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Canada Centre for Mineral and Energy Technology

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Centre canadien de la technologie des minéraux et de l'énergie
an XpS EXAMINATION OF CHEMICALLY REACTED SULPHIDE ORE: SUBMITTED BY THE RBS SECTION OF CANMET

Dr. J.R. Brown and L. Galbraith

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## INTRODUCTION

* Two samples of sulphide rich ore were submitted by RBS for ESCA (electron spectroscopy for chemical analysis). The samples were labelled "untreated" and "treated" and were in the form of 100 mesh powders.


## EXPERIMENTAL

An X-ray photoelectron spectrometer (XPS) model PHI 548 was used for the analysis. This analytical technique is surface sensitive (upper $25_{\mathrm{A}}^{\circ}$ ) and can be employed semi-quantitatively. The detection limit is $\simeq 10^{-9} \mathrm{~g} / \mathrm{cm}^{2}$ of surface ( $\simeq 0.1$ wt $\%$ bulk).

Each powdered sample was placed on a Al foil substrate ( $15 \mathrm{~mm} \times 10 \mathrm{~mm}$ ) using a piece of "double sided" sticky tape ( $10 \mathrm{~mm} \times 10 \mathrm{~mm}$ ). Enough powder was used to entirely cover the tape area to a depth greater than 1 mm . The Al foil strip was then attached to the instrument's sample holder using set screws so positioned to be well beyond the area of detection.

The sample holder was then mounted on the XPS insert probe and evacuated to $\simeq 10^{-5}$ torr in the preparation chamber for 15 minutes. XPS analysis were done at an UHV (ultra high vacuum) of $\simeq 10^{-8}$ torr in the main chamber using an X-ray gun system (Al anode) operating at 400 watts ( $10 \mathrm{KeV} \times 40 \mathrm{ma}$ ). Photons of energy 1486.6 eV characteristic of $\mathrm{AlK}_{\alpha}$ radiation were generated striking a sample area of $\simeq 1 \mathrm{~cm}^{2}$. The quantity of electrons and their kinetic energies photoejected from the sample were then monitered using a CMA (cylindrical mirror analyzer) and accessory electronics. A spectrum of peak intensity (\# of electrons) versus binding energy was then plotted. From such spectra it is possible to equate the surface content of a particular element and its chemical environment (oxidation state etc.).

After XPS analysis of these "as received" ores a fresh portion of the two samples were finely ground using an agate mortor for $\simeq 10 \mathrm{~min}$. This grinding was done so as to expose fresh surfaces for analysis. Identical handling procedures, sample mounting and instrument settings were employed as in the original analysis.

The ore samples were analyzed using two ESCA techniques:
a) Compound composition analysis by "surveying" (Figs. 1, 13,15,30)
b) Quantitative elemental analysis by "multiplexing"

Ultimate parameters for element identification by the survey technique were determined to be a Pass Energy (PE) of 100 electron volts (EV) and a range ( RG ) of 1000 eV . The actual analytical period was 15 minutes.

Ultimate resolution characteristics for the multiplex technique were determined by the settings: $P E=50 \mathrm{eV}$, and $R G=40,20$ or 10 eV depending on the proximity of one elemental peak to another, and on the complexity of the elemental peak patterns. The actual analytical period (for each specified element) was therefore $17.21,8.65$, or 4.36 minutes respectively. The carbon is signal was analyzed for 3.50 minutes and used as a charging reference. Sample charging was calculated using the standard carbon reference binding energy (C 1s) of 284.6 eV . Gold foil was used to calibrate the energy scale of the spectrometer (Au $4 f 7 / 2=83.8 \mathrm{eV}$ ). Sample charging was found to be identical having a value of 5.0 eV .

## DISCUSSION

The XPS analysis indicate this sample is a Zn , $\mathrm{Cu}, \mathrm{Fe}$ - sulphide assemblage with a matrix of complex Al-silicates and quartz. There is also appreciable fluorite $\left(\mathrm{CaF}_{2}\right)$ in the ore (Table 1,3).

The "untreated" sample results clearly indicate the powdered ore sulphides have been converted to sulphate species by the process of crushing and grinding (Table 1). Our grinding this material prior to XPS analysis did not expose fresh sulphide indicating the $>100$ mesh ore had been completely converted by the MSL prior to our acquisition. Interestingly, the treated (acid leached) sample showed a very high sulphide content, i.e. $\simeq 75 \%$ of the sulphur present (Table 1, Fig. 26). Grinding this leached material did not alter this ratio appreciably indicating the sulphide sulphur species is not a thin film coating the original sulphate particles

- (Fig. 17). Results here indicate the increased sulphide content of the ore
is caused by the precipitation of $\mathrm{Cu}_{2} \mathrm{~S}$ and/or copper metal during the leach. This treated sample also contains $\simeq 1.6 \mathrm{wt} \% \mathrm{Cl}$, probably as sorbed HCl or Cl not totally rinsed from the ore after leaching (Fig. 15, 27). Metal chloride species are unlikely as the binding energy ( $E_{b}$ ) of the Cl 2 p electrons ( 197.6 eV ) found is not correct for Cl bonded to metals. In addition the small concentration of Cl found by XPS is negative evidence.

The $E_{b}$ of $C u 2 p$ and its shape (lack of satellite structure) indicates the existance of Cu metal and/or $\mathrm{Cu}^{+}$(Fig. 19). The Cu 2 p Auger signal ( $\mathrm{V}_{3} \mathrm{LL}$ ) also indicates $\mathrm{Cu}^{+}$(Fig. 20). Leaching the ore removed the Zn and Pb content (below our detection of $\approx 0.1 \mathrm{wt} \%$ ), lowered the Fe , $\mathrm{Ca}, \mathrm{S}, \mathrm{O}$ and increased the $\mathrm{Si}, \mathrm{Al}, \mathrm{Cu}, \mathrm{F}$ and Sn . The increases of $\mathrm{Si}, \mathrm{Al}$ and $F$ can be related to a greater percentage of resistant minerals (fluorite, silica, Al-silicates) in the leached residue; these being only slowly attacked by HCl. Sulphide minerals however, are readily dissolved in acid. The large Cu increase is quite surprising noting the other metal sulphides ( $\mathrm{Zn}, \mathrm{Pb}$ ) are eliminated entirely. Investigation of this Cu anomaly indicates $\mathrm{Cu}_{2} \mathrm{~S}$ and/or Cu metal has precipitated. Solubilities of metal sulphide, oxides and chlorides of interest are shown in Table 2. Solubilities explain why the Cu increases while Zn etc. decline. During a static leach experiment, the solution quickly reaches equilibrium with the ore surfaces. The metal chloride species in solution react with the increasingly greater concentration of sulphur species ( $\mathrm{HS}^{-}, \mathrm{S}^{2-}$ ) present. The first sulphide to precipitate would be $\mathrm{Cu}_{2} \mathrm{~S}$. Note $\mathrm{ZnCl}_{2}^{0}$ etc. are very soluble and in concentrated HCl solutions the equilibrium condition will be strongly in their favour.

Tin is masked in the untreated ore ESCA analysis due to a strong Zn Auger signal occurring at the same $\mathrm{E}_{\mathrm{b}}$ (Fig. 1). One can't say if Sn is present at measureable levels. However, in the treated ore where Zn has been eliminated, the Sn 3 d signal is easily observed (Fig. 15). The $\mathrm{E}_{\mathrm{b}}$ position of Sn and its concentration ( $\simeq 1.5 \mathrm{wt} \%$ ) make it difficult to derive much pertinent information unambiguously. The $E_{b}$ portion for Sn 3 d , (Fig. 24) was found to be $487.2 \pm 0.4 \mathrm{eV}$ indicating $\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O} . \mathrm{SnO}_{2}$ and $\mathrm{SnS}_{2}$ are located at lower binding energies ( 486.5 eV ).

The Cl 2 p position of $197.6 \pm 0.4 \mathrm{eV}$ indicate an HCl type chlorine content (Fig. 27). However, the content is very low and it's possible the observed Sn is bound to Cl as $\mathrm{SnCl}_{2} \cdot 2 \mathrm{H}_{2} \mathrm{O}$.

The Si 2p position is 103.2 eV indicative of quartz; a shoulder on this peak at lower energy $(\simeq 102 \mathrm{eV})$ indicates the presence of Al-silicate type compounds (Fig. 28). The Al $2 p E_{b}$ position ( 74.5 eV ) also indicates Al-silicate type species present (Fig. 29).

Table 1 - Powdered ore (surface) analysis


## Sulphides

$$
\begin{equation*}
\mathrm{FeS}>\mathrm{ZnS}>\mathrm{PbS}>\mathrm{CuS}>\mathrm{Cu}_{2} \mathrm{~S} \tag{19}
\end{equation*}
$$

$-\log \mathrm{Ksp}$
(23)
(28)
(37) (49)*

## Oxides

$-\log \mathrm{Ksp}$
$\mathrm{PbO}>\mathrm{ZnO}>\mathrm{Fe}_{2} \mathrm{O}_{3} ? \mathrm{SnO}_{2}>\mathrm{CuO}>\mathrm{Cu}_{2} \mathrm{O}$
(4)
(15)*

Chlorides

$$
\begin{aligned}
& \mathrm{ZnCl}_{2} \gg \mathrm{FeCl}_{2} \cdot 2 \mathrm{H}_{2} 0>\mathrm{CuCl}_{2} \cdot 2 \mathrm{H}_{2} 0 \gg \mathrm{SnCl}_{2}>\mathrm{SnCl}_{4}> \\
& \mathrm{g} / 1 \text { (4000) (160) (110) (84) (?) } \\
& \begin{array}{ccccc}
\mathrm{FeCl}_{3}>\mathrm{CuCl}_{2}>\mathrm{FeCl}_{2} \gg \mathrm{PbCl}_{2} \gg \mathrm{CuCl} \\
\mathrm{~g} / \mathrm{C}(75) & (70) & (65) & (1.0) & (0.60)
\end{array}
\end{aligned}
$$

*Note $\quad \mathrm{CuCl}>\mathrm{Cu}_{2} \mathrm{O} \gg \mathrm{Cu}_{2} \mathrm{~S}$
$\mathrm{Cu}_{2} \mathrm{~S}$ should precipitate in a chloride rich solution as the $\mathrm{HS}^{-}, \mathrm{H}_{2} \mathrm{~S}$ and $\mathrm{S}^{2-}$ content increases during leaching.

Untreated ore

| Element | Peak energy eV | Assignments |
| :---: | :---: | :---: |
| C 1s | 284.6 |  |
| 0 1s | 533. | indicative of $\mathrm{SiO}_{2}$ and Al-silicates |
| Zn 2p 3/2 | 1024. |  |
| Cu 2p 3/2 | 933. | $\mathrm{Cu}^{+}$cuprite/chalcopyrite |
|  | 935.2 | $\mathrm{Cu}^{2+}$ sulphate |
| Sn 3d | 487.0 |  |
| Fe 2p 3/2 | 712.2 | oxide/sulphate |
| $\mathrm{Pb} 4 \mathrm{f} 7 / 2$ | 139.6 | sulphate |
| Si 2p 3/2 | 102.6 | Al-silicate/some $\mathrm{SiO}_{2}$ |
| Ca 2p 3/2 | 349. | fluorite |
|  |  | $\mathrm{CaF}_{2}$ |
| F 1s | 686.8 | flyorite |
| Al $2 \mathrm{p} 3 / 2$ | 74.6 | $\mathrm{Al}_{2} \mathrm{O}_{3}$ type |
| S 2 p 3/2 | 169.4 | $\left(S^{6+}\right)$ |
|  | 162. | $\left(\mathrm{S}^{2-}\right)$ |

Treated ore

C 1s 284.6
0 1s 533.6
Zn 2p -
$\mathrm{Cu} 2 \mathrm{p} \quad 933.2$
$\mathrm{Cu}\left(\mathrm{L}_{3} \mathrm{VV}\right)$
569.6

Sn 3d
487
Fe 2 p
Pb $4 f$
Si 2p 3/2
103.2

Ca 2p 3/2
348.6

F 1s
688.2

Al $2 \mathrm{p} 3 / 2$
S2p 3/2
$\mathrm{Cl}^{2}$
74.5
169.6
162.4
197.6
no satellite $\left[\mathrm{Cu}^{+}, \mathrm{Cu}^{\circ}\right]$
$-1487=917.4 \quad\left[\mathrm{Cu}_{2} \mathrm{~S}, \mathrm{Cu}^{\circ}\right]$
quartz some Al-silicate 102.?
A B
$\mathrm{CaF}_{2}+(\mathrm{SiF})_{n}$
$S^{6+} 25 \%$
$\mathrm{S}^{2-} 75 \%$
small; guanidine HCl 197.6



$\Phi$ esca multiplex
$E L=Z N 1$
$03 / 12: 81$
$P E=50$
$\mathrm{SF}=.140$
AL. $10.0 \mathrm{KV}, 40.0 \mathrm{MA}$

$$
O A T=8.65
$$

FSLE: ECSE20
Uurfegrito mes fitsn
18, 992

$$
3618 \mathrm{cps}
$$

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4
4 Esch

$$
P E=50
$$

$$
\begin{aligned}
& E=H: 1 \\
& S F=.010 \\
& D A T=8.65
\end{aligned}
$$

AL. $\cdot 10.0 \mathrm{KV}, 40.0 \mathrm{MA}$
fね£: ECS620
UATHEATED GRE FAESH
FICURE 非12







$E L=C U_{1}$
$03 / 13 / 81$
$\mathrm{PE}=50$ $\mathrm{SF}=.157$

$$
O R T=8.64
$$

AL, $10.0 \mathrm{KV}, 40.0 \mathrm{MA}$ ORT $=8.64$
TREATEO ORE FAESH












