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Article

Influence of Temperature on the Formation of Ag Complexed in $S_2O_3^{2-}$-O_2 System

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Abstract: Metallic elements of higher economic value occurring in the mineralogy of Zimapán are Pb, Zn, Cu and Fe, said elements are sold as concentrates, which, even after processing, generally include significant concentrations of Mo, Cd, Sb, Ag and As that could recover through different leaching methods. In this work the influence of temperature was studied in the complexation of silver in the $S_2O_3^{2-}$-O_2 system. Chemical and mineralogical characterization of concentrated Zn from the state of Hidalgo confirmed the presence of the silver contained in a sulfide of silver arsenic ($AgAsS_2$) through the techniques of Atomic Absorption Spectrophotometry (AAS), X-Ray Diffraction (XRD) and Scanning Electron Microscopy-Energy-Dispersive X-Ray Spectroscopy (SEM-EDS). The mineralogical species identified allowed the construction mineralogical species Pourbaix diagrams in the range of 298 K to 333 K, through which the Eh-pH conditions to obtain silver in solution were determined. The formation of $Ag(S_2O_3)_2^{3-}$ complex was confirmed by characterizing liquors leached using the technique Infrared Spectroscopy Fourier Transform (FTIR).

Keywords: silver; dissolution; thiosulfate; characterization; complex; temperature; arsenic

1. Introduction

Currently, the search for alternative leaching agents to traditional extraction process is presented in an essential way to the scientific and industrial interest to combat the cyanidation disadvantages. The limited selectivity and high toxicity involving the use of cyanide have directed efforts of different research fields to the use of leachetes such as thiourea, thiocyanates and thiosulfate [1], processes by which have been achieved profitable recoveries with a lesser extent ecological impact [2].

The thiosulfate is one of the most promising reagents for leaching precious metals [3]. It has shown that by maintaining sufficient concentrations of thiosulfate, ammonia, copper and oxygen in the solution, and under suitable Eh-pH conditions, precious metals such as gold can be extracted easily with a low consumption of reagents [4]. In the last decade, recoveries with thiosulfate are optimized with the use of oxidizing agents such as O2 and the addition of metal ions with catalyst character, reaching recoveries up to 97.13% Ag (I) in $S_2O_3^{2-}$-O_2-Zn^{2+}, at 40 gL^{-1} $S_2O_3^{2-}$ concentration, O_2 partial pressure of 1 atm and temperature of 318 K during 4 hours [5].

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Leaching with thiosulphate from sulphurous ores involves a complex chemical which requires a comprehensive thermodynamic analysis prior to experimental tests in order to determine the conditions in which precious metals are solubilized to interference from other metals present in the system. Some studies have clarified the dissolution chemistry of leaching systems by calculating the distribution of species and making Pourbaix diagrams determining the ratio between ore concentration and reagents [6], in addition to performing thermodynamic calculations that show the favorable recovery of Ag (I) in which conditions the complex formed with leaching agent is stable in solution [7].

This study shows the characterization of concentrated Zn from Zimapán, whose particles were bounded to 74 microns and subjected to a leaching process in the $S_2O_3^{2-}$-O_2 system in order to study the influence of temperature on the formation of complexed silver.

2. Materials and Methods

Prior to experimental tests, the ore zinc concentrate from the mining district of Zimapán, Hidalgo was dried and homogenized to obtain a representative sample. Later it was analyzed by Atomic Absorption Spectrophotometry (AAS) technique using a Perkin Elmer-Analyst 200 spectrophotometer in order to identify and quantify the elements present in zinc concentrate.

The morphological study of the representative sample was performed by X-Ray Diffraction (XRD) technique using INEL X-ray diffractometer, model EQUINOX 2000 with a Co-Ka1 radiation (1.789010 Å) operating at 30 mA and 20 KV, 220V voltage and 0.095 FWHM resolution; and Scanning Electron Microscopy-Energy-Dispersive X-Ray Spectroscopy (SEM-EDS) technique using an JEOL electron microscope, model JSM 6300 with a 30 KV voltage and a 21 mm field depth at different magnifications with secondary electrons and backscattered in order to identify the mineralogical species present in Zn concentrate powders.

According to the mineral species identified by XRD silver complexing agent and proposed for the leaching system ($S_2O_3^{2-}$), the thermodynamic simulation of the system was made with two metallic elements (Ag and As) and three nonmetallic (S, H and O_2), by building Pourbaix diagrams at different temperatures to establish a framework for the behavior of these elements in an aqueous system using HSC Chemistry software 5.11.

To perform the silver dissolution was used a glass reactor with 500 mL capacity on a Thermo Scientific Super Nuova hot plate fitted with magnetic stirring, oxygen was injected through a diffuser and regulated to 1 atm by a flowmeter with a 200 psi maximum capacity. A series of experiments were performed disolusión at different temperatures (298, 313 and 333 K) keeping all other parameters constant. The leaching process of Ag (I) was monitored by taking successive 10 mL aliquots at different times for 360 minutes, which were analyzed by AAS. Leached liqueurs were characterized by Infrared Spectroscopy Fourier Transform (FTIR) technique to confirm the formation of the silver-thiosulfate species using a Fourier Transform Infrared Spectrometer model Tensor 27, Bruker, with a MIR source.

3. Results

3.1. Chemical analysis by Atomic Absorption Spectrometry (AAS)

Figure 1 shows the analyzed elements in Zn concentrate by AAS technique, the obtained results determined a 0.25% (255 g ton^{-1}) silver content. Besides the presence of 48% Zn as a major component, followed by Fe and Cu concentrations. Sb, Pb and Cd were identified as less abundant elements in the concentrate.

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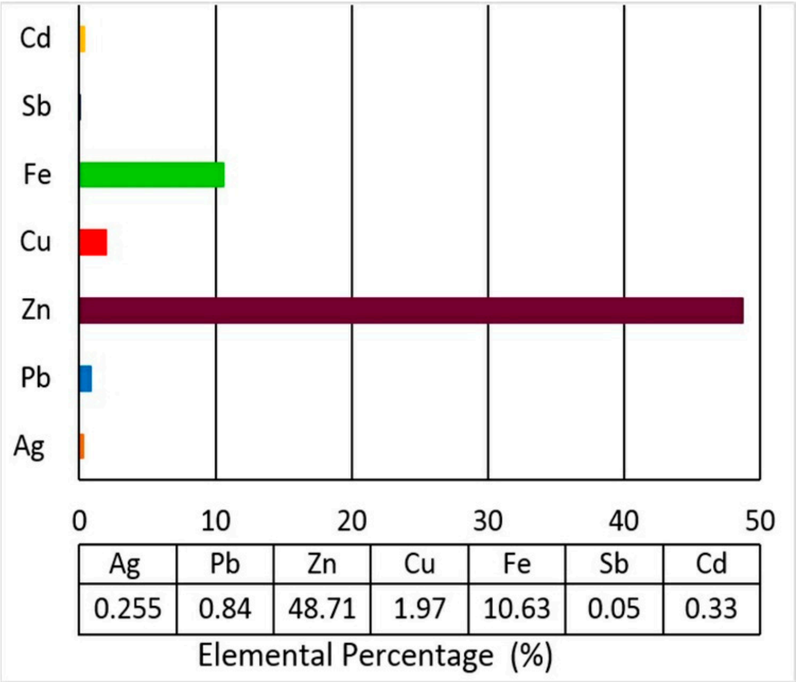

Ag	Pb	Zn	Cu	Fe	Sb	Cd
0.255	0.84	48.71	1.97	10.63	0.05	0.33

Figure 1. Average elemental composition of the ore sample.

Also performed triple digestion of powders held in 200, 270 and 325 mesh, Tyler series to known its silver and arsenic content. AAS analysis for these samples reported a uniform silver content for all measured particle diameters and high arsenic concentrations, as shown in Table 1.

Table 1. Ag and As content in Zn concentrate per mesh.

Mesh number	Micrometers (µm)	Ag (g/ton)	As (g/ton)
200	74	255	541
270	53	253	846
325	44	228	952

3.2. Characterization by X-Ray Diffraction (XRD)

Figure 2 shown diffractogram obtained by X-Ray Diffraction technique, in which is observed the following spectra corresponding to ore species: ZnS (PDF: 00-391-363) identified as ore matrix of this concentrate and metal sulfide $CuFe_9S_{16}$ (PDF: 00-270-165). The mineral species containing the precious metal in the concentrate of Zn was identified as a silver sulfide corresponding arsenic (PDF: 00-431-406).

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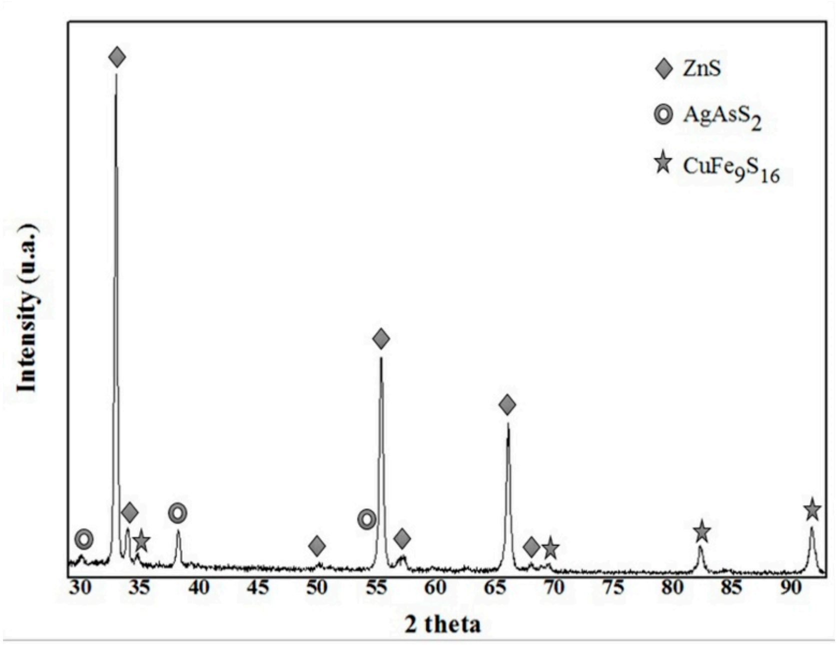

Figure 2. X-Ray diffractogram of the powders of pull size ore concentrate of Zn.

3.3. Characterization by Scanning Electron Microscopy-Energy-Dispersive X-Ray Microanalysis (SEM-EDS)

Figure 3 obtained with secondary electrons reported that the heterogeneous morphology of the particles corresponds to hemispherical and polygonal shapes with smooth angles. General EDS spectrum (refer with: Figure 4) reveals the elemental composition of concentrate, which is consistent with chemical analysis by AAS determining Zn, Cu and Fe as main metal components of sample powder.

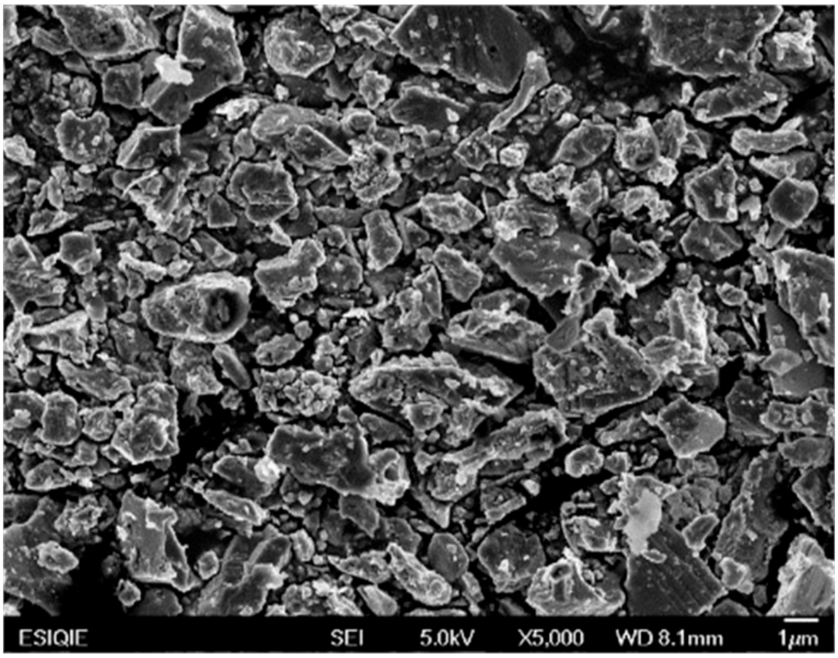

Figure 3. Micrograph of a powder sample in a Zn concentrate obtained by secondary electrons.

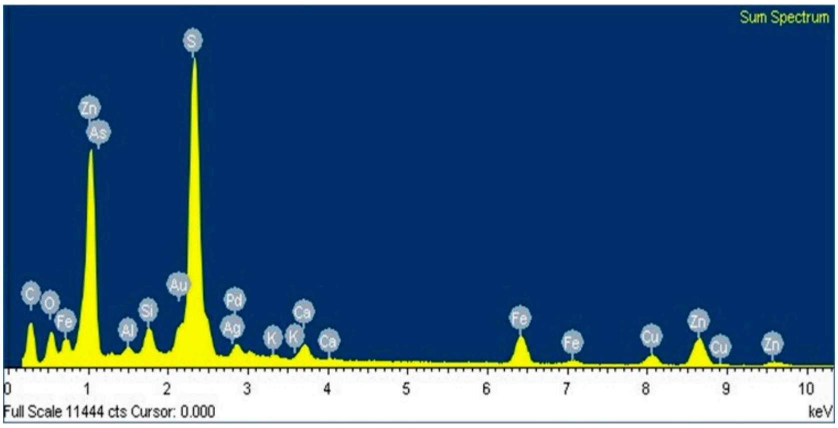

Figure 4. Energy-Dispersive X-Ray Spectrum performed to an all-in-one powder sample of Zn concentrate.

In the mapping performed to concentrate particles Zn shown in Figure 5, which shows the sulfur as the most abundant element in the sample and is mainly related to metallic elements such as Zn, Fe and Cu, suggesting the presence of mineral species such as wurtzite, pyrite and chalcopyrite.

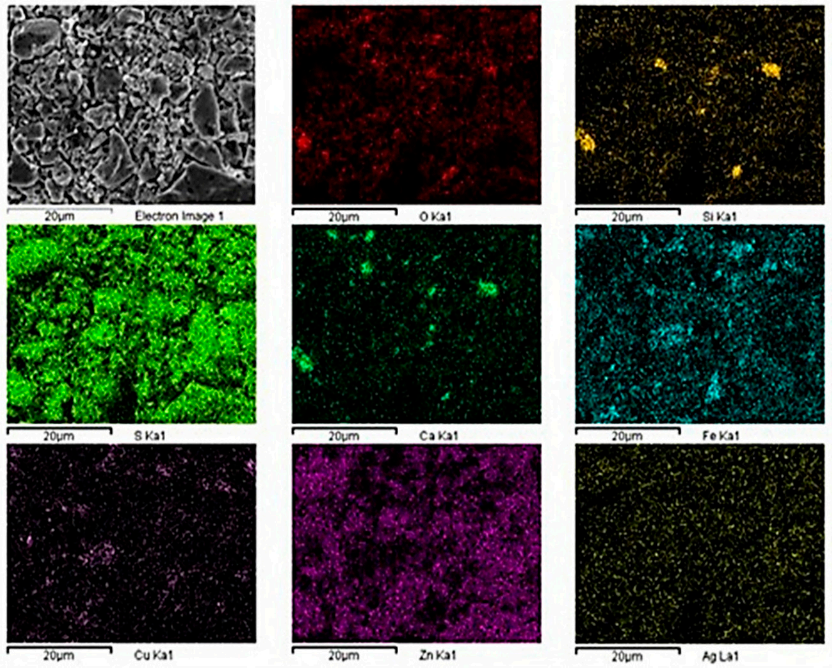

Figure 5. Mapping made to concentrate Zn powders.

3.4.. Thermodynamic Simulation of Ag (I) dissolution

In the diagrams performed at different temperatures presented in Figures 6 and 7 shows that at pH = 9 and in a range of Eh = -0.1 to 1.4 volts species $Ag(S_2O_3)_2^{3-}$, corresponding to the Ag (I) complexed with a lixiviant species is obtained, thereby confirming, the pH range is broad dissolution compared to potential range.

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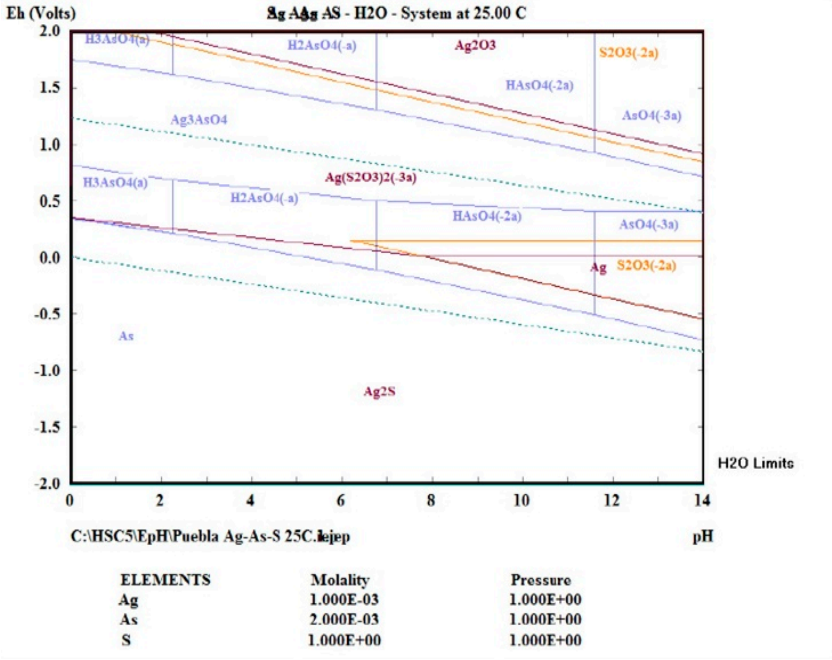

Figure 6. Diagram Eh-pH for the Ag-As-S-H2O system at 298 K.

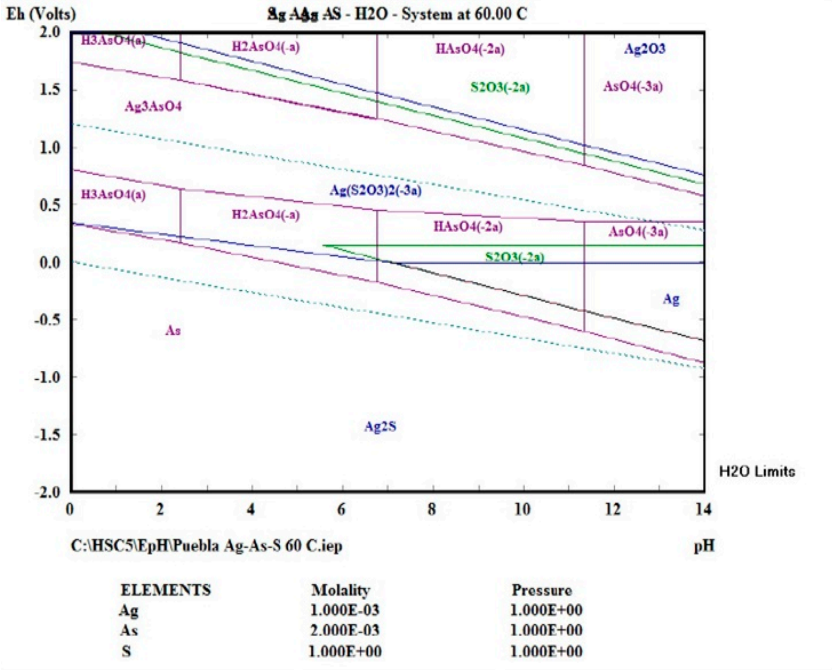

Figure 7. Diagram Eh-pH for the Ag-As-S-H2O system at 313 K.

3.5. Dissolution of Ag (I) at different temperatures

The mesh more concentrated distribution of silver was selected, in this case 200 mesh, as appropriate particle size to study the influence of temperature on the silver solution. Experimental conditions for leaching of Ag (I) in $S_2O_3^{2-}$-O_2 system show in the table 2:

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Table 2. Experimental conditions constant.

Constant Parameters	Measurement
Amount of mineral	40 gL^{-1}
$[S_2O_3^{2-}]$	0.5 M
Stirring speed	670 min^{-1}
pH	9
[NaOH]	0.1 M
Partial Oxygen Pressure	1 atm
Volume of Solution	500 mL

The graphical representation of the values obtained in the series of experiments shown in Figure 8 where it can be seen that the higher the temperature, the percentage of silver is raised in the leached solution.

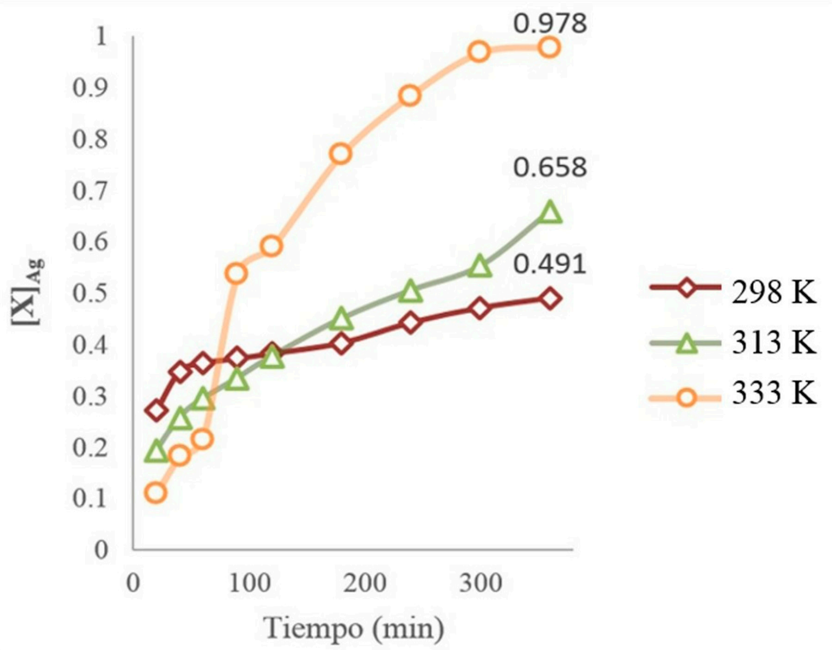

Figure 8. Graphic representation of the effect on leaching temperature of silver.

A temperature of 333 K the conversion of silver is 0.978 in an attack time 360 minutes, which represents 97.8% recovery of silver in solution.

3.6. Identification of the complexed species of Ag^+-$S_2O_3^{2-}$-O_2 system

The vibrations of the species $Ag(S_2O_3)_2^{3-}$ retain the same intensity by increasing the solution temperature range of 298 K to 333 K as shown in Figure 9.

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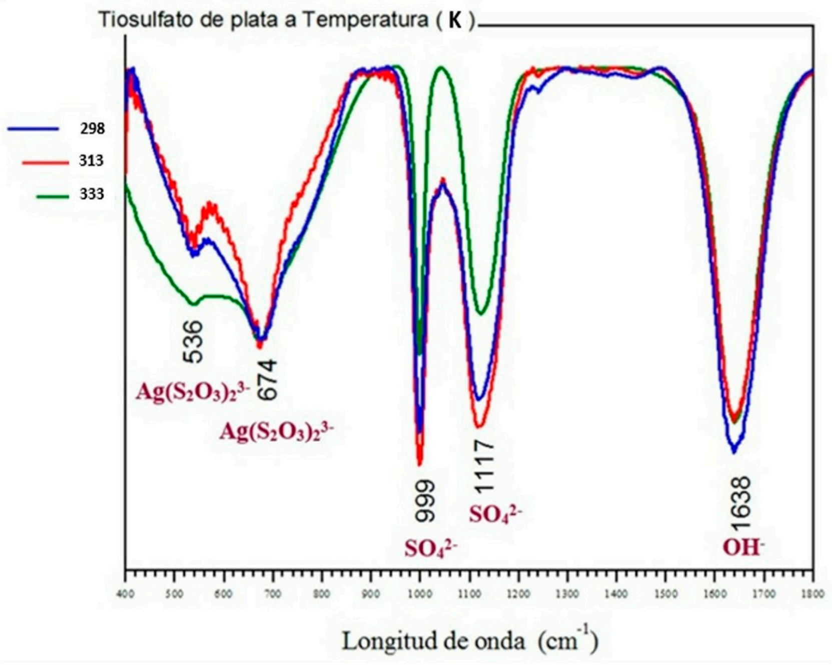

Figure 9. Infrared spectrum corresponding to silver thiosulfate at 298 K, 313 K and 333 K.

4. Discussion

Zimapán mining district is characterized by a varied and complex mineralogy consisting primarily of sulphides and oxides with significant metal concentrations outstanding among which are elements such as Fe, Se, W, Zn, Cu, Pb, Cd and Mo [8]. Among the endemic minerals of this district and of greater commercial interest, such as pyrite, chalcocite, chalcopyrite, galena, covelite and sphalerite, it has confirmed the formation of compounds where the sulfur combines with settleable such as As, Sb or bi and relate to important contents of Ag as pyrargyrite (Ag_3SbS_3) and proustite (Ag_3AsS_3) [9]. The presence of As, Ag and S confirm in turn mineralogical silver species identified by XRD. Ca content in the concentrate of Zn was detected by the mapping, confirming the alkaline nature of the pulp and corresponds to the presence of non-metal species such as calcite ($CaCO_3$) [10, 11]. Silver is observed homogeneously distributed in the sample, as indicated by the chemical analysis of different sizes particular.

A potential reducing silver is in the form solid products such as metallic silver and silver sulfide while potential greater than 1.4 volts silver precipitates as oxide. It can be seen that the stability domain of the species of complexed silver covers the entire range of pH stability within the area of water. As in the case of element directly related to the content of Ag in the concentrate of Zn, it presents in elemental form potential reducers, while above -0.3 volts, As can be oxidized in AsO_4^{3+} that dissolves as $AsO_4$3-, $H_3AsO_4^+$ and $HAsO_4^{2-}$ below a pH=11.5. Previous studies have reported that dilute concentrations of the mineral species and higher concentrations of thiosulfate increase silver recoveries [3], so dilute concentrations of Ag and As, and a saturated concentration of S to construct diagrams were considered Pourbaix within the range of 298 K to 333 K, in which no influence of temperature was observed in the complexation of silver.

Based on the species identified in the Pourbaix diagrams to pH = 9 and oxidizing conditions, the reaction stoichiometry dissolution was formulated proposed system, which is shown in equation 1:

$$4AgAsS_2 + 6NaS_2O_3 + 8H_2O + 21O_2 + 28e^- \rightarrow 4Ag(S_2O_3)_2^{3-} + 4HAsO_4^{2-} + 12\,NaOH + 4SO_4^{2-} \qquad (1)$$

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Through the technique Infrared Spectroscopy Fourier Transform (FTIR) silver complexed by thiosulfate presence in leach liquors made of solutions at different temperatures, in addition to the formations SO_4^{2-} ions which are formed by identified decompotion thiosulfate inherent in basic medium and in the presence of oxidizing agents [12] as shown in equation 2:

$$S_2O_3^{2-} + 2O_2 + 2OH^- \rightarrow 2SO_4^{2-} + H_2O \qquad (2)$$

The behavior of complex $Ag(S_2O_3)_2^{3-}$ shown stably regardless of the temperature increase is made as obtained by FTIR vibrations. The temperature has a favorable effect on the dissolution of silver [13, 14] to increase recoveries in a 55.76%.

5. Conclusions

- The species containing silver in Zn concentrate is a silver-bearing sulfide arsenic (AgAsS2) whose reflections were identified by XRD and its composition confirmed by the exact analysis performed to fine particles by SEM-EDS.
- EDS microanalysis confirmed the presence of Cu, Zn, S, Fe and Pb elements, whose concentrations were analyzed by AAS. Micrographs obtained by SEM allowed to identify the composition of typical ores as wurtzite (concentrate matrix), glance and chalcopyrite, whose reflections were also observed in the X-Ray Diffractogram.
- By thermodynamic simulation of the dissolution of the species in the $S_2O_3^{2-}$- $AgAsS_2$-O_2 system was found that at pH = 9 and Eh= -0.1 to 1.4 volts is achieved to obtain Ag (I) in solution at a temperature between 298 K and 333 K, because potential minor species are generated as sulfides silver arsenate and arsenic acid. This was confirmed by the experiments realized to different ranges of temperature, where it was observed the formation of silver complex even at high temperatures.

Author Contributions:

Aislinn M. Teja-Ruiz designed and performed the experiments; Julio C. Juárez-Tapia conducted the discussion of results and wrote the paper; Leticia E. Hernández-Cruz realized the thermodynamic simulation of Ag (I) dissolution; Martín Reyes-Pérez performed the characterization by FTIR and contributed the software used for Thermodynamic Simulation; Francisco Patiño-Cardona realized the chemical analysis and contributed to discussion of results; Ivan A. Reyes-Dominguez performed the characterization by DRX and mapping realized by SEM-EDS; Mizraim U. Flores-Guerrero realized the indexing of spectrum obtained by DRX; Elia G. Palacios-Baes performed the characterization by SEM-EDS.

Conflicts of Interest: The authors declare no conflict of interest

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