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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

ESCA ANALYSIS OF URANIUM MILL FEED (HEAD) AND HIGHLY LEACHED URANIUM TAILINGS RESIDUE: FOR M. SILVER, CANMET/MSL, OTTAWA

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ESCA Surface Analysis

Electron spectroscopy for chemical analysis (ESCA) is highly surface sensitive, direct and non-destructive. ESCA can probe qualitatively to semi-quantitatively the outermost 1-5 nm region of a sample's surface. All elements except hydrogen can be detected with an ultimate sensitivity approaching 10^{-9} gm cm^{-2} of surface. Usually it is possible to confirm chemical environment (oxidation state, co-ordination number) of an element from ESCA chemical shift information.

Extensive reviews of ESCA theory, instrumentation and application have been reported in the literature (1-3).

A model 548 Physical Electronics X-ray photoelectron spectrometer with an accessory specimen introduction system (PHI 2100) and multiple-technique analytical computer system (MACS) were used for this study.

Each specimen was placed on an Al foil substrate (15 mm x 10 mm) using double-sided 3M brand® sticky tape. Enough powder was used to entirely cover the tape to a depth where it was obscured (several mm's). The Al foil strip was then attached to the sample holder. This holder was then mounted on the specimen insert probe and evacuated to $\simeq 10^{-6}$ torr in the preparation/pumpdown chamber. ESCA analyses were done at $\simeq 10^{-8}$ torr in the analytical chamber using an Al X-ray gun operating at 400 watts (10 KeV x 40 ma). The resulting X-rays (AlK_{α}) of energy 1487 eV were directed onto an $\simeq$ 10 mm^2 area of the sample. The quantity of electrons photoejected from this area and their kinetic energies were monitored using a cylindrical mirror analyzer (CMA) and associated electronics. This entire analytical operation is computer controlled. A spectrum of peak intensity (no. of electrons) vs. binding energy is then plotted. It is thus possible to equate the surface content of a particular element and its chemical environment from this spectrum. Samples are normally analyzed using two ESCA scanning modes: (a) initial "surveying" for determining all elements present and (b) "multiplexing" specific regions of the survey at greater resolution for quantitative and chemical bonding information.

Optimum parameters for element identification by the "survey technique" are at a binding energy (E_b) range of 1000 eV and a pass energy (P_e) of either 200 or 100 eV. The time of analysis can be varied but is usually 15 or 30 minutes.

For the "multiplex technique" ultimate resolution is achieved at lower pass energies, typically 25 or 50 eV and E_b ranges of either 10, 20 or 40 eV depending on the complexity of the individual peak envelope and on the proximity of one peak to another. Analytical times for multiplex spectra vary, usually less than 15 minutes is required for an acceptable S/N ratio, typically 5 minutes. The carbon (C 1s) signal is used as a binding energy calibrant for sample charging; an electron flood gun (specimen neutralizer) can also be used to greatly reduce charging of insulators and hence eliminate identification problems due to differential charging "ghost" peaks.

All peak positions are referenced to the accepted hydrocarbon binding energy for C 1s of 284.6 eV.

Gold foil is used to calibrate the energy scale of the spectrometer ($Au4f_{7/2}$ = 83.8 eV). We have found the electron flood gun can actually overcompensate for sample charging, lowering the observed C 1s signal to ≈ 284.0 eV in some samples.

REFERENCES

1. Bancroft, G.M., Brown, J.R. and Fyfe, W.S. "Advances in, and Applications of, X-ray Photoelectron Spectroscopy (ESCA) in Mineralogy and Geochemistry"; Chemical Geology, 25, 227-243; 1979.

2. Hercules, D.M. "Electron Spectroscopy"; Anal. Chem., 42, 20A-40A; 1976.

3. Jenkin, J.G., Leckey, R.C.G. and Liesegang, J. "The Development of X-ray Photoelectron Spectroscopy: 1900-1960"; J. Electron Spectrosc., 12, 1-35; 1977.

ERL/CATALYSIS - ESCA SURFACE ANALYSIS

SAMPLE AL SLUDGE - HEAD DATE 5/28/81

PROJECT MSL - M. SILVER

COMPOSITION

(A)

	XPS		Bulk (Wt. %) (±5%)	Remarks
	At. % (±10%)	Wt. %		Surface
Si	1.6	2.4	—	SiO, Al_2O_3 type } silicate type.
Al	2.8	4.1	—	
Fe	2.8	8.5	11.37	Fe^{3+} (Fe_2O_3) or FeOOH
Ca	5.3	11.6	17.7	CaO and $CaSO_4$ (or CaF_2)
Mg	3.9	5.2	—	MgO ~~trace~~
Ti	—	—	—	
Na	—	—	—	
K	—	—	—	
S	3.3	5.8	13.4	S^{6+} as (SO_4^{2-})
C	44.2	28.9	—	no CO_3^{2-}
O	34.9	30.4	—	
1. Th	0.2	2.0	2.03	ThO_2
2. F	1.0	1.0	—	silicate or CaF_2 - MgF_2
3. U	—	—	0.009	
4.				
5.				
TOTAL	100	100		

COMMENTS

(1) Neutralized on illuminate

(2) oxygen to satisfy cations (oxides) + SO_4

Σ(Si, Al, Fe, Ca, Mg, Th, S) = 34.5 At %

observed oxygen = 34.9 At %

(3) 2 Ca species 40% CaO, 60% $CaSO_4$ observed From spectrum (C

confirm. Ca = 5.3 At %; S = 3.3 At % as $CaSO_4$ leaves 2.0 % Ca as CaO $\frac{2.0}{5.3} : \frac{3.3}{5.3} \simeq 40 : 6$

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ERL/CATALYSIS - ESCA SURFACE ANALYSIS

SAMPLE AL SLUDGE - FINAL DATE 5/28/81

PROJECT MSL - M. SILVER

COMPOSITION

(B)

	XPS		Bulk (Wt. %) (±5%)	Remarks
	At. % (±10%)	Wt. %		Surface
Si	2.2	3.6	—	silicate type
Al	3.9	6.1	—	
Fe	4.4	14.2	23.11	Fe^{3+} Fe_2O_3 or FeOOH
Ca	—	—	5.8	no Ca observed (trace?)
Mg	4.9	6.8	—	MgO (silicate)
Ti	—	—	—	
Na	—	—	—	
K	—	—	—	
S	0.1	0.2	0.66	very low level (S^{6+})
C	51.6	35.8	—	(no CO_3^{2-})
O	30.7	28.4	—	
1. Th	0.3	4.0	—	
2. U	—	—	0.024	
3. F	1.0	1.0	—	
4.				
5.				
TOTAL	100	100		

COMMENTS

(1) Neutralize or eliminate

(2) Oxygen observed 30.7 At %

Oxygen required to satisfy XPS 23 At. %

our expt. value low because XPS saw no Ca and very little S species on the surface

Note Iron content by XPS may be underestimated (due to ① high level presa ② broad linewidth ③ baseline shift

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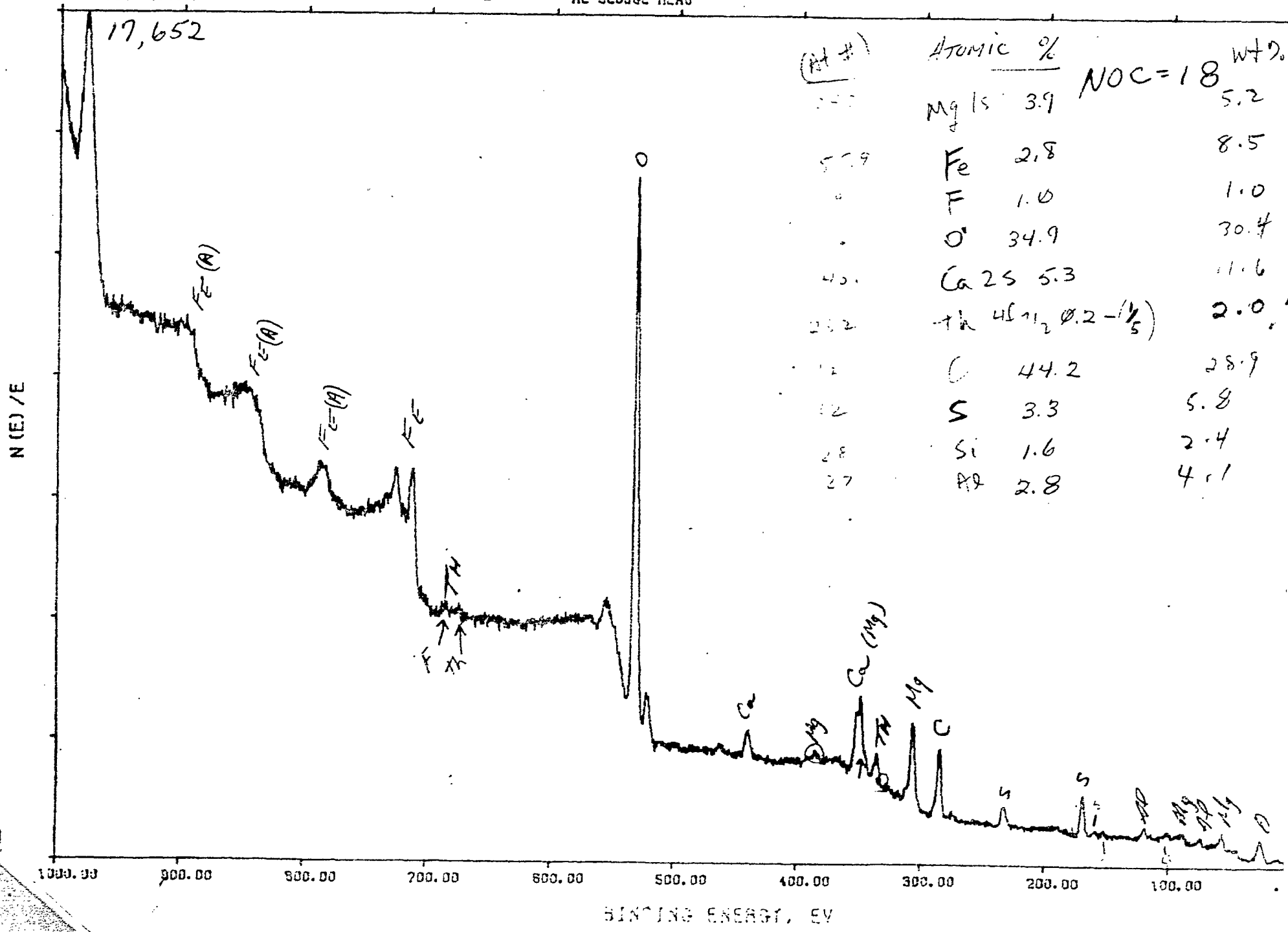
PE= 100
AL, 10.0KV, 40.0MA
FILE: ECS887

(A)

SF= 2.781
DAT= 30.30
AL SLUDGE HERO



(Ref #)		Atomic %	
	Mg ls	3.9	5.2
	Fe	2.8	8.5
	F	1.0	1.0
	O	34.9	30.4
	Ca 2s	5.3	11.6
	Th $4f_{7/2}$ Ø.2 – 1/5		2.0
	C	44.2	28.9
	S	3.3	5.8
	Si	1.6	2.4
	Al	2.8	4.1

NOC = 18 Wt%

ESCA SURVEY
PE= 100
AL, 10.0KV, 40.0MA
FILE: ECS690

SF= 3.190
DAT= 30.30
AL SLUDGE FINAL

05/29/81