Final Technical Report
OSM Project at PVAMU (Grant #S06AC12337)

Improved Static Test Prediction of Acid Generation Potential: A Surface Analysis Approach

(*X-Ray Photo-electron Spectroscopy (XPS) Shows Potential for Sulfur Speciation in Mining-Related Samples)*

Hylton G. McWhinney[1], Paul T. Behum[3], Jon E. Brandt[2] and Tony Grady[1]
[1]Prairie View A&M University, Prairie View, Texas; [2]Rail-Road Commission of Texas, Austin, Texas; [3]Office of Surface Mining, Mid-Continent, Illinois.

Abstract

These studies target one of the gravest environmental problems of the coal mining industry, acid mine drainage, by the application of non- traditional solid-state characterization method of mine soils and rocks to determine relative amounts of sulfur specie present in minerals. X-Ray photoelectron spectroscopy (XPS) a surface analytical tool is applied to the characterization of minerals common to mining operations. Real samples from mine sites were also analyzed with XPS. Results from these studies indicate that the XPS method holds very strong potential as a complimentary tool to traditional bulk methods for deriving information on the mineral chemistry of mine materials. Results show that this cutting edge technique can identify and distinguish among the presence of sulfur species such as jarosite, galena, barite, and anhydrite. The technique can also differentiate between the reduced and oxidized forms of sulfur in these complex samples. Semi-quantitative XPS results of pyritic and oxidized sulfur contents in samples as low as 0.4 bulk percentage sulfur, compare favorably with results determined by traditional methods from similar samples.

Background

Acid mine drainage or acid rock drainage (AMD/ARD) is one of the costliest environmental problem of the mining industry, resulting from mineralogy and mining activities at mine sites. One of the effects is that surface and subsurface waters can be loaded with metals (arsenic, copper, cadmium, zinc, etc.) [1]. Acid drainage is a consequence of ambient pyrite weathering that is summarized in the following equation.

$$FeS_2 + 15/4O_2 + 7/2H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad [2]$$

Chemolithotrophic bacteria (mainly *Thiobacillus Ferrooxidans* and *Leptospirillium Ferriphilum*) in the environment enhance the acid producing reaction [3 to 5].

Heavy reliance is placed on Acid-Base predictive tests and models for the identification, prevention, and mitigation of AMD/ARD. Acid-Base Accounting (ABA) methods and its implementations have several shortcomings which can lead to over or underestimation of future acid generation [6 to 14]. Some common sources of errors associated with ABA are:

- Over compensation for reactive sulfur content by including sulfate from $CaSO_4$ and $BaSO_4$ and other non-acid forming sulfates in the total sulfur determination;
- In the determination of neutralization potential (NP), strong acids may cause the dissolution of stable minerals giving rise to erroneous results;
- The presence of carbonates of dolomite [$CaMg(CO_3)_2$] and siderite ($FeCO_3$) can contribute to (NP) in the lab setting but none in the field;
- The formation of metal hydroxides in titrations involving NaOH can also lead to problems in calculating NP;
- Jarosite [$KFe_3(SO_4)2(OH)_6$], a common secondary mineral at mine sites, is acid forming, but can be under-quantified in acid potential (AP); and
- Galena (PbS) is not an acid generating mineral, but may be included as such.

Mineral speciation is helpful in understanding the complex chemistry of soils and rocks associated with mining. Great importance is being placed on the application of cutting edge characterization techniques that could assist in reducing errors in ABA. The XPS analytical technique is capable of elemental and chemical speciation at depths of approximately 5-150 Angstroms (0.05 to 1.50 micrometer) from the surface of a sample. The semi-quantitative information is given as the relative % of chemical species. In very fine powders, these semi-quantitative results are observed to be comparable to bulk concentrations [15].

We investigated the application of XPS in the following to:

- Routine elemental and mineral composition characterization of mine site materials.
- Provide chemical information, not gained from traditional methods, but relevant to future regulatory, remedial and mitigation practices at mine sites.
- Identify and estimate reactive sulfide (i.e., pyritic-S) species relative to all other types of sulfur in mine samples.
-
- Distinguish among sulfur mineral compounds (barite, anhydrite, jarosite) that may be present in mine materials.
- Gain some insight to its limitation in mining-related sample characterization.

Experimental

Surface analysis was carried out with a PHI 5400 chemical imaging XPS equipped with a hemispherical analyzer, operating at 10^{-10} Torr (1.33×10^{-8} Pa) base pressures. The spectrometer provides a spectral resolution of ~0.2 eV, employing Mg & Al standard-monochromatic X-rays [14. Spectral reduction was carried out using the PHI Multipak reduction software. The internal standard for measuring chemical binding energy shift was the adventitious C1s core electron (284.6 eV). Species composition was given as XPS Relative % conc. Bulk sample analyses for total sulfur, pyritic-S, sulfates, and organic sulfur were carried out at Energy Labs Inc. in College Station, Texas. A LECO Sulfur Analyzer was employed to calculate bulk % sample concentration based on standard operating procedures, SOP ELI-T-50-114-00 (EPA -670/2-74-070: Mine Spoil Potential [7]). All samples used in bulk and XPS analyses were ground to pass a 60-mesh (0.251 mm) sieve.

Results & Discussions

Figures 1 to 5 show the XPS spectra of the sulfur 2p regions for the studied minerals and field samples. Table I lists the chemical shifts (binding energy of the Sulfur 2p photo electron lines for several mineral samples. Table 2 lists a comparison of bulk sulfur species ratios with semi-quantitative XPS surface species ratios of selected mine samples.

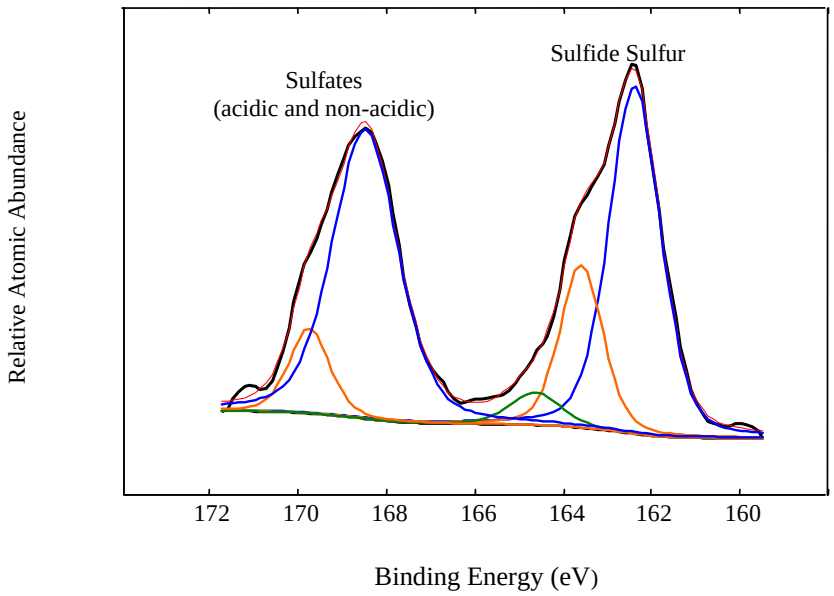

Figure1. XPS spectrum of oxidized surface of pyrite showing the reduced (sulfides) and oxidized (sulfates) species.

Figure 1 is an XPS binding energy S 2p spectrum of air-oxidized, planar-polished euhedral pyrite. It establishes the basis on which we indentified the general sulfur species in terms of sulfates and 'pyritic sulfur'. Sulfates are located at 166 -171 eV (oxidized) and sulfides (i.e., pyritic sulfur) at 160-165.5 eV (reduced). Figure 2 plots the XPS spectra of the S 2p region for several minerals of interest (barite, pyrite, galena, jarosite, anhydrite, and siderite; sample Store-1). Store-1 was a bulk secondary reference sample comprised of weathered acid sulfate mine spoil materials from a lignite mine in central Texas that were crushed to pass a 10-mesh (2-mm) sieve and homogenized. The sulfur oxidation products on planar euhedral pyrite are represented by a peak position of 168.54 eV with jarosite at 168.91 eV, barite at 169.15 and anhydrite at 169.70 eV. We

are able to distinguish between the different minerals in terms of their sulfur chemistry and respective binding energies, despite the small differences in the S 2p energies. Table 1 lists the binding energies of the S2p lines, determined at full width half maxima for each photoelectron peak. Figure 3 plots the S 2p regions of a mixture barite mineral, anhydrite mineral and a field collected jarosite sample. The de-convoluted spectrum shows distinct chemical shifts for the minerals corresponding to their predetermined binding energies in Figure 2. Peak positions in this spectrum also correlate with the minerals jarosite, barite and anhydrite. Figure 4 depicts spectral plots of real field samples ranging from 0.3 to ~ 2.5 bulk % sulfur. A typical de-convoluted spectrum of such samples is shown in Figure 5. A comparison of the bulk pyrite/total sulfur ratio versus the XPS determined pyrite/total sulfur ratio for three analyses is presented in Table 2. There appears to be good correlation between semi-quantitative XPS results and bulk traditional results. Irrespective of the sample type, the XPS spectra did not show improved resolution at the higher bulk concentrations over the lower concentrations. Mine samples with bulk sulfur contents of less than 0.3% did not give rise to spectra of any analytical worth and suggests that this is the lower limit of detection of sulfur in these complex mineral systems.

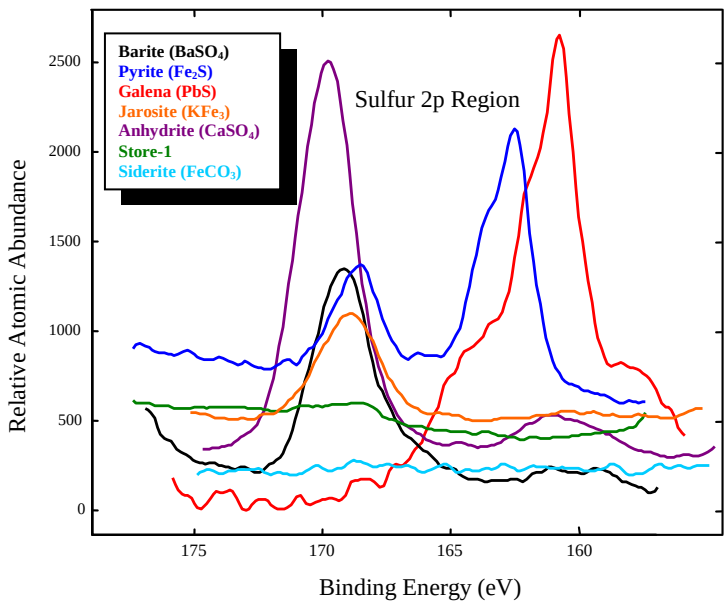

Figure 2. Sulfur 2p spectra of mineral standards and a field sample (Store 1) having a bulk composition of 0.45% total sulfur

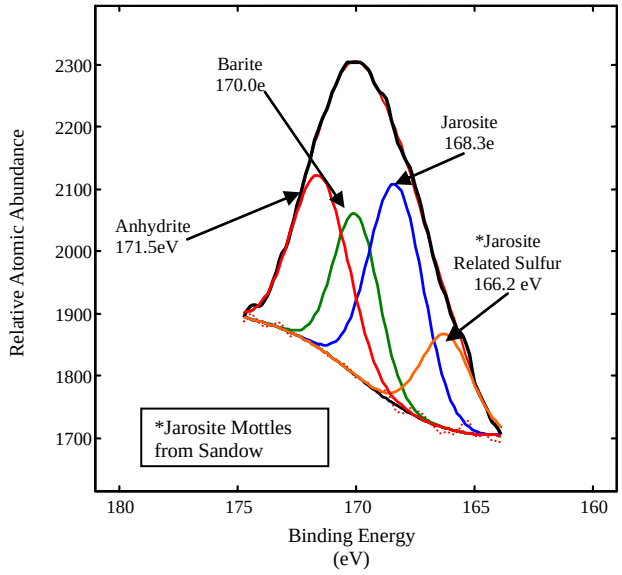

Figure 3. XPS of mixture of barite, anhydrite and jarosite minerals (S 2p chemical shifts)

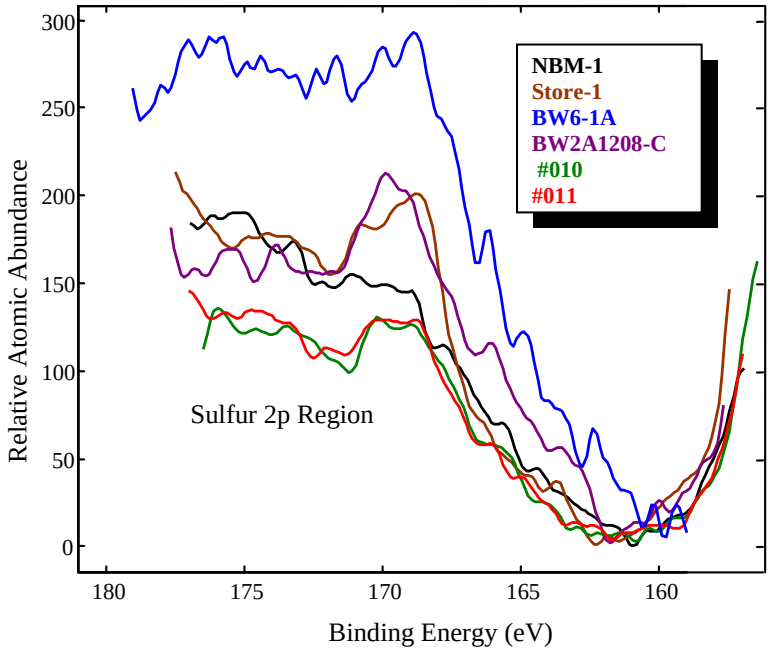

Figure 4. XPS spectral overlays of the S 2p region for field samples ranging between 0.3 and 2.5 bulk %

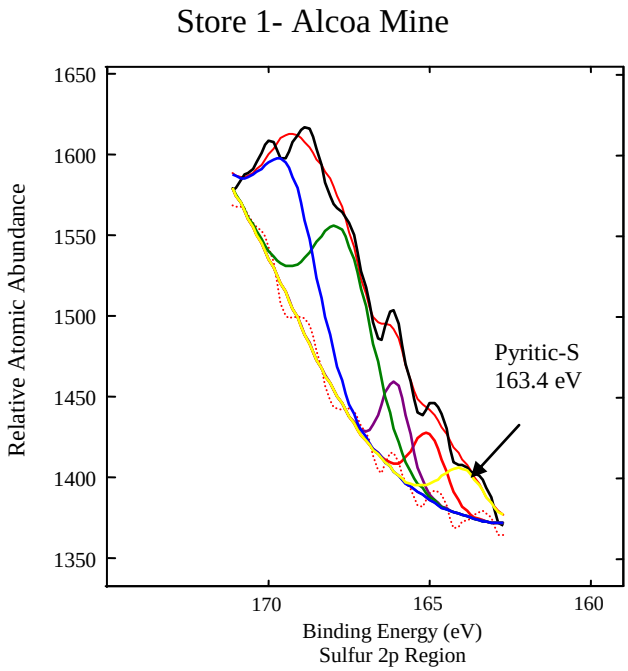

Figure 5. Examples of XPS de-convoluted spectrum of a mine sample (0.49% total S and 0.04% pyritic-S bulk). The bulk percent ratio of pyritic-S/total sulfur is 8.0%. The XPS % pyritic-S/total sulfur is 6.0%. The small difference is typical of all other comparisons.

Table 1. XPS binding energies in the sulfur 2p region for minerals of interest

Minerals	Sulfates (eV) (acidic and non-acidic)	Pyritic Sulfur (eV)
Barite	169.15	----
Pyrite	168.54	162.53
Galena	----	160.66
Jarosite	168.91	----
Anhydrite	169.70	----
Store-1	168.62	----
Siderite	----	----

Table 2. Comparison of bulk sulfur species ratios with XPS surface species of selected mine samples.

Sample ID	**Bulk Sulfur (%)**			**Surface Sulfur (Rel. %)**
	Pyritic	Total S	Pyritic /Total S	Relative %/Total S
BW6(1A)#2	0.03	0.34	9.0%	8.0%
BW2A1208C	0.11	0.45	24.0%	20.0%
Store-1	0.02-0.06 (~0.04)	0.49	8.0%	6.0%

Conclusions

Surface oxidation of planar euhedral pyrite occurs within minutes of exposure to air, giving rise to sulfur oxidation products in the range of 166-171 eV and the reduced forms between 160-166 eV. Galena (PbS) is easily distinguished from pyrite (FeS_2) by a large chemical shift in the vicinity 0f 164-159 eV. In addition, there are, as expected no oxidation products associated with galena. XPS shows strong potential for the routine analysis of mine related soils and rocks. Identification of jarosite, barite and anhydrite sulfate minerals in mine soil samples through spectral de-convolution of the S 2p photo-electron region is easily achieved by XPS. The semi-quantitative XPS estimation of the pyritic-S/total S relative concentrations, compared to bulk composition of field samples, suggests that this method holds strong potential for characterizing the various types of sulfur fractions in mining-related samples. Limitations in the application of XPS appear exist below bulk sulfur concentrations of 0.3%. While these findings are only preliminary in nature, it is worthwhile to further investigate the application of XPS to coal mining operations and the important field of environmental science and technology.

References

[1] Natarajan, K.A., Subramanian, S., and Braun, Jean-Jacques. Environmental Impact of Metal Mining, Journal of Geochemical Exploration. 88 (2005) 45-48.

[2] Carrucio, F.T. 1967. An evaluation of factors affecting acid mine drainage production in various strata of the Allegheny group and the groundwater interactions in selected areas of western Pennsylvania. Ph.D. Diss. Penn. State Univ. (Diss. Abstr. 29-245-B).

[3] Ehrlich, Henry L., 1996. How Microbes Influence Mineral Growth and Dissolution. Chemical Geology 132 pg. 5-9

[4] Blake, II, R.C., Ohmura, N., Inkumsah, M. and McWhinney, H,G. (2008) "Acidithiobacillus ferrooxidans and Leptospirrilium ferriphilum adhere to different sites on the surface of pyrite", in (Young, C.A., Taylor, P.R., Anderson, C.G., and Choi, Y., eds.) Hydrometallurgy2008, Society of Mining, Metallurgy, and Exploration, Inc., Denver, CO, pp 464-473

[5] Fortin, D., Beveridge, T.J., The role of the bacterium Thiobacillus in formation of silicates in acid mine tailings. Chemical Geology, 141 (1997) 235-250.

[6] Jennings, S.R. and Dollhopf, D.J. Acid base account effectiveness for determination of mine waste potential acidity, Journal of Hazardous Materials 41 (1994) 161-175

[7] A. A. Sobek, W. A. Schuller, J. R. Freeman and R. M. Smith, Field and Laboratory methods applicable to overburdens and mine soils. Cincinnati, OH, US Environmental Protection Agency Environmental Protection Technology, EPA-600/2-78-054, 1978

[8] Coastech Research Inc., Investigation of prediction techniques for acid mine drainage, mend project 1.16.1a. Canada Center for Mineral and Energy Technology, Energy, Mines, and Resources Canada (1989)

[9] Duncan, D. and Bruysnesteyn, A. Determination of acid production potential of waste materials. Metallurgy Society, AIME, paper A (1979) 79-29

[10] Ferguson, K.D. and Morin, K.A. Prediction of acid rock drainage-lessons from database: Second International Conference on the Abatement of Acid Drainage, Conference Proceedings, 1- 4(1991).

[11] Lapakko, K. Predictive testing for waste drainage quality in mine operation and closure, Sponsored by EPA and others April 27 – 29, 1993. Helena. MT (1993a).

[12] Lapakko, K. Mine waste drainage quality prediction. A Literature Review Minnesota Department of Natural Resources, Division of Minerals, St. Paul, MN (1993b).

[13] Lawrence, R., Jaffe, S., and Broughton, L., In-house development of net acid production test method, Coastech Research (1998).

[14] Lawrence, R., Prediction of behavior of mining and processing waste in the environment. In Proc. Western Regional Symposium on Mining and Mineral Processing Wastes. Edited by Fiona Doyle, Published by the Society for Mining, Metallurgy and Exploration, Inc., Littleton, CO (1990)

[15] C. Wagner, W. Rigs, L. Davis and J. Moulder, in Handbook of x-ray photoelectron spectroscopy, edited by G. E. Muilenberg, Perkin Elmer Corporation, Eden Prairie, Minnesota, 1979).