Review

X-ray Photoelectron Spectroscopy in Mineral Processing Studies

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Featured Application: This article reviews the applications of X-ray photoelectron spectroscopy in beneficiation and hydrometallurgy of sulfide minerals and ores of base and precious metals aiming at understanding the surface phenomena and reaction mechanisms required to improve the flotation and leaching performance.

Abstract: Surface phenomena play the crucial role in the behavior of sulfide minerals in mineral processing of base and precious metal ores, including flotation, leaching, and environmental concerns. X-ray photoelectron spectroscopy (XPS) is the main experimental technique for surface characterization at present. However, there exist a number of problems related with complex composition of natural mineral systems, and instability of surface species and mineral/aqueous phase interfaces in the spectrometer vacuum. This overview describes contemporary XPS methods in terms of categorization and quantitative analysis of oxidation products, adsorbates and non-stoichiometric layers of sulfide phases, depth and lateral spatial resolution for minerals and ores under conditions related to mineral processing and hydrometallurgy. Specific practices allowing to preserve volatile species, e.g., elemental sulfur, polysulfide anions and flotation collectors, as well as solid/liquid interfaces are surveyed; in particular, the prospects of ambient pressure XPS and cryo-XPS of fast-frozen wet mineral pastes are discussed. It is also emphasized that further insights into the surface characteristics of individual minerals in technological slurries need new protocols of sample preparation in conjunction with high spatial resolution photoelectron spectroscopy that is still unavailable or unutilized in practice.

Keywords: X-ray photoelectron spectroscopy; sulfide minerals; surface; oxidation; flotation; leaching

1. Introduction

Surface composition and structure are critically important for minerals behavior in a variety of natural processes and for mineral processing, particularly the recovery and separation of base metal sulfides by flotation, as well as their leaching in hydrometallurgy [1–4]. The products of surface oxidation and reactions of sulfides with flotation reagents and precipitates from the mineral slurries, which render hydrophobic/hydrophilic properties and phenomena that determine the ability of mineral particles to break the wetting water film and attach to a millimeter air bubble in the flotation process, are not well understood so far [5–10]. The characters of the reacting and modified surfaces as well as the near-surface regions affect the rates of dissolution and leaching, which are often very slow and considered as “passivation” of still debatable nature (for example, [11–14]).

Application of surface-sensitive techniques to this field, which is necessary in order to gain insights into the surface composition and chemistry, however, faces with a number of difficulties. The X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis ESCA) is a powerful method for surface studies in materials science, catalysis, and other areas [15,16], and is widely utilized for characterization of mineral surfaces and interfaces [10,17–24].

Alternative techniques such as Auger electron spectroscopy (AES) [25,26] and secondary ion mass-spectrometry (SIMS, TOF-SIMS) [27] are less informative regarding chemical bonding and also require an ultra-high vacuum environment (UHV). X-ray absorption spectroscopy (XANES/EXAFS), infrared spectroscopy (ATR-FTIR) and Raman spectroscopy are not generally surface-sensitive and unable to determine the total surface composition [18,19,22–24,28–32]. The photoelectron spectroscopy is based on the analysis of electrons emitted under X-ray irradiation from the core levels and the valence band in atoms of materials located in the near-surface region as a function of the binding energy (BE) [15]. The binding energies of the photoelectrons are derived from the known energy of the incident X-ray photons ($h\nu$) and the measured electron kinetic energy (KE) as $BE = h\nu - KE - \phi$, where ϕ is the work function of the photoelectron analyzer. The intensities and chemical shifts of the photoelectrons provide information about the surface composition and the chemical state of the elements. The probing depth can be estimated by the electron inelastic mean free path (IMFP) in solid that depends on the kinetic energy of the electron (and on the solid constituents) and is usually in the range of 1–5 nm for laboratory instruments with Mg K α (1253.6 eV) or Al K α (1486.6 eV) irradiation of the X-ray tube anodes, but can be substantially varied with the excitation photon energy, particularly, using synchrotron radiation facilities (SR-XPS) [10,15,16,24]. XPS measurements traditionally have required ultra-high vacuum (UHV) because: (i) the detector needs to operate under this pressure regime, (ii) the surface contamination should be minimized, and (iii) potential inelastic collisions of the ejected electrons in their way to the detector should be also minimized since if the photoelectrons lose energy, then information is also lost. This is the main problem of XPS in studies of the solid/gas and solid/liquid interface [33]. Another problem is very complex multi-phase and multi-component composition of aqueous dispersions of minerals with practical solid-to-liquid weight ratios from 1:1 to 1:5 [1–4].

In this review, we consider applications of XPS with regard to the most common metal sulfide minerals (galena PbS, sphalerite ZnS, chalcopyrite CuFeS₂, pyrrhotite Fe_{1-x}S, pyrite FeS₂, and some others), and their ores. The metal sulfides are the main source of base metals in nature, and are also of vivid interest for materials science. In comparison with the previous reviews of mineral surface studies [5–10,17–24], this contribution is focused on methodological aspects, modern trends and developments of XPS along with the limitations concerning elusive (volatile, unstable or buried) entities on sulfide minerals, and the techniques aimed at (quasi) in situ approach. Only some important papers from the XPS application history are overviewed here, and only selected results are discussed in detail as examples. The studies, which utilized XPS for examination of concrete mineral systems, as well as those on the chemical bonding in metal sulfides, mineralogical and geochemical issues, are largely left aside, and we refer the readers to the articles summarizing the findings on specific minerals and the bibliography therein [13,34–39].

2. Speciation of Surface Products

2.1. Oxidized Surfaces of Metal Sulfides

2.1.1. Detection of Elemental Sulfur, Sulfate, and Oxysulfur Species

Some important possibilities and complications of the XPS method have been highlighted in early studies performed at single minerals and synthetic metal sulfides. Manocha and Park [40] have undertaken one of the first XPS (ESCA) research on sulfide minerals to resolve contradictions about the products of PbS oxidation under various conditions found with common surface-insensitive techniques. It has been stated that lead sulfate is the major product of oxidation of PbS in air and aqueous environments, while elemental sulfur formed in the early reaction stages; another product is PbO followed by slow adsorption of hydroxide ions. Brion [41] has compared oxidation of main sulfide minerals in air and water and found sulfate and, in the case of Fe-bearing minerals, Fe(III) (hydr)oxides as the main surface products, with the rate of sulfation decreasing in the order FeS₂ > CuFeS₂ ≥ PbS > ZnS, which looks debatable at present [10,35–39]. Evans and Raftery [42] have studied the initial surface

oxidation of natural PbS crystals using angle-resolved photoelectron spectroscopy and pointed out that elemental sulfur tends to be lost in vacuum but some S remained trapped under an oxidized layer. Luttrell and Yoon [43] have characterized chalcopyrite surfaces with a focus on the formation of elemental sulfur as a hydrophobizing agent under collectorless flotation conditions and suggested that the presence of polysulfide species could explain some contradictions between XPS and other methods.

Buckley and Woods [44–55] have performed a series of studies on the sulfide minerals reacted in air, flotation- and leaching-related aqueous media, and highlighted the existence of metal-deficient surfaces involving S-S bonding and the necessity to cool the samples down to liquid nitrogen (LN) temperatures in order to preserve volatile surface species. In particular, galena crystals oxidized in air or reacted with aqueous solutions and then dried with Ar flushing were cooled to about 180 K during evacuation and measured at LN temperatures [44]. Elemental sulfur formed due to oxidation of galena was demonstrated to remain at the frozen samples and to volatilize after warming up to room temperature in UHV. Furthermore, Laajalehto et al. [56] have shown that the sulfur can be kept on such cooled samples under intense synchrotron radiation.

2.1.2. Metal-Deficient and Polysulfide Surfaces

Buckley and Woods have also found [44–55] that oxidation of metal sulfides in atmosphere and aqueous media generally produces surfaces depleted in metal and so enriched in sulfur. The initial oxidation typically yields metal oxides and hydroxide with no oxidized sulfur species, suggesting the formation of “defective metal-deficient” sulfide surfaces. If the deficit of a metal becomes large, the S 2p lines at higher binding energies arise, suggesting S-S bonding and “polysulfide” surfaces. These effects were found for a majority of sulfide minerals, including pyrite [49,57,58] containing disulfide groups, which is the most resistive to oxidation so quantities of polysulfide are the smallest in comparison with other sulfides. The surface non-stoichiometries induced by the preferential release of metals from the lattice are important phenomena for mineral processing and adjacent areas because they affect hydrophobic/hydrophilic characteristics (polysulfide surface is commonly assumed to be hydrophobic [10,17,18]), reactivity and mechanisms of various reactions of metal sulfide phases, including passivation in the hydrometallurgical leaching. Even small, within the error of XPS analysis, stoichiometry deviations can dramatically change the semiconducting properties of metal chalcogenides, surface charge distribution, etc., as shown, for example, for galena [59–61].

The studies [62–68] performed with the aim to understand the surface S-S species have elucidated that the end atoms in polysulfide anions bear negative charges similar to that in disulfide groups with the S 2p_{3/2} BE about 162.5 eV. A small charge may be localized at S atoms nearest to the terminal ones [66], while intermediate atoms are close to elemental sulfur with almost no charge and BE between 163 and 164 eV. The occurrence of polysulfides on reacted sulfide mineral surfaces was confirmed with Raman spectroscopy (not quite surely, though) [57,69,70] and TOF-SIMS [71] and other techniques. Polysulfides are thought to be stable in the spectrometer vacuum, in contrast to elemental sulfur [44–58,63–68].

At the same time, Klauber et al. [72–74] have reported that the intensity of S 2p bands attributable to polysulfides at chalcopyrite decreased with time as the sample was kept in UHV at room temperature. The “polysulfide” lines have been suggested to belong to elemental sulfur adsorbed at metal-deficient surface and the sulfur gradually evaporated at room temperature, whereas polysulfides do not actually exist [72]. This, however, contradicts numerous findings, including the S-S species detected in much deeper sulfide layers and transformations of S-S bonding observed in (electro)chemical reactions [75–88]. The inconsistency seems to be resolved by using hard XPS depth profiling [89,90] which elucidated that the metal-depleted surfaces are composed of several layers with only the outer one containing polysulfide anions. Nasluzov et al. [68] found with DFT+*U* simulation and cryo-XPS of fast-frozen chalcopyrite (Figure 1) that the polysulfides as intermediates to elemental sulfur are surprisingly stable and hinder the release of elemental sulfur (see Section 3.3 for details).

Figure 1. X-ray photoelectron S 2p spectra of particulate chalcopyrite conditioned in water, 0.1 M HCl, and 0.05 M FeCl₃ + 0.01 M HCl, centrifuged, fast-frozen and measured at -160°C (a, a'), -40°C (a''), and $+25^{\circ}\text{C}$ (b, b'). The spectra a' and b' measured employing an electron flood gun. Reproduced from [67] with permission from ACS.

2.2. Flotation Reagents

Oxidation of sulfide minerals notably affects their hydrophobicity and floatability but flotation reagents play the main role in their recovery and separation [2,5,8–10,18,22,91–94]. Sulfhydryl collectors, particularly alkyl xanthates are the most common reagents [2,5,8,10], so we restrict this overview to xanthates as a representative example. The main efforts of researchers have been concentrated on elucidating the chemical state of adsorbates [10,18,22,23,29–31,95–103]. It has been established [92–103] that alkyl xanthates of alkali metals can be attached to sulfide mineral surfaces as chemisorbed xanthate radicals, metal xanthates, or dialkyl dixanthogens, depending on the nature of the mineral, collector concentration, electrochemical potential and mineral pre-oxidation, and other conditions. Nevertheless, a large amount of uncertainty still remains because the analytical techniques have insufficient surface sensitivity and the lack of in situ measurements, particularly in technological media.

In the case of XPS, it is necessary to discern weak signals of S atoms in xanthate-derived surface species having the S 2p_{3/2} binding energies of 162–162.5 eV for chemisorbed xanthate and metal xanthates and 163.5–164.2 eV for dixanthogens [92,95,98–103] from the spectra of di- and polysulfides in underlying metal sulfide phase; the spectra of O and C are usually less informative due to surface oxygen and carbon contaminations. To overcome this obstacle, higher xanthate concentrations are often utilized, which may lead to unpractical results. The samples evacuated at room temperature, typically rinsed to remove solution components, could lose interfacial volatile and soluble species of interest. When sulfide minerals reacted with xanthate solutions were dried and cooled to LN temperature [98–100], or prepared as fast-frozen wet particulate paste [102,103], XPS recognizes dialkyl dixanthogens, which otherwise evaporate in UHV. The cryo-XPS data (see Figure 2 for an example) show that dixanthogens are the major adsorbate at pyrite, dixanthogen and cuprous xanthate formed in the next stage on chalcopyrite and Cu-activated sphalerite and pyrite, while predominant chemisorbed xanthate is present on galena. In general, one can conclude that the quantities of dixanthogens were underestimated whereas those of metal xanthates overestimated previously. This may be explained in part by the fact that metal xanthates tend to form nanoparticles with lower visible surface [104,105], whereas dixanthogen continuously (but not completely) covers the mineral surface [106].

XPS has been extensively used for characterization of mineral surfaces modified with flotation activators, depressors and other reagents. Noteworthy, organic reagents, which are physically adsorbed on sulfides and volatile in the UHV, are not well suitable for XPS examination. Especially large attention has been paid to the interaction of Cu²⁺ with sulfide minerals, mainly sphalerite and pyrite, and following interaction with flotation collectors, including experimental, theoretical, and review works [103,107–119]. The XPS and SR-XPS studies, including those performed at low temperatures,

have established that copper deposits at sphalerite mainly forms a non-stoichiometric $\text{Cu}^+\text{-Zn}$ sulfide but not a single copper sulfide phase, with polysulfide anions formed due to oxidation of ZnS by cupric ions and dissolution of Zn ; some Cu^{2+} hydroxide colloids can precipitate on the surface under higher pH conditions [116]. Notwithstanding, there are still perceptual gaps in understanding the reaction mechanisms and surface products, and their relation to the flotation practice, which can be explained by a wide variety of factors influencing these processes, e.g., heterogeneity of minerals. Thus, the experimental techniques with a better spatial resolution and spectral sensitivity are required under conditions typical of a plant environment [116].

Figure 2. Cryo-XPS S 2p spectra from fast-frozen sphalerite (1) ground, (2) reacted with 0.1 mM CuSO_4 , the activated mineral treated with (3) 0.1 mM KBX and (4) 10 mM KBX. Right panels show the bands, normalized by the height and shifted to align the peak position, and the differences between the spectra. For clarity, only S $2p_{3/2}$ components are shown in the S 2p spectra fitting. Reproduced from [102] with permission from Elsevier.

2.3. Quantitative Analysis of Mineral Surfaces

XPS is crucial for the quantitative surface composition analysis, despite both inherent limitations, such as accuracy, different surface sensitivity for various spectral lines, effect of surface roughness, and some others [15,16], and additional difficulties arising from real mineral systems [10,17–19,23,24]. Possible loss of surface substances could occur due to washing or other pretreatment before the sample transfer to a spectrometer and in vacuum. In XPS, the concentrations of atomic species can be evaluated and attributed to visible surface area, which depend on morphology of the products, e.g., whether those form uniform coatings on the mineral or entities of notable height. In particular, atomic force spectroscopy showed [18,61,120–123] that the products, mainly elemental sulfur, form protrusions up to hundred nanometers in height so their quantities could be underestimated in XPS, even if sulfur sublimation is suppressed through freezing the sample. Another interesting example is so-called invisible gold in metal sulfides that was detected by XPS when presented as Au nanoparticles. The apparent Au concentration can become lower than the detection limit if Au forms micrometer-scale particles despite of its higher total content [124]. Furthermore, ultrafine particles of gangue minerals and other components of real slurries could cover sulfide minerals and complicate the surface analysis [17].

3. Spatial Resolution of Photoelectron Spectroscopy

The previous studies and findings of photoelectron spectroscopy, along with other techniques and mineral processing practice [10,17,117], have exposed the issues needed to be answered with XPS. For instance, it is known that about 50% monolayer xanthate coverage of a sulfide surface is enough for flotation recovery of the mineral [5,10], so the question arises of how the collectors, oxidation products, and other surface species are spatially distributed and how this influences the hydrophobicity

and flotation. It is also difficult to distinguish mono- and multilayer coatings of flotation reagents [125]. Knowing the distribution of reaction products is necessary in order to understand the origin of retarded reaction kinetics and “passivation” of metal sulfide oxidation and leaching. Therefore, researchers need XPS techniques having a high spatial resolution, both lateral and in-depth, which also cause minimize alterations of the mineral/aqueous interfaces upon measurements.

3.1. Ion Sputtering and Depth Profiling

Information about depth-resolved concentrations of elements and morphology of products, thicknesses of surface layers of adsorbates, etc., can be obtained in XPS by several methods [15,16]. First, atoms from outer layers can be removed by sputtering with heavy ions, usually Ar^+ ions, exposing deeper structures. The Ar^+ bombardment causes substantial disordering of crystal and electronic structures, reduction of some elements, and so on, so the information on the chemical state of atoms will be lost; moreover, elemental composition can change under the ion beam, too. For example, ion bombardment of pyrite results in preferential removal of S atoms, producing disordered layer with high-spin $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations and sulfide anions instead of singlet ferrous iron and disulfide groups [126,127]. Nevertheless, the Ar^+ bombardment is often employed for depth-profiling down to about 100 nm, although for rough and inhomogeneous surfaces of real, oxidized sulfide minerals it provides semi-quantitative concentration distributions at best. It is more convenient in such situations to use the ion bombardment together with Auger electron spectroscopy [25,26] because of the smaller size of an electron beam; see for example, studies of oxidized and leached pyrrhotite [76–79]. In addition to profiling, mild Ar^+ sputtering is used to clean surfaces from casual contaminations.

3.2. Surface-Sensitive Techniques

Non-destructive XPS with varying analysis depth is based on changing the thickness of the layer from which photoelectrons escape without loss of energy [15,16,128]. The thickness can be decreased by several times if the electron take-off angle is reduced from 90° to $15\text{--}20^\circ$ although this provides a limited probing depth range and is not very suitable for rough surfaces and especially for particulate materials. This option realized in many XPS instruments can be easily used to enhance surface sensitivity and to distinguish, for example, more or less uniform surface coating and bulk particles. Another easy way to estimate the depth distribution is by comparing the core level spectra with different binding energies (and the kinetic energy of emitted electrons), for example Cu $2p_{3/2}$ (BE of about 932 eV) and Cu $3p$ (60 eV), Fe $2p_{3/2}$ and $3p$ (709 and 54 eV, respectively), as the electron IMFP at high energies is roughly proportional to the square root of the kinetic energy [15].

Alternatively, the kinetic energies of photoelectrons can be changed by varying the energy of synchrotron excitation photons in the range from about 100 eV to tens of keV [15,128,129]. The soft SR-XPS has been applied in order to increase the surface sensitivity in a number of studies on the structure and initial reaction stages on fractured sulfide surfaces, adsorption of flotation collectors [130–151] and activators [152]. For example, S $2p$ spectra allowed to distinguish outmost S atoms having lower coordination with metals and S-S bonding arising at reconstructed or/and oxidized surfaces [130–137]. The high-flux synchrotron radiation could damage the surface layers due to heating and photodecomposition effects but the distortions can be significantly reduced at the samples cooled to LN temperatures. Thus far, the synchrotron studies [129–152] have been mostly fulfilled at compact mineral specimens with moderately modified surfaces.

3.3. Hard X-ray Photoelectron Spectroscopy

The probing depth can be increased with increasing energies of excitation photons far beyond those applied in the common laboratory spectrometers. The high-energy photoemission spectroscopy, or hard XPS (HAXPES) [128,153], most often utilizes the photon energies tunable from 2 keV to 10 keV at many synchrotron facilities and characterizes the layers extending up to 20–30 nm in depth. Commercial instruments employing hard X-ray sources, particularly with Cr (5.417 keV) and

liquid Ga (9.243 keV) anodes [154,155], are developed now too. The HAXPES is an effective tool for destruction-free examination of multilayered structures, and surfaces and interfaces buried under reaction products, which provides information about both the concentration as a function of the excitation photon energy (depth profiles) and the depth-resolved chemical form of elements [130]. Certain shortcomings of the compositional analysis arise for samples with complex morphology of near-surface regions due to multiple elastic scattering, and because the photoionization cross-sections of core shells essentially depend on the excitation energy [128,153–155]. HAXPES looks as a very promising technique for characterization of real heavily reacted and contaminated surfaces in mineral processing but, to the best of our knowledge, only few HAXPES investigations of sulfide minerals were reported in the literature.

As an example, Mikhlin et al. [88,89] have applied HAXPES in conjunction with Fe K- and S K-XANES, and DFT+*U* simulation to study polycrystalline chalcopyrite, pyrite, and pyrrhotite plates oxidized in air and aqueous Fe^{3+} solutions and developed Fe-depleted surfaces. It has been known that the metal deficiency induced by chemical reactions is not just a surface phenomenon and extends in depth up to hundreds nanometers as established with AES depth profiling [11,76–79], X-ray absorption and emission, and Mössbauer spectroscopy [80,81,87–89,148,149] but the nature of such heavily disordered structures has remained puzzling. HAXPES study discovered that the near-surfaces of mineral samples beneath some surface Fe oxides are stratified (Figure 3) and composed of an outer layer with high S excess and polysulfide species, and then a metal-deficient zone with mono- and disulfide anions, whose composition and thickness varied from a few nm to several tens of nm, depending on the nature of mineral and reaction conditions. The underlayers up to a hundred nm in depth had no variations in the composition discernible in HAXPES but the changes in XANES suggested their high defectivity. The polysulfide centers located in the 1–2 outmost atomic layers were found to be energetically favorable under the oxidation conditions [68], so arresting the yield of elemental sulfur and promoting the formation of thick metal-depleted layers. These findings shed new light on the origin of metal-deficient surfaces and highly debatable mineral “passivation” [11–14,71–74,156–160].

Figure 3. Atomic ratios and the results of fitting of the S 2p and Fe 2p spectra as a function of excitation photon energy for pyrrhotite leached in acidic 0.5 M FeCl_3 solution (top panels), and scheme illustrating layered structures of pyrite and pyrrhotite oxidized in air and the aqueous solution as derived from HAXPES and XANES. Adapted from [88] with permission from Elsevier.

3.4. Lateral Resolution of Photoelectron Spectroscopy

Natural mineral systems are composed of plentiful phases with the particle size less than 100 μm after the comminution [1,2], with the surfaces of single mineral particles being further inhomogeneous in terms of crystal faces exposed, roughness, impurity distributions, and so on. Conventional laboratory and synchrotron photoelectron instruments have resolutions on the order of a hundred μm and several μm , respectively, at best. The high spatial resolution methods available at present are scanning X-ray photoelectron microscopy (SPEM, or XPEM) and photoemission electron microscopy (PEEM) [161–164]. In synchrotron SPEM, the photon beam focused to a spot of about 100 nm scans over the surface. Emitted photoelectrons are collected with an analyzer, providing local photoelectron spectra similar to conventional XPS or/and spectromicroscopy images with submicrometer resolution at selected excitation photon energies [161,162].

PEEM can be realized both as laboratory and synchrotron set-ups, with the latter often coupled with XANES technique [163,164]. PEEM provides surface chemical imaging by parallel acquisition of the photoelectrons emitted from the illuminated area. This allows reaching the lateral resolution as good as 10 nm at short measurement times, but information on chemical bonding is limited and should be extracted from a coupled technique, e.g. XANES. The methods have been applied to image distributions of various phases in natural mineral samples, including surface oxidation products across natural samples [164–167].

Interesting SPEM studies on reacted sulfide minerals have been performed by Gerson and co-workers [168–170]. The experiments were carried out using polished mineral slabs frozen after the treatment and measured using about 100 nm photon beam at LN temperatures at the ESCA Microscopy Beamline (ELETTRA). It has been found, for example, that Fe–O bonds form prior to Fe–OH bonds in initial stages of pyrite oxidation, S oxidation proceeds through interactions of OH radicals formed at the Fe sites, and sulfate forms, via thiosulfate/sulfite intermediates, in the patches, where adsorption of oxygen has been localized and Fe oxidation occurred. Chalcopyrite dissolution in 4 mM Fe^{3+} solution has been observed to be spatially heterogeneous at the submicrometer scale, producing di- and polysulfide anions, elemental sulfur, sulfite, and sulfate (Figure 4). The surface heterogeneity has been concluded to indicate that the minerals are not passivated by these products.

Figure 4. S 2p SPEM speciation maps (a) S^{2-} , (b) S_2^{2-} , (c) S_n^{2-} , (d) S^0 and (e) SO_3^{2-} collected from a region ($100 \times 100 \mu\text{m}$) on the chalcopyrite surface partially dissolved with pyrite for 10 days containing spots 4A–4D (S 2p XPS spectra are shown in top left corner). Reproduced from [170] with permission from Elsevier.

In general, PEEM and SPEM are not broadly used in mineral processing studies until now, in particular, because these methods require rather flat surfaces and well-conducting materials, in addition to access to SR facilities. XPS measurements spatially resolved in lateral dimension remain a challenge.

4. Towards in Situ XPS

4.1. XPS Studies of Solid–Liquid Interfaces

The application of in situ and *operando* XPS [33,171–179] is a vital problem in catalysis, materials science, electrochemical power sources, and other fields, and the minerals processing is not an exception. The behavior of minerals occurs at the interface between the aqueous phase and the (oxidized) minerals, which decays upon routine sample preparation and drying. XPS operation in the systems containing aqueous solutions is complicated by the high pressure of water vapor “forbidden” for the UHV installation and the attenuation of photoelectrons in gas and liquid phases. At present, there are two main approaches to this problem.

4.1.1. Ambient Pressure XPS

(Near) ambient pressure photoelectron spectroscopy ((N)AP-XPS) is a fast-developing technique allowing to characterize a sample at pressure up to about 100 mbar by using differentially pumped spectrometers [33,172–177]. Such equipment first advanced by Salmeron and co-workers [172] can work as backfilling system, in which the whole chamber is filled with gas, or the enhanced pressure is created in a reaction cell connected to the analyzer. Usually, the brilliant synchrotron radiation is utilized because of the photoelectron attenuation, but laboratory instruments equipped often with high-energy X-ray sources (e.g., Cr anode) are available now too [173,179].

Several types of the cells have been proposed for samples containing a liquid [33,173,174]. The liquid microjet set-up, in which the liquid stream is injected with a high speed through the nozzle having a diameter of 20 μm or smaller, is used for XPS studies of aqueous solutions, liquid-vapor and liquid-solid (nanoparticles) interfaces [179]. A “dip and pull” method has been utilized for a solid surface coated with a thin liquid layer up to 10 nm which has been fabricated by partially pulling up from a liquid reservoir placed in the analysis chamber; both the solution species and underlying substrate with adsorbates can be analyzed with XPS (HAXPES) [178]. In a technique based on SR or conventional X-ray tube sources, an environmental cell containing liquid, gas, or multiphase samples is sealed with a thin membrane (graphene, Si, Si_3N_4) as a window transmitting photoelectrons and separating it from the environment [33,172,173,178,179].

To the best of our knowledge, NAP-XPS has not been used in mineral processing research to date; the main tasks here seem to be a creation of experiment methodology and proper cells.

4.1.2. Cryogenic XPS

A number of works considered above have employed low-temperature XPS for retaining surface substances unstable in vacuum at room temperature. In fact, the preparation, sometimes referred as “freeze-drying” [171], combined cooling and drying the sample in the entry lock chamber under controlled conditions in order to remove water but preserve volatile species of interest (sulfur, polysulfide, dixanthogens, and others). This procedure is usually preceded by washing to eliminate undesirable surface products and solution remnants since, otherwise, non-volatile solutes could uncontrollably precipitate at the interface.

Burger and co-workers [180] have proposed XPS as a tool for examination of aqueous solutions and demonstrated that their quick freezing to LN temperatures preserves the solution chemistry and prevents precipitation of solutes. More recently, Shchukarev [171,181–183] has developed the cryogenic XPS analysis of solid/aqueous phase interfaces using fast-frozen wet particulate materials, which allows retaining the volatile species together with a thin frozen film of adjacent aqueous phase.

In a typical “fast-freezing” procedure [183], an aqueous dispersion is centrifuged and the supernatant is discarded; the wet paste is placed on a sample holder cooled to a liquid nitrogen temperature, and kept in the spectrometer lock chamber under a flow of dry N₂ or Ar for 30–60 s prior to pumping to a vacuum of 10^{−6} to 10^{−7} mBar in order to freeze the paste and evaporate (sublimate) excessive water (ice). The sample is transferred to the pre-cooled manipulator in the analysis chamber; its temperature is kept below −150 °C with the vacuum on the order of 10^{−9} mbar during the experiment. After the measurement, the samples are usually warmed up in the vacuum and reexamined at room temperature. The technique allows to study mineral/solution interfaces with the water (ice) layer thickness of about 1 nm and electrolyte concentrations below 0.05–0.1 mol/L [183]. The laboratory-based cryo-XPS has been successfully employed for exploration, among many others, of ion adsorption and electrical double layer structures [182,184], sulfur oxidation products of the reaction of goethite and lepidocrocite with aqueous sulfide [185], surfaces of chalcopyrite upon chemical and bacterial leaching [68,186], xanthate-derived collectors adsorbed on the main sulfide minerals [102,103], and other interfaces (see Figures 1 and 2 as examples). Interestingly, some signatures of surface nanobubbles, whose role in flotation is discussed at present [101,186–190], were observed as highly inhomogeneous electrostatic charging of sulfide mineral particles reacted with butyl xanthates [102,103] probably due to widespread cavities and rare ice islets on the hydrophobic surfaces.

The cryo-XPS of fast-frozen pastes is a promising method for quasi in situ studies in mineral processing, especially as that can be easily implemented in commercial laboratory instruments. Some questions regarding this technique still need to be answered. Particularly, it is not quite clear yet how thick the adjacent ice films are at specific materials [183], or how very fine particles (slimes) occurring in mineral slurries [191] upon freezing and collecting the spectra will manifest themselves.

4.2. Sampling and Exploring Natural Mineral Dispersions

The majority of XPS studies have been conducted with single minerals or their simple mixtures, whereas real ores, industrial products, and their pulps are very complex in terms of chemical and phase composition, with low concentrations of valuable sulfides and abundant gangue minerals, wide particle size distribution, and presence of solutes and colloids. These entities can interact with sulfide mineral surfaces modifying their characteristics and behavior, and could essentially complicate XPS studies by screening the surface of interest and causing inhomogeneous electrostatic charging. Smart [17] has published a sampling procedure aimed at prevention of ex situ oxidation of the mineral surfaces and rejection of pulp solutes and slimes. Slurry specimens were purged with nitrogen, followed by their sealing and freezing to arrest possible reactions until examination. After thawing, the sample was deslimed through several steps of sonication/decantation, and the aqueous solution was removed after filtering. Then the thickened slurry was loaded into the spectrometer and remaining water was evaporated without contact with air during the pumping. This, or a slightly modified protocol, has been utilized in numerous studies on sulfide minerals and ores, and their interaction with flotation reagents. It can be combined with freeze-drying or fast-freezing techniques [171] to retain volatile species.

Meanwhile, ultrasonic treatment and discarding the slimes may result in the loss of important information about real mineral surfaces in their dispersions. In particular, it was demonstrated that smaller sulfide mineral particles are more oxidized and attract more ferric hydroxides after the comminution in steel mills than coarser ones [192]. The grinding of sulfide ores was found to produce ultrafines in quantities comparable with, or exceeding the amounts of flotation reagents [193,194], particularly serpentine gangues [194–196] which bear positive charge and adhere to negatively-charged sulfide minerals, suppressing their flotation. Thus, correct procedures of sampling and handling of mineral dispersions for XPS exploration still need to be elaborated.

The heterogeneous electrostatic charging can emerge as a serious problem when studying multiphase particulate dispersions with abundant dielectric phases. Usually, an electron flood gun is utilized to eliminate the sample charging [197], but this could be insufficient when bright synchrotron radiation is applied in HAXPES or high lateral resolution XPS and SPEM. Strong charging effects were

also observed for lab-based cryo-XPS of moderately hydrophobic particles of single minerals [102,103]. Therefore, more sophisticated methods such as a high-energy electron gun [198], low-energy ion beam or gas ionization in AP-XPS [172–175] would be necessary.

Table 1 briefly summarizes the pros and cons of the photoelectron spectroscopy techniques and examples of their utilization in studies on specific sulfide minerals.

Table 1. Principal possibilities and shortcomings of X-ray photoelectron spectroscopy techniques, and examples of the application to sulfide minerals.

Technique	Possibilities and Findings	Drawbacks	Mineral Samples
Conventional XPS	Analysis of surface reaction products and adsorbates, non-stoichiometry	Loss of volatile species; decay of solid/water interface	numerous minerals, ores
Freeze-drying	Detection of volatile species (S, dioxanthogens, etc.)	Decay of solid/water interface	PbS [44,56] FeS ₂ [99,100]
Fast-freezing	Characterization of volatile species and solid/water interfaces	Uncertainty about the effect of freezing	CuFeS ₂ [68,102,186], FeS ₂ , PbS [102], ZnS [103] PbS [56,138–140,143], FeS ₂ [58,130,132,141,142, 144,152], CuFeS ₂ [135,136,147–150], ZnS [137], FeAsS [131,133], NiAsS [134], Fe _{1-x} S [145], Cu ₅ FeS ₄ [147], (Fe, Ni) ₉ S ₈ [151]
Soft SR-XPS (hν = 100–1000 eV)	Tunable excitation energy and surface sensitivity; high spectral sensitivity and resolution	Need of access to SR facilities, potential sample damage and loss of volatile species, decay of solid/water interface	Fe _{1-x} S, FeS ₂ [89], CuFeS ₂ [90]
HAXPES (hν = 2000–10000 eV)	Non-destructive depth profiling	Mainly buried layers and interfaces, need of SR facility access (mostly)	FeS ₂ [168], CuFeS ₂ [169,170]
SPEM	Lateral resolution down to 100 nm	Strict requirements to samples; access to SR facilities	CuFeS ₂ [165–167], (Ni,Fe) ₉ S ₈ [165], Fe _{1-x} S [165], FeS ₂ [167]
PEEM	Lateral resolution down to 10 nm	Limited chemical information; access to SR facilities (mostly)	
AP-XPS	N situ analysis of solid/gas and solid/liquid interfaces	Lack of appropriate techniques; need of SR facility access (mostly)	–

5. Conclusions and Outlook

XPS became at present a routine technique for characterization of solid surfaces in mineral processing and related areas. XPS and surface-sensitive SR-XPS successfully specified products formed at mineral surfaces upon their interaction with flotation reagents, including flotation collectors. The method discovered the phenomenon of surface non-stoichiometry caused by the preferential release of metal cations from the sulfide lattices, while depth-resolved high-energy XPS (HAXPES) found that the metal-depleted near-surface is composed of several layers with polysulfides occurring only in the outmost one. It should be stressed that many surface species (elemental sulfur, dioxanthogens, polysulfides, etc.) are volatile in the spectrometer vacuum at room temperature so the samples should be cooled before or during their evacuation. The cryogenic XPS of fast-frozen particulate minerals is one of the most promising techniques for (quasi) in situ exploration not only of the unstable surface species, but also adjacent aqueous phase, double electrical layers and adsorbates. This technique is worthy of further development and wider application. The near-ambient pressure XPS, whose application rapidly

progresses in catalysis and other fields, practically is not in use in mineral processing. Photoelectron microscopy (SPEM and PEEM) methods having high lateral resolution could provide interesting results but are not well suited for common measurements yet. HAXPES, a powerful method for the characterization of thick layers and buried interfaces, is underestimated in the mineral processing studies, especially as commercial laboratory instruments equipped with innovative hard energy X-ray sources are becoming available. The problem of surface studies on real ores is far from being solved; development of spatially resolved methods both in the depth and lateral dimensions together with appropriate sample preparation procedures is still pressing.

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