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ASIAN JOURNAL OF SCIENCE AND TECHNOLOGY

ISSN: 0976-3376

Asian Journal of Science and Technology
Vol.07, Issue, 03, pp.2509-2515, March, 2016

RESEARCH ARTICLE

COMPARATIVE STUDIES OF BULK AND SURFACE COMPOSITION OF OXIDIZED ZINC ORE SAMPLES FROM AN IRANIAN LEAD AND ZINC MINE

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ARTICLE INFO

Article History:
Received 16th December, 2015
Received in revised form
12th January, 2016
Accepted 22nd February, 2016
Published online 31st March, 2016

Key words:

Oxidized zinc ore,
EDX; XPS,
Surface composition,
BulkComposition.

ABSTRACT

Studies of surface and bulk chemical properties of minerals can aid in understanding the mechanism of collector attachment and also the behavior of the oxide minerals during flotation process. In this paper, the surface and bulk properties of oxidized zinc ore samples were examined by means of X-Ray Photoelectron Spectroscopy (XPS) or Electron Spectroscopy for Chemical Analysis (ESCA) andenergy-dispersive X-Ray analysis (EDX).Three size fractions,-250+200µm;-200+150µm and-150µm, were examined XPS results show that there are no significant differences between zinc percentage nor the for other elements of the three size fractions. According to these results, it can be concluded that the measurement of surface composition by means of XPS are approximately the same for all three-size fractions. A comparison between the data obtained from XPS (surface composition) and from EDX Analysis (bulk composition) showed that there are some differences for some elements. For example, Si, Fe, and Al content in the oxidized zinc ore samples. These differences between XPS and EDX technique could be based on the amount of measured oxygen for each technique.

INTRODUCTION

The flotation behavior of oxide and silicate minerals is highly pH dependent and their flotation behavior can be very similar because of their surface chemical similarities (Rao *et al.,* 2004; Bulatovic, 2007; Wills, 2010). Surface chemistry is also the principal determinant for selective separation of the various mineral phases. In order to optimize the froth flotation, a detailed evaluation of the surface chemistry of both value and non-value minerals by phase and stream in a process is essential (Gerson *et al.,* 2013). There are numerous spectrometric and spectroscopic techniques that can be employed to study both mineral bulk and surface chemistry. Several studies have been carried out for flotation of oxidized zinc ores (Hosseini *et al.,* 2006 a,b; Hosseini *et al.,* 2007; Ejtemai *et al.,* 2008; Mehdilo *et al.,* 2008, Hosseini*et al.,* 2009; Mehdilo *et al,* 2010; Irannajad *et al.,* 2011; Mehdilo *et al.,* 2011; Hosseini *et al.,* 2011; Hosseini *et al.,* 2015).

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The Angooran lead and zinc mine located in Zanjan province, Iran is one of the largest mines of its kind in the Middle East. This mine is located 100 km. south west of Zanjan by road with an altitude of roughly 2950 m above sea level on a latitude of approx. 47º 20´and a longitude of 36º 40´. The major zinc mineral is smithsonite with hemimorphite and hydrozincite as minor minerals while the major lead mineral is cerrusite with mimetite as a minor mineral. Generally, the associated minerals are mainly calcite and quartz, which are accompanied with minor amount of mica, hematite, goethite, kaolinite, and montmorillonite. The daily feed to the Dandy beneficiation plant, which is located 20 km from the Angooran mine, is approximately 1000 tons. Figure 1 shows the location of Dandy mill plant in Zanjan, Iran. In general, the tailings of cerrusite flotation is the zinc concentrate containing 20-25% Zn, which is leached by sulfuric acid to extract the zinc. Dandy plant has been designed to handle low and high-grade zinc ores. The high-grade ore contains 10% lead and 35% zinc while the low-grade ore averages 7% lead and 22% zinc. The normal products of the plant include lead concentrate grading 60% lead, zinc concentrate with 38% zinc and a calcined zinc concentrate with 52% zinc. This plant includes the following sections: rock crushing, heavy media separation (HMS), milling, flotation, filtration and calcination. If the feed is of the low-grade type, it is first upgraded by HMS cyclones and the

concentrate obtained is introduced along with the high grade feed into the milling circuit and subsequently concentrated in the flotation unit.

2. X-Ray fluorescence (XRF), X-Ray diffraction (XRD), wet chemical assay and also optical microscopy were used for preliminary characterization of oxidized zinc ore.

Figure 1. Dandy beneficiation plant location in Iran

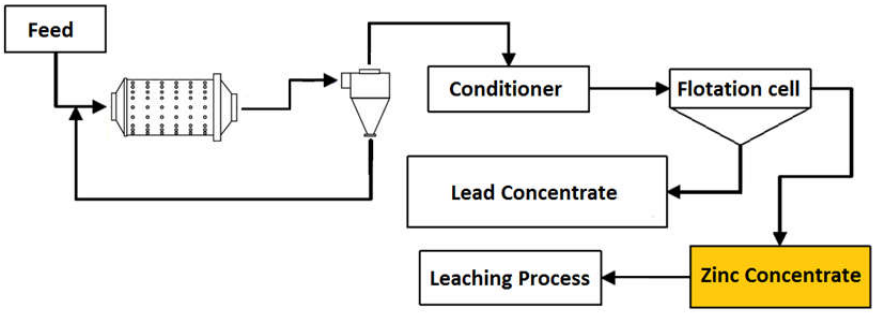

Figure 2. Schematic flow diagram of Dandy Mineral Processing Plant for very low grade

Table 1. Results of XRF Test

Elements or Oxides	Weight %	Elements or Oxides	Weight %	ElementsorOxides	Weight
SiO_2	61.9	F	0.21	MnO	0.022
Al_2O_3	15.2	As_2O_3	0.18	V_2O_5	0.022
ZnO	8.9	CdO	0.14	ZrO_2	0.016
K_2O	2.15	S	0.102	Cl	0.013
Fe_2O_3	1.95	NiO	0.058	Sb_2O_3	0.007
PbO	0.85	P_2O_5	0.046	La_2O_3	0.006
TiO_2	0.65	Cr_2O_3	0.044	Rb_2O	0.0052
MgO	0.60	Co_3O_4	0.026	SrO	0.0041
CaO	0.30	WO_3	0.025	L.O.I	6.57

Material <2mm in size, which is not introduced into the HMS circuit, is milled and added to the low grade flotation route. Finally, after the rougher, cleaner and scavenger stages of the lead flotation route, a concentrate with 60% lead is obtained and the corresponding tailingsare dewatered and sent to the zinc concentrate stockpile. A part of the zinc concentrate is sent to the calcination unit to obtain a calcined product containing 52% zinc. The schematic flowsheet of present concentration process in Dandy mill plant is shown in Figure

In the present work, XPS and EDX have been utilized in order to study the characterization of the surface and bulk composition respectively. The results of this research work will help improve understanding of the surface chemistry on the flotation process for size fractions of 150-200 µm (D. J. Vaughan *et al.,* 1995). The objective of this paper is to determine the bulk and surface composition of oxidized zinc ore samples from Angooran lead and zinc mine and comparethe obtained results to each other.

Experimental

MATERIALS

The representative samples collected from Angooran lead and zinc mine, have been examined to determine the bulk chemical composition of particles including some minerals such as smithsonite (ZnCO3), quartz (SiO2), goethite (FeOOH), rutile (TiO2) and other minerals. Table 1 and Table 2 show the result of chemical composition of oxidized zinc ore. By combining the results obtained from chemical analysis (Tables 1,2), XRD and optical microscopy, the ore samples contain the approximate mineralogical compositions: smithsonite (16%), mimetite (0.6%), quartz (52%), sericite (16.5%), kaolinite (12%), Iron oxides minerals (1.5%), rutile (0.4%) and other minerals (1%). Figure 3 and Table 3 illustrate the results of XRD measurements on oxidized zinc ore and library data for a Siemens XRD instrument. As it can be seen, the strongest line in the X-ray powder pattern reference is 2.75(1), and the others are 3.558(0.5), 1.703(0.45), 2.328(0.25), 2.109(0.25) and 1.948(0.25).

Table 2. Results of wet chemical tests

Oxides	Weight %
SiO2	62.5
Al2O3	16.5
K2O	2.25
TiO2	0.45
PbO	1.36
Fe2O3	1.85
ZnO	9.60

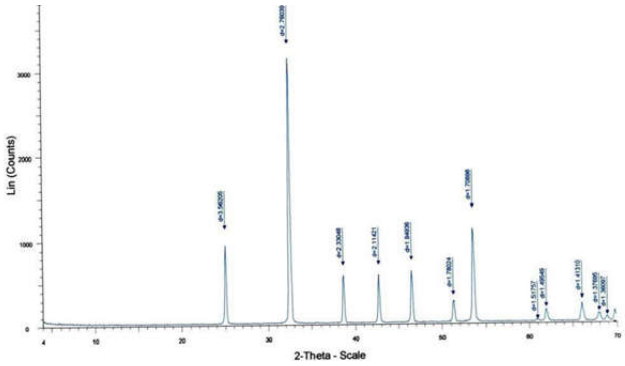

Figure 3. XRD pattern of oxidized zinc mineral sample

Table 3. XRD data of oxidized zinc ore samples vs. Siemens library data

Interplanar spacings(d) Experiment data	Interplanar spacings(d) Siemens library data
1.3609	1.3568
1.3769	1.3734
1.4131	1.4096
1.4954	1.4941
1.5175	1.5143
1.7089	1.7027(0.45) D3(I/I0)(hkl)
1.7802	1.7754
1.9493	1.9481
2.1142	2.1092
2.3304	2.3280
2.7603	2.7502(1) D1(I/I0)(hkl)
3.5621	3.558(0.5) D2(I/I0)(hkl)

The representative sample, which was collected from Angooran lead andzinc mine, has been used to determine the chemical surface and bulk composition of the particles including some minerals in three size fractions of - 250 +200 µm; -200 +150 µm and -150µm. Sieve analysis of the samples using standard screens (150, 200 and 250 µm) for three types of samples were prepared: sample No: H1250 (-250 +200 µm), sample No: H2200 (-200 +150 µm) and sample No: H3150 (-150µm). There are a number of methods thatcan be used to mount the powders for XPS analysis. Perhaps the most widely used method is too carefully and lightly dust the powder on a polymer film based adhesive tape with a camel hairbrush. The powders must be dusted on lightly, with no wiping stokes across the powder surface. It has been used successfully in the 10^{-9} Torr range (Moulder, 1995). The non-conducting samples in EDX analyzer are coated with a thin layer of carbon. Metallographic embedding, polishing, and sectioning are available for samples requiring special preparation. Samples are usually mounted and coated and introduced into the vacuum chamber (Goodhew, 1983).

METHODS

Surface Composition Study

One of the techniques utilized for determining the surface composition of materials, is XPS. XPS, also known as ESCA determines the chemical composition of a surface using the photoelectric effect. In general, when a surface is bombarded with atomic and subatomic particles, ions, electrons and atoms are emitted. Bombardment with X-Ray photons leads to the emission of electrons, these are called photoelectrons. These particles typically are emitted from an l0 nm surface layer. The chemical state of a surface can also be monitored by analyzing the photoelectrons emitted from a surface on bombardment with X-Rays.

The sample is irradiated with X-ray photons and electrons are emitted from the sample if the photon is of sufficient energy. Photoelectrons are counted at each kinetic energy value and a spectrum of intensity vs. binding energy is generated from the above equation. The binding energy of an electron is characteristic of the element, orbital and chemical environment therefore XPS can determine the bonding state and/or oxidation states of materials and surface concentrations. To produce the low energy X-ray, a 10 KeV electron gun was aimed at an aluminum target. MgKα X-Rays (1253.6 eV) or AlKα X-Rays (1486.6 eV) are ordinarily used. Besides the normal peaks for elements in plotting the spectrum, we can see auger peak shifts. The reason for that is the Auger electron is generated by the internal atom de-excitation (the atom recovers from a higher energy state caused by the loss of the photoelectron) The Auger electronkinetic energy is always independent from the source nature. At first glance it is not easy todistinguish on a spectrum Auger electron peaks from photoelectron peaks (J. F. Moulder, 1995).

Bulk Composition Study

EDX was used for bulk composition studies. In fact, it is a common accessory, which gives the scanning electron microscope (SEM) a very valuable capability for bulk chemical analysis. (Hren *et al.,* 1979). The energy holding electrons in atoms (the binding energy) ranges from a few eV up to many kilovolts. Many of these atomic electrons are dislodged as the incident electrons pass through the specimen, thus ionizing atoms of the specimen. Ejection of an atomic

electron by an electron in the beam ionizes the atom, which is then quickly neutralized by other electrons. In the neutralization process an X-Ray with an energy characteristic of the parent atom is emitted. By collecting and analyzing the energy of these X-Rays, the constituent elements of the specimen can be determined. (Norden *et al.,* 1997)

RESULTS AND DISCUSSION

Tables 4-6 show the results of XPS measurements for surface composition of zinc ore sample with three different size fractions. Figures 4-6 show the peak result of XPS measurements for zinc ore samples.

Table 4. Resultsof XP Sonzinc ore sample (-150µm)

Element	Area (cts- eV/s)	Sensitivity Factor	Atomic Concentration (%)	Weight (%)
Fe2p3	6595	1.791	0.45	1
O1s Al2p	352649	0.711	60.89	48
Si2p Cls	12476	0.193	7.94	10
K2p Ca2p	35533	0.283	15.41	21
Zn2p3	24347	0.296	10.10	6
F1s	13270	1.300	1.25	2
Mg1s	5741	1.634	0.43	1
	85586	3.354	3.13	10
	1914	1.000	0.23	0.5
	1786	1.433	0.15	0.5

Table 5. Resultsof XP Sonzinc ore sample (-200 +150 µm)

Element	Area (cts- eV/s)	Sensitivity Factor	Atomic Concentration (%)	Weight (%)
Fe2p3	4783	1.791	0.45	3
O1s Al2p	263502	0.711	62.26	47
Si2p Cls K2p	8744	0.193	7.61	10
Ca2p Zn2p3	27782	0.283	16.49	22
F1s	13485	0.296	7.65	4
Mg1s	9557	1.300	1.24	2
	4277	1.634	0.44	1
	68699	3.354	3.44	11
	1573	1.000	0.26	0.5
	1311	1.433	0.15	0.5

Table 6. Resultsof XP Sonzinc ore sample (-250 +200 µm)

Element	Area (cts- eV/s)	Sensitivity Factor	Atomic Concentration (%)	Weight (%)
Fe2p3	5288	1.791	0.48	1
O1s Al2p	272991	0.711	62.33	48
Si2p Cls	9468	0.193	7.96	10
K2p Ca2p	29168	0.283	16.73	23
Zn2p3	13531	0.296	7.42	4
F1s	9642	1.300	1.20	2
Mg1s	4212	1.634	0.42	1
	64855	3.354	3.14	10
	1284	1.000	0.21	0.5
	964	1.433	0.11	0.5

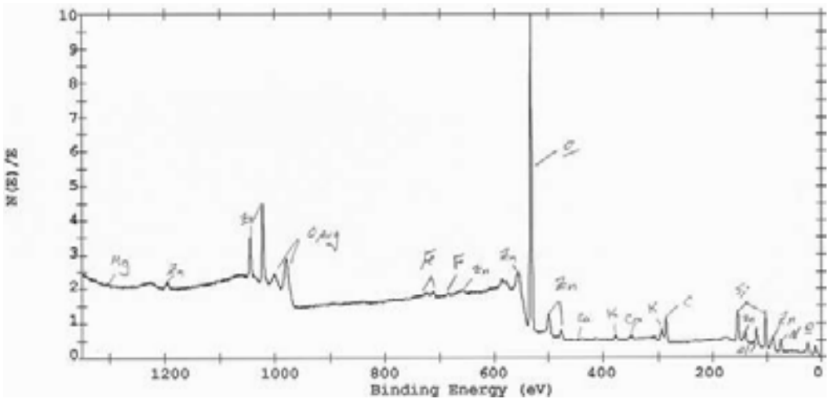

Figure 4. XPS peak results of zinc ore sample (-150µm)

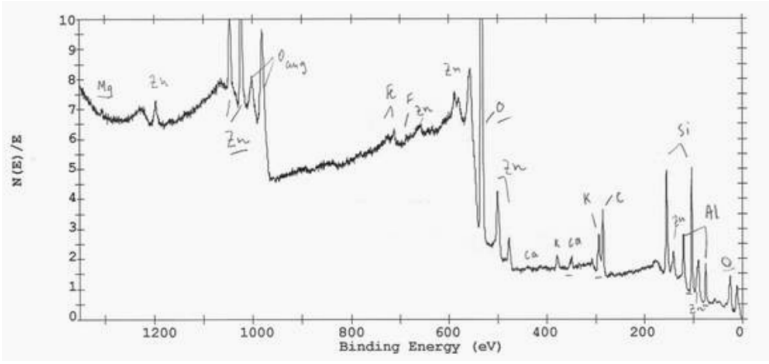

Figure 5. XPS peak results of zinc ore sample (-200 +150 µm)

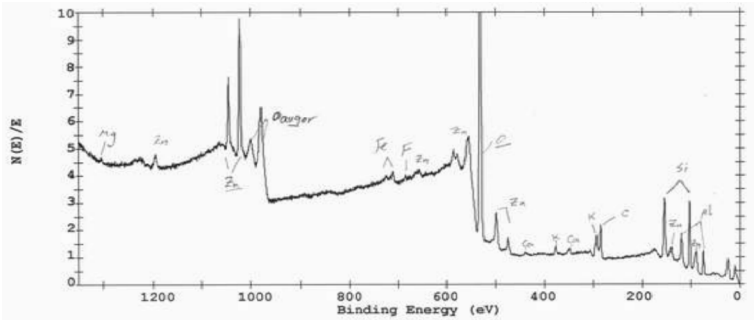

Figure 6. XPSpeak results of zinc ore sample (-250 +200 µm)

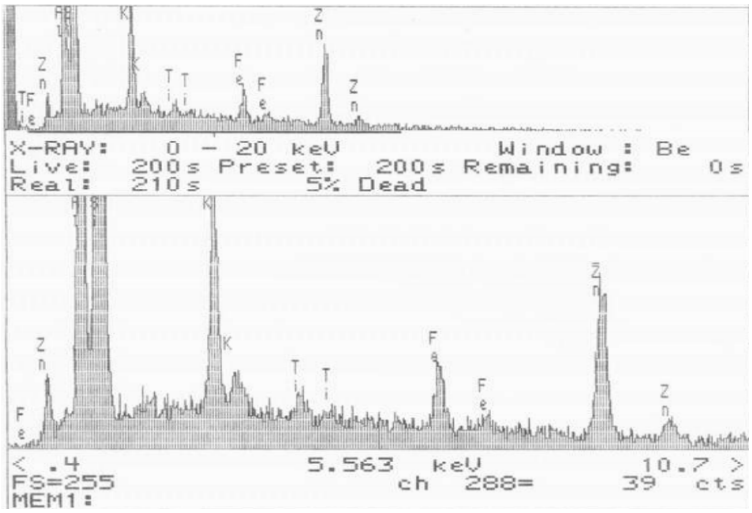

Figure 7. EDX Peak results of zinc ore sample (-150µm)

Spectrum File-LF011204
Live Time (Spec.)= 200
TILT =0.00
ELEV=30.00
AZIM =0.00
ENERGY RES AREA
7.1 76.08 120609
Total AREA= 33838
Peak at 0.98 KeV Peak at 3.30 KeV Peak at 3.62 KeV FIT INDEX = 4.99
ZAF-PB CALCULATIONS
3 ITERATIONS G-FACTOR =7.993
20.00 KV TILT= 0.00 ELEV=30.00 AZIM=0.00 COSINE=1.00

SPECTRUM:

All Elements analyzed

ELEMENT	AREA	AREA/BGND	%CONC	FST	NORM. %
Al K	3788+- 105	3.032+- .412	23.72	0.671	29.41
Ti K	223+- 55	.129+- .032	0.62	1.293	0.76
Si K	10586+-156	7.274+- .692	41.47	.863	51.42
Fe K	638+-71	.531+- .061	2.36	1.542	2.92
Zn K	1635+-102	2.256+- .169	12.50	1.719	15.49

Table 7. The results for Bulk Chemical Analysis using EDX for zinc ore sample (-150µm)

Table 8. Comparison the results for Bulk & Surface Chemical Analysis of zinc ore samples

Analysis Technique	Zinc ore sample (-150μm)					Zinc ore sample (-200 +150 μm)					Zinc ore sample (-250 +200 μm)				
	Weight %					Weight %					Weight %				
	Sii	Al	Zn	Fe	Ti	Si	Al	Zn	Fe	Ti	Si	Al	Zn	Fe	Ti
EDX	51.4	29.4	15.5	2.9	0.76	51.5	29.6	15.2	3.1	0.78	52.1	28.8	16.1	3.2	0.88
XPS (ESCA)	21	10	10	1	---	22	9.73	11	3	---	23	10	10	1	---

Figure 7 and Table 7 also illustrate the result of EDX for finest zinc ore sample (-150μm). According to the obtained results, it was observed that these results have no difference in element percentage for three different size fractions. It can be said that they areapproximately the same for all three size fractions. The desired size for flotation process thathas the maximum degree of liberation is the size fraction (-200 +150 μm). In comparison of the data obtained from XPS (surface composition), EDX Analysis (bulk composition), there are differences between obtained data (Table 8).

For example, the reason fordifferences of Zn% for XPS in comparison with EDX, may be for the oxygen content. It means that the Zn% in EDX is based on oxygen content, but in XPS the oxygen % is determined individually. The results of XPS show that these have no difference especially in Zn percentage and also for other elements for three size fractions. It can be concluded that the surface composition are approximately the same for both three-size fractions.

Conclusions

The following conclusions were obtained from the present research:

- The bulk composition studies were carried out using EDX. The results of EDX technique showed no significant differences. The comparison of the elemental weight % obtaining by EDX revealed reasonable agreement between bulk compositions for three size fractions of fine, middle and coarse oxidized zinc or samples.
- The surface composition analyses were carried out by means of XPS technique. The obtained results of XPS for all elements were similar and it was not observed significant variations between the obtained results.
- A comparison of the data obtained from XPS (surface composition) and from EDX analysis (bulk composition) shows that there are some differences for the Si, Fe, and Al content in the zinc ore samples. These differences between XPS and EDX technique could be based on the amount of measured oxygen for each technique.

Acknowledgements

The author wishes to thank Calcimine Co. for providing the samples used in this work. The assistance of colleagues at Islamic Azad University, South Tehran branch, Mining Engineering Department is also much appreciated. I also would like to thank Mr. Patrick Kerr (MINEPROMET) for helping me linguistically to improve the English version of this paper.

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