of synthetic sulfide mineral systems were investigated, and the results are discussed below.

The XPS spectrum obtained for millerite is shown in Fig. 3a. The binding energy of Ni(2p₃) peak has been reported to be in the range from 853.6 to 855.2 eV for Ni, from 852.9 to 857.4 eV for Ni⁺⁺, and approximately 861.0 eV for Ni⁺⁺⁺⁺ compounds (Clifford, Purdy, and Miller, 1975). In the present investigation, the Ni(2p₃) spectrum exhibited the most intense peak at 857.0 eV and had a broad shoulder or a separate peak at 860.0 eV. However, when millerite sample was conditioned in 10⁻³ kmol/m³ FeCl₂·4H₂O, the X-ray photoelectron spectrum also contained Fe(2p₃) peak at 712.0 eV of binding energy (Fig. 3b).

This suggests that the ferrous ions are adsorbed on the millerite surface as indicated by the conclusion from the electrophoretic results that ferrous ions are adsorbed on the millerite surface electrostatically (Acar, 1985).

The spectrum obtained for millerite conditioned in 10⁻² kmol/m³ CuCl₂·2H₂O is shown in Fig. 4. It was reported earlier that surface conversion of millerite to covellite is thermodynamically possible (Acar, 1985). In fact, Cu(2p₃) peak at 932.6 eV suggests such reactions are taking place on the millerite surface.

As shown in Fig. 5a, the synthetic covellite spectrum displays a most intense copper peak at 934.1 eV for Cu(2p₃). A secondary peak is located at 956.2 eV of binding energy. Conditioning of the covellite particles in 10⁻² kmol/m³ FeCl₂·4H₂O results in another peak at the binding energy of 860.0 eV.
electrokinetic experiments suggest that the nickel species adsorb electrostatically at this acidic pH range (Acar, 1985).

The ESCA spectrum of synthetic pyrrhotite is given in Fig. 7a. The most intense Fe photoelectron line (2p) is located at the binding energy of 710.6 eV, which is in agreement with the published reports (Perkin Elmer). Auger peaks of Fe are also very clearly seen at 553.0 and 607.6 eV of binding energies.

Pyrrhotite is the most unstable of the sulfide minerals chosen for this study (Acar, 1985). Therefore, conditioning of pyrrhotite particles in copper or nickel solutions should be expected to result in significant surface conversions. The results of the ESCA spectrum of FeS in the presence of 10^{-2} kmol/m3 CuCl2 (Fig. 7b) and 10^{-2} kmol/m3 NiCl2 (Fig. 8) support such surface conversions of pyrrhotite to covellite or to millerite, respectively. Spectra show intense copper and nickel peaks at the binding energies of 934 eV and 857 eV along with an Fe peak at about 714 eV, respectively.

Conclusions

ESCA studies have proven to be useful in investigating the surface composition of natural and synthetic sulfide minerals after various treatments. Thus, comparison of spectra obtained for millerite in the absence and in the presence of CuCl2 showed copper to be present on the millerite surface when treated with CuCl2. Similar results were also obtained for pyrrhotite conditioned in CuCl2 or NiCl2 solutions. Since the mineral particles were rinsed several times with triple-distilled water prior to surface analysis, these results show that dissolved mineral species can strongly interact with the min-

![Fig. 5-XPS spectrum of covellite (a, left) and covellite conditioned in 10^{-2} kmol/m3 FeCl2.4H2O (b, left).]

714.6 eV, which is the Fe(2p) peak (Fig. 5b). Presence of this iron peak on the covellite contacted with FeCl2 solution suggests that ferrous ions, i.e. Fe^{2+}, the only major species at the natural pH of 5.1, do adsorb on the negatively charged covellite. This was also seen from the electrokinetic data reported previously (Acar, 1985).

The spectrum of covellite treated with 10^{-2} kmol/m3 NiCl2.6H2O is given in Fig. 6. Although the resolution of Ni(2p) peak is not good, this figure suggests that nickel ions can adsorb on the covellite surface when contacted with NiCl2 solution. This is also attributed to the adsorption of positively charged nickel species on the negatively charged mineral surface. Correlation of this result with that obtained from

![Fig. 6-XPS spectrum of covellite conditioned in 10^{-2} kmol/m3 NiCl2.6H2O.]

![Fig. 7-XPS spectrum of pyrrhotite (a, left) and pyrrhotite conditioned in 10^{-2} kmol/m3 CuCl2.2H2O (b, right).]
eral surfaces and alter their surface properties. It is to be noted that presence of such species can cause non-selectivity in separation processes using flocculation or flotation of mineral mixtures (Acar and Somasundaran, 1985; Acar, 1985).

Acknowledgment

The authors acknowledge the National Science Foundation for financial support of this work.

References


Perkin-Elmer, Physical Electronics Division, Handbook of Chemical Analysis.
