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CHARACTERIZATION OF A MINERAL OF THE DISTRICT OF ZIMAPAN, MINA CONCORDIA, HIDALGO, FOR THE VIABILITY OF THE RECOVERY OF TUNGSTEN

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Abstract

A sulfide-type mineral of the district of Zimapan, Hidalgo, Mexico, was chemically and mineralogically analyzed with the aim of detecting minor species with added value for their subsequent beneficiation. Apart from the usual species of the site, the X-ray diffraction analysis (XRD) detected the presence of tungsten sulfate (WS_2) and the mineral species typical of a base-metal sulfide site, as well as impurities such as: orthoclase, quartz, magnesium-silicon oxide, magnesioferrite, monticellite, andradite, magnetite and calcite, the latter being the mineral matrix. The Scanning Electron Microscopy (SEM) mapping confirmed the presence of the typical elements of the mineral: W, Si, O, Mg, Ca, C, Al, K, Fe, S, Zn and Cu. The Inductively Coupled Plasma Spectroscopy (ICP) analysis indicates an average concentration of 380 g W ton^{-1}, as well as 1.81% Zn, 3.41% S, 0.15% Cu, 2.36% Fe, 0.78% Pb, 0.04% Mn, Sb 0.05% and 0.01% Ag. This mineral is a potential source for the extraction of tungsten .

Introduction

The main economic ores of tungsten are wolframite [(Fe, Mn) WO_4] and scheelite ($CaWO_4$), and approximately two thirds of the world's reserves consist of scheelite deposits [1]. Tungsten is one of the most important refractory metals used in several industrial applications due to its robust performance and resistance to heat in the form of tungsten carbide. Most of the tungsten ores contain less than 1% WO_3 [2]. The main sources of tungsten are the high grade concentrates of wolframite and scheelite ores, with concentrations of 60-70% WO_3 [3]. These ores are crushed, ground and subject to separation processes, such as flotation, magnetic separation, gravity, and electrostatic separation.

One of the conventional methods to process scheelite concentrates is the route based on hydrochloric acid used in some companies in the last century [4]. In this leaching process, the formed solid layer of tungstic acid makes it very difficult for the HCl to penetrate into the ore's core, which leads to a very low leaching yield [5, 6, 7]. In order to improve the leaching process and obtain a high tungsten yield, the HCl concentrations were increased and high temperatures were used. However, HCl is extremely corrosive and highly volatile, thus causing difficulties in the operation; as a consequence this process is rarely adopted today by the tungsten metallurgical companies [8]. Nowadays, the scheelite digestion with sodium hydroxide through an autoclaving process is mainly applied in western countries [1,9]. A good yield can be achieved through this method by using a large amount of Na_2CO_3, high temperatures and high pressures, reaching tungsten recoveries of 98% in 1,5 to 4,0 h, at typical digestion conditions of 190-225 C, a corresponding pressure of 12- 26 bar, and a Na_2CO_3 concentration of 10.18% [10]. A thermo-grinding process especially designed for the digestion of a scheelite concentrate through sodium hydroxide has had a successful commercial application [11,12]. The thermo-grinding process makes a good use of mechanical activation to kinetically improve the leaching process. Since operating at low liquid/ solid proportion conditions is necessary for the grinding process, an involuntarily higher concentration of sodium hydroxide is obtained inside the thermo-grinding reactor with a dose of sodium hydroxide, which makes the operation difficult [13]. In normal operating circumstances, medium grade tungsten concentrates have seen their commercial value reduced, making them difficult to place in the market [5].

The value of tungsten exports in Mexico has drastically dropped since 2006, with a 78% loss by 2011 [14]. A production of 287 tons of tungsten was reported in 1995, while there was no production of this metal in 2013 [15]. Although the minerals coming from mining districts in the state of Hidalgo have high tungsten concentrations, the lack of knowledge of new technologies for the extraction of this metal at industrial levels limits their use.

This piece of work presents the chemical and mineralogical characterization of a mineral coming from the mine *Mina Concordia* in the mining district of Zimapan, Hidalgo, Mexico, with the purpose of knowing the aspects of its composition that could affect its subsequent processing for the extraction of tungsten.

Experimentation

We collected a mineral sample from the mining district of Zimapan, Hidalgo. It was totally dried, homogenized and repeatedly chopped up to obtain a representative 500 g sample. The mineral dusts were mounted in epoxy to know their morphology and to identify the mineral species present in the ore by using Scanning electron microscopy-Energy-dispersive X-ray spectroscopy (SEM-EDS). The dust in the sample was also mineralogically analyzed through the X-ray diffraction technique (XRD). The chemical analysis was performed in triplicate using 1 g of mineral digested with aqua regia (3 parts HCl for 1 part HNO_3) and heated until dry. A smaller volume of aqua regia was then added, the insoluble was filtered and the remaining solution was gauged at 0.1 L.

Experimental methods

The identification and quantification of the elements present in the mineral sample was conducted by Inductively Coupled Plasma Spectroscopy (ICP) using a Perkin Elmer 8300 spectrometer. The equipment used for the mineralogical study was the following: INEL EQUINOX 2000 X-ray diffractometer, with a Cu-Ka1 radiation of 1.540598 Å, operation at 30 mA and 20 KV, 220V and a resolution of 0.095 FWHM. JEOL JSM 6701F scanning electron microscope, with a voltage of 25 KV and a depth of field of 16.5 mm at different magnifications with secondary electrons.

Results and discussion

Table 1 shows the chemical analysis, performed by Inductively Coupled Plasma Spectroscopy (ICP), of copper (Cu), zinc (Zn), sulfur (S), iron (Fe), molybdenum (Mo), antimony (Sb), tungsten (W), silver (Ag), lead (Pb), and manganese (Mn) for different mesh sizes.

Table 1. Chemical analysis of the mineral by mesh size

Element Percentage (%)	Mesh Size								Average Percentage (%)
	100 149 μm	150 90 μm	200 74 μm	270 53 μm	325 44 μm	400 37 μm	500 25 μm	-500 -25 μm	
Cu	0.110	0.137	0.139	0.148	0.164	0.152	0.166	0.180	0.15
Zn	1.811	1.896	1.958	2.005	1.926	1.747	1.703	1.444	1.81
S	4.099	3.856	3.392	3.260	3.806	3.230	3.176	2.438	3.41
Fe	3.005	2.763	2.530	2.446	2.312	2.015	2.076	1.722	2.36
Mo	0.008	0.008	0.005	0.005	0.008	0.006	0.005	0.007	0.01
Sb	0.092	0.093	0.088	0.099	0.999	0.098	0.114	0.127	0.05
W (g ton^{-1})	355.50	384.22	402.88	374.00	325.70	352.02	381.04	356.06	0.038
Ag (g ton^{-1})	133.76	136.32	137.50	158.03	117.51	142.58	163.68	155.36	0.01
Pb	0.674	0.718	0.749	0.852	0.784	0.746	0.875	0.838	0.78
Mn	0.030	0.032	0.034	0.035	0.038	0.042	0.046	0.067	0.04

In average, S is the most abundant element, with 3.41%, followed by Fe and Zn, with 2.36% and 1.81% respectively. Pb, Cu, Sb, Mn and Mo are among the minor elements. The concentration of both the major and minor elements is shown in a homogeneous fashion regarding the mesh sizes, as observed in figure 1.

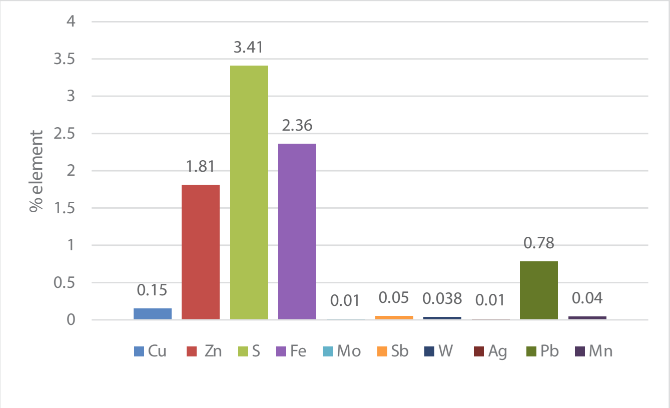

Figure 1. Average elemental composition of the mineral sample.

The highest concentration of tungsten appears in the mesh size measuring 74 µm, with 402.88 g ton^{-1} of mineral (see Figure 2a). On the other hand, the highest concentration of silver was found in the 25 µm mesh size, with 163.68 g/ton of mineral (see Figure 2b), so it could be considered as a metal of interest for its extraction. Both elements are evenly present in the sample in the range between 325.7 and 402.88 g/ton for tungsten, and between 117.51 and 163.68 g/ton for silver. The lowest concentrations of both metals were reported in the mesh size measuring 44 µm.

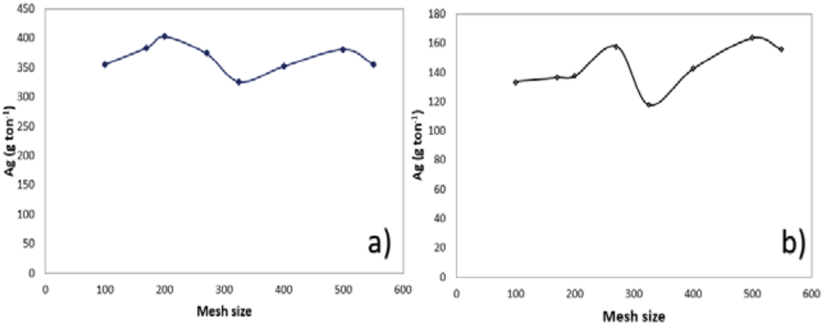

Figure 2. a) Tungsten distribution (g ton^{-1}) by mesh size. b) Silver distribution (g ton^{-1}) by mesh size.

Calcite ($CaCO_3$) was identified as the matrix of the mineral in the diffractogram obtained from the dust sample of the pull size ore. Other species that are present in the sample are quartz (SiO_2), franklinite ($Zn_{0.98}Fe_{2.02}O_4$), Bornite ($Cu_{1.25}Fe_{0.25}S$) and tungstenite (WS_2); the latter is the species where the tungsten content was identified, as is the case with the analysis performed for white and whitish particles (see Figure 3).

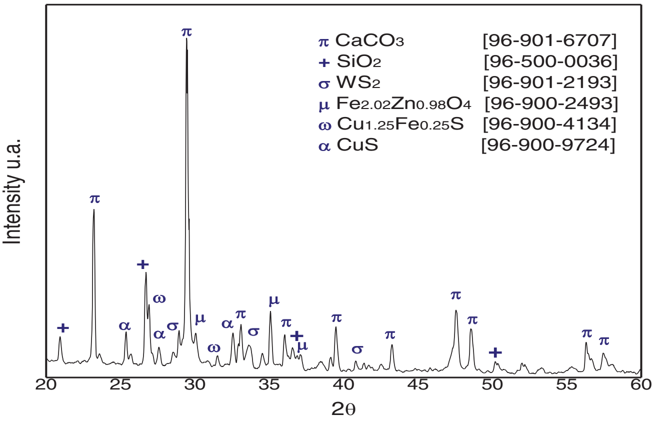

Figure3. X-ray diffractogram of the dusts of pull size ore.

We performed a handpicked separation of the run-of-mine by color. It included black, gray, white and dark gray particles (magnetic particles); they were pulverized and characterized by XRD. The mineralogical analysis performed through this technique allowed us to determine calcite ($CaCO_3$) as the matrix of the mineral in all of the particles except for the gray and grayish particles, whose mineralogical matrix was identified as orthoclase ($AlKSi_3O_8$). Some minor mineral phases were also found, whose reflection numbers are shown in table 2 for particles with different colors.

Table 2. Mineral species present in particles with different colors.

Particle Colors	**No. PDF**	**Composition**	**Mineral Shases**
Dark gray (Magnetic particle)	[96-900-6904]	Fe_2O_4 Zn	Franklinite
	[96-900-1077]	$CaMgO_4Si$	Monticellite
	[96-901-1801]	FeS	Mackinawite
	[96-900-6284]	$Ca_{1.08}Fe_{3.92}O_{12}Si_3$	Andradite
	[96-101-0929]	$CCaO_3$	Calcite
	[96-900-9724]	$Ca_{0.63}Fe_{4.37}O_{12}Si_3$	Almandine
White particles	[96-900-5841]	Fe_3O_4	Magnetite
	[96-901-1453]	$CaCO_3$	Calcite (Wallastonite-2M)
	[96-710-3015]	SiO_2	Quartz
	[96-900-9146]	WS_2	Tungstenite
Black particles	[96-901-5843]	FeS_2	Pyrite
	[96-901-6707]	$CaCO_3$	Calcitae
	[96-900-8219]	$AlKSi_3O_8$	Sanidine
	[96-901-3322]	SiO_2	Quartz
Gray particles	[96-900-0163]	$AlKSi_3O_8$	Orthoclase
	[96-901-6707]	$MgSiO_3$	Magnesium-silicon oxide
	[96-900-7274]	Fe_2MgO_4	Magnesioferrite
	[96-901-3322]	SiO_2	Quartz

By using grayscale contrast, an SEM-EDS micrograph, which is shown in figure 4 was obtained. An irregular, varied morphology can be observed in the mineral dusts. For the mapping performed on mineral particles sieved with sizes of 25 microns, the micrograph was first obtained by second electrons. The elements identified in the mapping were Si, K, Mg, Ca, Al, S, O and Fe, of which a strong relation between S and Fe can be observed. This confirms the presence of pyrite and mackinawite in the sample. The presence of large amounts of Si, Mg, Ca and O evenly distributed in the mineral indicate that calcite is the mineral's matrix.

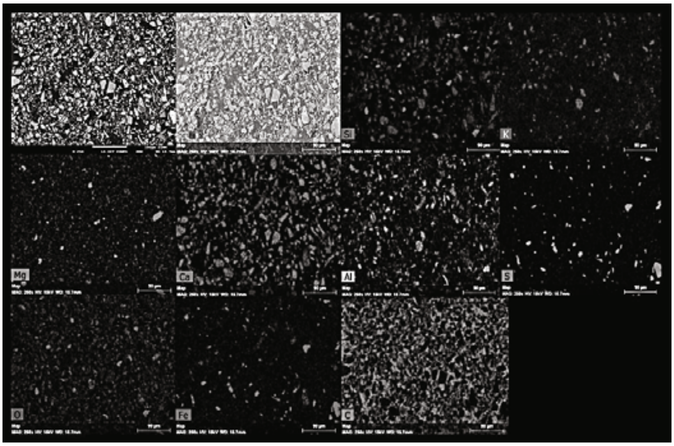

Figure 4. Mapping of polished particles sieved at a mesh size of 25 µm

The punctual analysis performed on a light colored particle reports a metal composition associated to iron sulfides. The energy dispersive analysis performed on the dark particle indicates the presence of Ca, Al, Si, Fe and O, which suggests the existence of andradite and calcite in the mineral, as with the particles smaller than 25 microns.

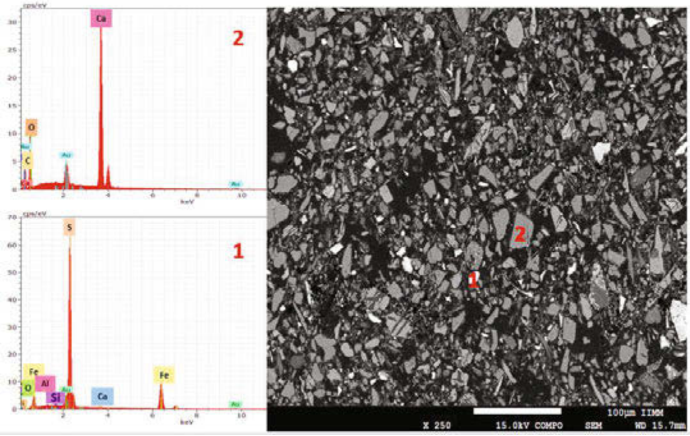

Figure 5. Punctual analysis of particles sieved at a mesh size of 25 µm.

Figure 9 shows the mapping performed on particles sieved at a mesh size of 37 µm, where Si, K, Mg, Ca, Al, S, C, O and Fe were identified, as well as an important concentration of W evenly distributed in the mineral. The relation between Fe and S is present in the same manner as the previous samples, and it was confirmed by the energy dispersive microanalysis performed on the particle seen in the bottom micrograph in figure 6.

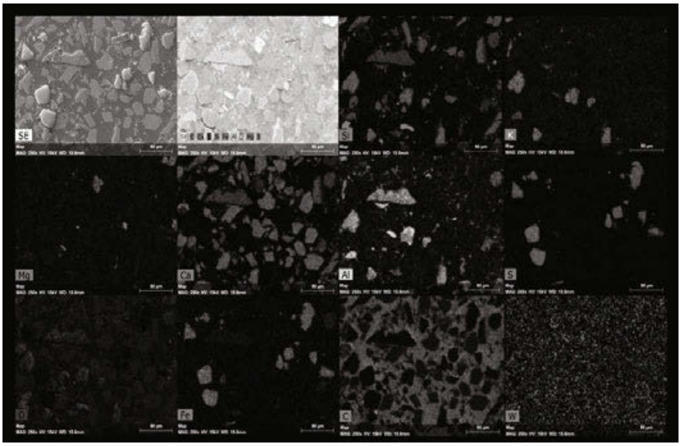

Figure 6. Mapping of polished particles sieved at a mesh size of 37 µm

The element O was observed to be evenly distributed; however, in this case, Ca is concentrated in larger particles, and it is associated to Si and Al. The punctual analysis performed on the particle shown in the top micrograph of figure 7 reveals the presence of S, Fe, and Mg, which suggests the existence of magnesioferrite.

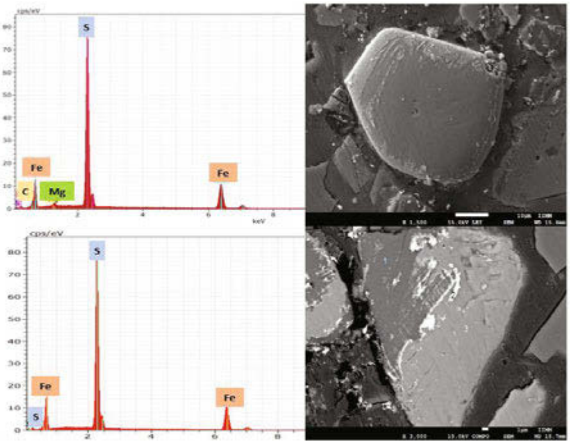

Figure 7. Punctual analysis of particles sieved at a mesh size of 37 µm.

Conclusions

By means of the XRD technique, tungstenite (WS_2) was identified as the mineral species that contains tungsten; this element was confirmed by the mapping performed through the SEM-EDS technique on particles sieved at 37 microns, as well as the elemental chemical analysis by ICP. This suggests that the mineral from the *mina Concordia* mine is a viable source for the extraction of tungsten, with the highest concentration of 402.88 g ton^{-1} identified in particles sieved at 74 microns. However, tungsten is likewise present in the pull size ore sample. Elements typical to the ore, such as S, Fe, and Zn, confirm the presence of abundant metal sulfides that were identified through XRD and SEM-EDS; they are contained in the mineral sample, whose matrix is mainly composed of calcite and quartz. Among the minor elements, important concentrations of silver can be observed which coincide with the even presence of tungsten at the different mesh sizes at which the sample was sieved.

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