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Zeta Potential of Molybdenite to Fine Sizes

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Abstract: ***The zeta potential (ζ) of molybdenite at fine sizes has been obtained in the present work, this determination was carried out with electroacoustic equipment, where the variation of this electrokinetic parameter with respect to pH was obtained. In relation to studies carried out, the obtained results confirm that in the molybdenite particles, as the face / edge ratio decreases the zeta potential (ζ) increases; same variation of increase occurs as the pH increases; being always negative, with values between -65 to -80 mV for the tested range. The magnitude of these values and the increase that it suffers when increasing the pH, is due to the fact that when you have an increasingly fine grinding of the particles, a larger number of edges is generated, and this is where the load originates in the surface of the molybdenite particles, from the oxygenated sites on said edges, causing the formation of molybdate ions (MoO_4^{-2}) and hydromolybdates ($HMoO_4^{-1}$).***

Keywords: zeta potential, mineral fines, pH and faces/edge ratio

1. Introduction

The purpose of this work is to carry out research that could be a potential reference, in terms of knowledge of the surface (electrokinetic) properties of fine particles (60% -10μm) of molybdenite, to be used in Floc-Flotation studies, with a view to achieving a better recovery in your process of concentration.

For the recovery of molybdenite, its surface properties and the chemical nature of its crystalline structure are used, since due to these characteristics it is a natural hydrophobic mineral and this makes it respond to the flotation process.

The crystalline structure of molybdenite was determined in 1923 by Dickinson and Pauling, which presents a hexagonal unit formed by a sheet of atoms of Mo that is sandwiched between two sheets of S atoms, giving the three a layered structure. The strength of the bonds within the layers are much stronger than between these, resulting in excellent exfoliation; between the atoms of the crystalline structure is established two types of bonds, the covalent, associated between atoms of sulfur and molybdenum (S-Mo bond) and van Der Waals, between layers of S-Mo-S, which are considerably weaker than the first.

The structural characteristics of molybdenite, result in the surface of the particles of this mineral, two different types of surfaces that can be found as: sites created by the rupture of van der Waals type bonds, which are called faces, and other sites created by the breaking of S-Mo links called edges. as seen in Figure 1.

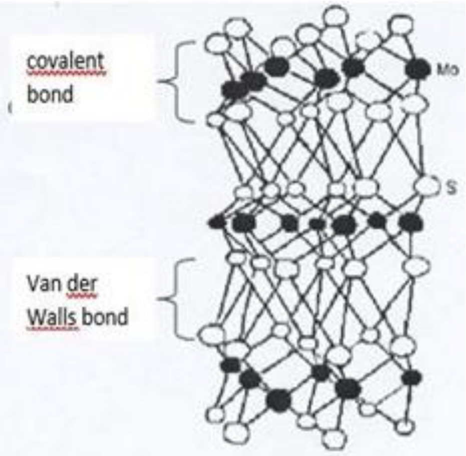

Figure 1: Crystal structure of molybdenite, where the faces and edges are observed (Ornelas et al., 2006).

The zeta potential is a physical property which is exhibited by a particle in suspension. It has been widely recognized that the zeta potential is a very good index of the magnitude of the interaction between colloidal particles and the measurements of it are commonly used to ensure the stability of the colloidal systems, said stability plays a very important role in many industries, for example, food, paint, pharmaceutical, water treatment, and particularly in the materials (minerals) that is our area of work.

If the particles in suspension have a large negative charge or in their case a positive zeta potential then they will tend to repel one another and therefore there is no tendency to join, that is, this leads to maintaining a state of dispersion. However, if the same particles have low values of zeta potential then there will be no force to prevent the particles from agglomerating; This is the suspension becomes a state of instability that allows the aggregation of particles, this fact is used in the mining industry in the recovery of fine particles (-10μm) which represent a significant percentage that usually most of the time it is lost or in the best of cases low recoveries are achieved. which negatively affects the economy of the company, which may at a given time or situation, put at risk the continuity of operations and in the extreme case make a mining project unviable.

The general division line between stable and non-stable suspensions is generally taken as +30 or -30 mV. Particles with zeta potential more positive than +30 mV or more negative than -30 mV are considered normally stable.

Origins of the surface charge.-
Most colloidal dispersions in an aqueous medium carry an electrical charge. There are many origins of this surface charge depending on the nature of the particle and its surrounding environment, here we will mention some of the mechanisms only:

a) Dissociation of ionogenic sites (ionization of groups on the surface).
   The surface charge can be reduced to zero by eliminating surface ionization by lowering the pH in the case of negatively charged particles or by increasing the pH in the case of positively charged particles. In both cases the magnitude of the surface charge depends on the acid or basic concentration on the surface and on the pH of the solution.
b) Differential loss of ions from the crystalline structure.
   As an example, consider a crystal of silver iodide placed in water, the ionization of said compound will occur.
c) Adsorption of charged species (ions or ionic surfactants).
   The ionic surfactants can be specifically adsorbed on the surface of a particle allowing, in the case of cationic surfactants, a positively charged surface and in the case of anionic surfactants, it produces a negatively charged surface.
d) Ionization of amphoteric groups on the surface of metal oxides.
e) Isomorphic substitution in the crystalline network of the solid.

In silicates in the tetrahedron SiO_2, an atom of Si^{4+} can be replaced by Al^{3+}. Also Al^{3+} by Mg^{2+} or Fe $^{+2}$ in the octahedron of Al_2O_3. Therefore, the surface acquires a negative electric charge. The negative charge is compensated by metallic cations. The double electric layer. The development of a net charge on the surface of the particle affects the distribution of ions (ionic density) in the surrounding interfacial region resulting in an increase in concentration of the counterions, that is to say ions of charge opposite to those of the particle next to the surface. Then a double electric layer exists around each particle (Figure 2).

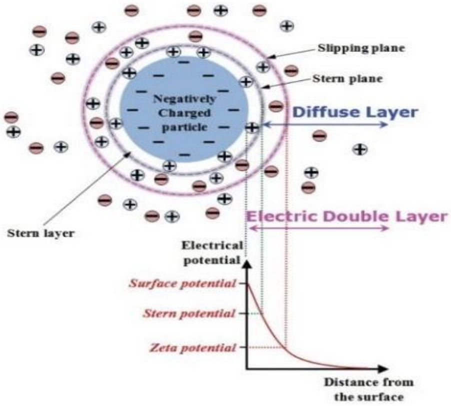

Figure 2: Electric double layer model

The maximum value of the potential occurs at the surface of the particle. The surface of the charged particle and the diffuse layer of most charged ions of opposite sign compress the double electric layer. Its thickness is defined as the distance from the surface of the particle at which the electric potential falls to (1/ e) of the maximum potential (potential at the surface) and is commonly referred to the length of the Debye-Hückel parameter (k^{-1}) [1].

1.1. Potential zeta (ζ)

The layer of liquid surrounding the particle exists identifying itself formed of 2 parts; an inner region (Stern layer) where the ions are strongly united and an external region (diffuse) where said ions are weaker in their union. The union between the bonds of the charge close to the particle (Stern layer) and the diffuse layer is identified by the curved line of the figure. That surface, which separates the junction of the charge from the diffuse charge around the particle, where the solution and the particle move in opposite directions when an external field is applied. At this point it is known as a cutting surface or sliding surface.

The zeta potential (ζ), also called the electrokinetic potential, is defined as the value of the electric potential in the plane of the particle cut [2], this potential is shown schematically in Figure 3.

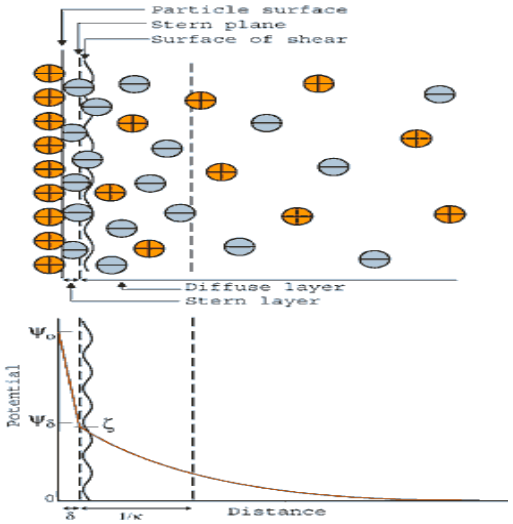

Figure 3: Representation of the zeta potential

The isoelectric point (iep), is the potential in the slip plane = 0
In as much the Point of zero charge (pzc), it is the potential in the surface = 0
The objective of the present investigation is to obtain the values of the Zeta Potential for molybdenite at fine sizes when the pH varies, and that they represent another element in the search to improve efficiency in its recovery.

2. Methodology

2.1 Mineral sample

The sample used for the development of this study was that corresponding to a molybdenum concentrate from the "La Caridad" Mining Unit located in Nacozari in the State of

Sonora, Mexico. Said concentrate was taken to a purification stage in order to increase the degree of Mo, eliminating as much as possible the impurities it contains, as well as sulfur.

Remnants of leaching solution and reagents used in the previous concentration. Once obtained, the purity of the base sample for the research study, we proceed to obtain a sample of fine particle size, the above is achieved through the grinding of the sample of purified MoS_2, in a disk type planetary mill , control of particle size was achieved using a Gilsonic Autosiever microsizer, with an aperture micrograph of 10 µm, until a size of 60% at -10 µm was obtained. The following tests are then carried out: Chemical analysis, MEB, DRX and Zeta Potential.

2.2 Chemical analysis

Through chemical analysis, the most significant elements and compounds that are present in the molybdenite sample will be quantified. This information is used to determine the mineral species that make up this sample. The analysis was carried out in a Perkin Elmer brand atomic absorption spectrophotometer, model 3110, determining the following elements: Mo, Cu, Fe, SiO_2

2.3 X-ray diffraction analysis (XRD)

X-ray diffraction analysis is an important tool to determine which minerals are present in a sample, due to the great certainty of the results obtained. Based on its measurement principles, this analysis technique was used to determine if there were mineral species above a concentration of 5%. For which a Rigaku DMAX Model 2200 brand equipment was used.

2.4 Analysis by Scanning Electron Microscopy (SEM)

For this study we used the Scanning Electronic Microscope (SEM), Philips brand, Mod XL-30, which has an EDAX Mod DX-4 dispersed energy spectrometer coupled to it. The SEM is a fundamental tool for the characterization of the molybdenite sample. The EDS detector with backscattered electrons (BSE) was used for the identification and quantification of mineral species. The secondary electron detector (SE) was also used to observe the morphology of the molybdenite particles

2.5 Potential zeta (ξ)

The zeta potential was determined by varying the pH in a Zet-meter, model Zeta probe-T6A, from Colloidal Dynamics (Figure 4). The measurements were carried out under the following conditions: a suspension at 2.8% by weight was used, with $2x10^{-3}$ mol / l, KCl; prepared with deionized water. HCl and KOH solutions were used to control the pH.

Figure 4: Zetámetro, model Zeta probe-T6A, of Colloidal Dynamics

3. Results and Discussion

3.1 Chemical analysis

Table 1 shows the chemical composition of the molybdenite sample before and after purification, thereby increasing the MoS_2 concentration from 82.8 to 94%.

Table 1: Chemical analysis before and after purification.

Product	% Mo	% SiO2	% MoS2
Samples/ Purify	49.7	3.67	82.8
Purified Sample	56.4	1.62	94.0

3.2 X-ray diffraction analysis (XRD)

The XRD pattern of the purified molybdenite sample is presented in Figure 5, and shows that the main mineral species, due to its high concentration, corresponds to molybdenite (MoS_2). Due to the specific operating characteristics of the X-ray equipment (XRD), it is possible to establish that the sample analyzed is of high purity and that it confirms the result obtained in the chemical analysis of Table 1, since all the difractorama peaks coincided with the Molybdenite card, which implies that there are no impurities greater than 5%.

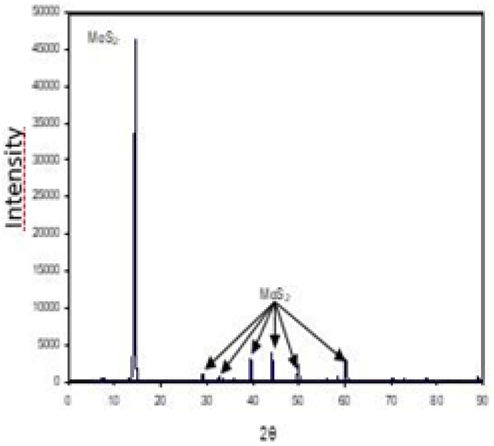

Figure 5: XRD pattern of the purified molybdenite sample

3.3 Study by Scanning Electron Microscopy (SEM)

Through the analysis of images obtained by this technique, it is observed that there are MoS_2 particles of different shape and size, as can be seen in Figure 6.

Figure 6a presents several molybdenite particles released below a size of 10 µm, in Figure 6b, impurities of SiO_2 and FeS_2 can be observed in the sample of molybdenite; these impurities at fine sizes are a problem in their processing, since they originate the obtaining of low grade concentrates, and this diminishes also their recovery [3].

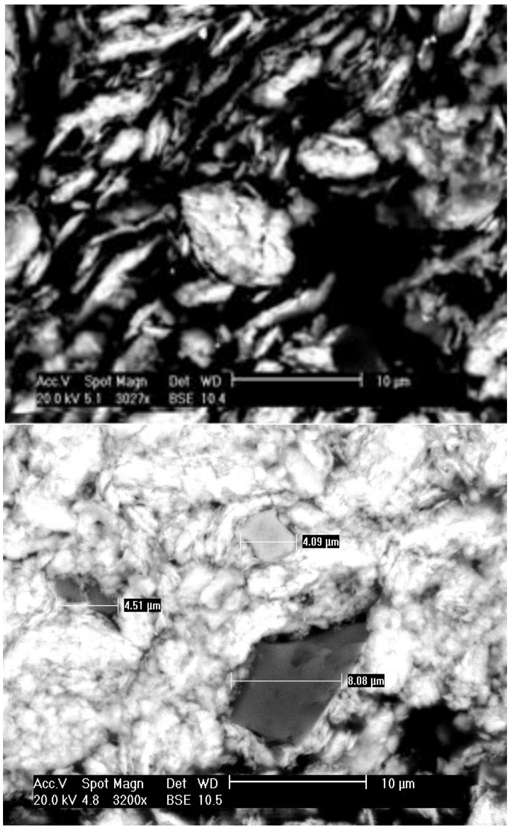

Figure 6: Photomicrographs obtained in SEM. a) MoS_2 particles, released in different sizes; b) Different impurities (FeS_2 and SiO_2), present in the molybdenite sample.

3.4 Zeta potential (ζ), for the molybdenite sample.

Figure 7 shows the variation of zeta potential in relation to pH, for molybdenite according to several authors [4] , where it can be observed that the corresponding electrokinetic curves differ from each other. The main reason being the different face / edge ratio used in the base molybdenite particles of the study; based on this fact, it emerges from the same figure that when increasing the face / edge ratio in the particle, the magnitude of the zeta potential is smaller in absolute value.

A common characteristic in all the electrokinetic curves of the same Figure 7, is that each value of the zeta potential is always negative at any pH value, this implies that at a low pH a zeta potential is also low, while at a pH alkaline the zeta potential is bigger.

Fuerstenau and Chander [5], have explained that the zeta potential of molybdenite particles is due to the generation of electric charges at the edges of the particles since the faces have only van der Waals forces. The edges of molybdenite can produce thiomolybdate ions as follows:

$$MoS_xO_y + H_2O \leftrightarrow \left[MoS_xO_{y+n/2}\right]^{-n} + 2H^+ \quad (1)$$

$$\left[MoS_xO_{y+n/2}\right]^{-n} + H^+ \leftrightarrow \left[MoS_xO_{y+n/2}H\right]^{-n+1} \quad (2)$$

These reactions explain the pH decrease of molybdenite powders dispersed in water. The hydromolybdates are dissolved as follows:

$$HMoO_4^{-1} \leftrightarrow H^{+1} + MoO_4^{-2} \quad pK = 5.9 \quad (3)$$

The predominant species, under alkaline conditions, are $MoO_4{}^{2-}$ anions, according to reaction 3, which explains the high negative zeta potential values under these conditions.

The aforementioned, is the product of the results obtained in studies carried out by different researchers on molybdenite particles (Figure 7), under specific conditions and when doing the interrelation with the results obtained in the present work, the following is observed:

The zeta potential (ζ) of the sample of molybdenite under study with a size of 60% -10µm (thinner than the one used in the mentioned investigations), as a function of the pH of the suspension, is shown in Figure 8 , where it is observed that the zeta potential of the molybdenite particles increases in absolute value when increasing the pH value; being always negative in the whole range used. The values thereof vary approximately between -65 to -80 mV for the pH range tested. The magnitude of these values and the increase that they suffer when increasing the pH, is due to the variation of the face / edge ratio present in the molybdenite particles. Since the edges are responsible for the measured potentials, according to the mentioned mechanism, where the charge on the surface of the molybdenite particles originates from the oxygenated sites on the edges, causing the formation of molybdate ions ($MoO4^{-2}$) and hydromolybdates ($HMoO4^{-1}$)

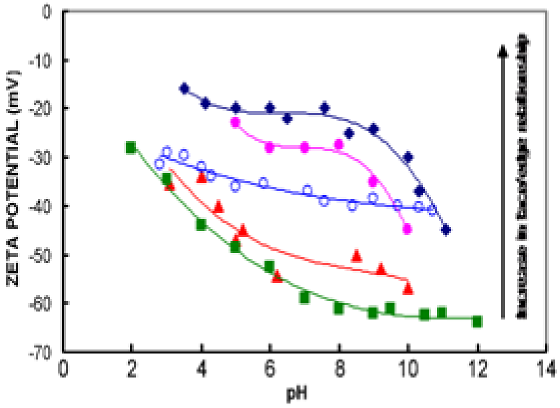

Figure 7: Zeta potential of molybdenite particle as a function of the pH. ✂ López Valdivieso (1980); ✎ Hoover and Malhotra (1976); ✚ Raghavan and Hsu (1984); ▲ Chander and Fuerstenau (1974); ▯ Madrid Ortega (2005).

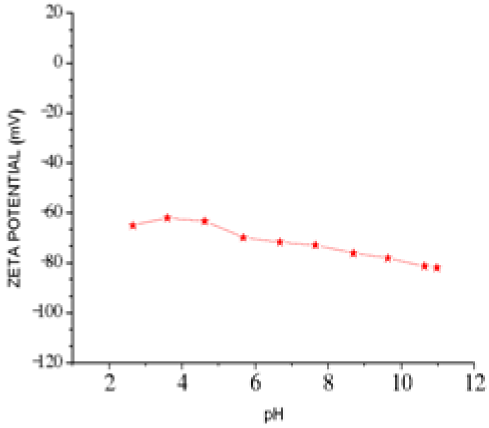

Figure 8: Variation of the zeta potential (ζ), with the pH, for the MoS_2 sample, at a size of 60% at -10 μm.

4. Conclusions

As the face / edge ratio decreases, the zeta potential of the molybdenite particles tends to increase in absolute value, in relation to the results obtained in the previous studies; due to the fact that more and more edges are being generated, due to a finer grinding of the particles; 60% -10μm and being chemically active sites by the breaking of the covalent bond S - Mo, in the structure of molybdenite, it is here where the electric charges are generated due to the formation of $HMoO_4^-$ and MoO_4^{-2} ions. Likewise, it was obtained that the zeta potential increases, when the pH increases and this is due to the fact that the $MoO4^{-2}$ ions are generated in the solution predominantly at alkaline pH.

5. Acknowledgements

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Author Profile

PhD. Antonio Lòpez Mendoza, Research Professor full-time of the Academic Unit of Earth Sciences of the Autonomous University of Zacatecas 1987-present, and responsible for the career of metallurgist mining engineer (2006 to 2010), I obtained the doctorate in sciences in the Institutional Doctorate of Engineering and Materials Science, UASLP; I received a Master's Degree in science from the Metallurgy Institute of the University's Engineering Faculty, UASLP, and a degree in Metallurgical Engineering from the National Polytechnic Institute of Mexico: publications of scientific articles, extensive memoirs and participation as a lecturer in congresses of mining.

PhD. Josè Angel Delgadillo Gòmez, Secretary of Planning of the Faculty of EngineeringAutonomous University of San Luis Potosí,January 2017 - Present, Research Professor Level VI, SNI I. Incorporated into the Faculty of Engineering and the Institute of Metallurgy as a full-time Professor-Researcher since July 2007. His research is aimed at the Simulation of particle classification processes using Computational Fluid Dynamics (CFD) as the tool, the element method discrete (DEM), population balance as well as other innovative techniques in the development of modeling. He has experience in the field of design and optimization of circuits in mineral processing at industrial level in companies such as Gold Corp, Peñoles; Minera México, Minera Rio Tinto and Mexichem Fluor. In addition to having funding from public institutions such as FAI-UASLP, Conacyt and PROMEP.