Mexican Contribution to Sulfide Minerals Electrochemistry: A Review

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Abstract. The electrochemical study of sulfide minerals has emerged as a vital area for enhancing sustainable methods for extraction and recovery of metals. This field encompasses diverse investigations. The use of Mineral Carbon Paste Electrodes (CPE) is one of the strategies developed in México, and their application for analyzing systems of extractive metallurgy range from analyses of bacterial-mineral interactions to key studies that have delved into understanding mineral dissolution mechanisms, with a particular focus on minerals such as galena, sphalerite, copper sulfides, and silver minerals. In addition, research efforts have been directed towards exploring copper and zinc concentrates leaching, as well as cyanidation refractoriness. These studies aim to advance extraction efficiency and sustainability in the mining industry.
Keywords: Sulfide minerals; electrochemistry; extractive metallurgy.

Resumen. El estudio electroquímico de los minerales de sulfuro ha surgido como un área vital para mejorar los métodos de extracción y recuperación de metales de manera sostenible. Este campo abarca diversas investigaciones. La utilización de electrodos de pasta de carbono (CPE) es una de las estrategias desarrolladas en México, y su aplicación para analizar sistemas de metalurgia extractiva abarca desde análisis hasta interacciones bacteria-mineral. Estudios clave se han centrado en comprender los mecanismos de disolución mineral, con un enfoque particular en minerales como la galena, la esfalerita, los sulfuros de cobre y los minerales de plata. Además, los esfuerzos de investigación se han dirigido a explorar la lixiviación de concentrados de zinc y la refractariedad a la cianuración. Estos estudios tienen como objetivo avanzar en la eficiencia y sostenibilidad de la extracción en la industria minera.
Palabras clave: Sulfuros minerales; electroquímica; metalurgia extractiva.

Introduction

The electrochemistry of sulfides has been studied from various perspectives. Initially, thermodynamics specialists constructed the first Eh-pH diagrams, defining the stability conditions of various sulfide mineral systems. These were applied, for example in explaining the metal matte refining process, the dissolution kinetics of sulfides and particularly the electrochemical mechanisms involved. Another trend was to study the electrochemical characteristics of sulfide minerals, such as their resistivity, finding that under certain conditions they could behave like metals, although most of them behaved as semiconductors [1].

The production of sulfuric acid through the oxidation of pyrite in an autoclave may be considered as one of the earliest hydrometallurgical processes involving sulfide minerals. Several reports studied the effect of conditions such as oxygen pressure, temperature, and acidity, among others [1]. Initially, there was discrepancy regarding the dissolution mechanisms; some researchers assumed that leaching occurred over the whole area of

the exposed pyrite surface, by adsorbed oxygen through a completely molecular route to sulfates, as sulfur formation was not observed during the oxidation process of pyrite. Peters and Majima [2] adopted Woodcock's suggestion [3] that anodic dissolution from the bottom of deep pits could explain the constant dissolution rate if the rate-limiting step was oxygen reduction and considered that this could be demonstrated through an electrochemical study of pyrite. The Peters and Majima study [2] was the first to show that pyrite could dissolve both anodically and cathodically, followed by various studies on the mechanisms and kinetics of mineral leaching to explain the results of experimental sulfide systems.

On the other hand, regarding the application of electrochemistry in sulfide flotation, the earliest studies were conducted by Woods [4], who employed cyclic voltammetry to investigate the oxidation of ethyl xanthate using a galena electrode. This was the first study to use an electrode other than mercury or platinum, which are commonly used for studying electrochemical reactions related to adsorption.

Following the studies of Ernest Peters and Ronald Woods, a series of investigations were conducted using bulk mineral electrodes to study various aspects of mineral leaching and flotation processes. Additionally, through the combination of spectroscopic and electrochemical techniques, some bases of the surface speciation were established to define the mechanisms and processes of these two important unit operations in extractive metallurgy. Most of these studies were reported in the proceedings of the ECS (Electrochemical Society) symposia on *Electrochemistry in Mineral and Metal Processing I to VIII (1984-2010)* [5-12].

The mentioned electrochemical studies required the construction of a working electrode made of bulk mineral, that was as simple as encapsulating in resin a piece of the massive mineral and preparation of the probe obtained to expose the mineral surface. Later, the construction of mineral electrodes was as advanced as preparing rotating disk [13] and even rotating-ring disk electrodes [14,15], hence enabling in-depth kinetic and mechanistic studies. However, construction of these types of electrodes is not always suitable for all minerals, due to conductive characteristics, such as the case of sphalerite, or when they are contained in concentrates or mineral waste. The electrochemistry group at UAM-Iztapalapa took advantage of the so-called carbon paste electrode technique (CPE) to solve these issues, but unlike other groups that used commercial carbon paste to prepare the electrodes [16,17], UAM´s group developed a technique where ground mineral was mixed with graphite powder and then silicon oil was added to obtain the paste. In this way, this group led by Ignacio González [18-22] was able to demonstrate the advantages offered by carbon paste-mineral electrodes (CPME), highlighting the reproducibility of the electrochemical response obtained.

The development of the CPME at UAM-Iztapalapa triggered a wide range of mineral electrochemistry studies, particularly aimed at understanding flotation, leaching, and reactivity aspects, involving sulfide minerals and this has been the cradle of many researchers that are either starting or already have consolidated careers at different universities and research centers throughout Mexico. The following is an account of contributions over a span of more than 30 years.

Electrochemical Interactions Between Bacteria and Mineral Surfaces (early approach)

Early studies focused on the interaction between bacteria and minerals in solution, particularly how bacterial adhesion to mineral surfaces is affected. The use of CPME, allowed characterization of fresh mineral samples [21,22], as well as of mineral samples that had been subjected to chemical or biological processes [23].

Cruz et al [24] examined the electrophoretic mobility of the bacterium *A. ferrooxidans* and arsenopyrite (FeAsS), finding that the bacterium shows low electrophoretic mobility and consistently presents a negative charge, regardless of pH. It was observed that at pH levels below 2.5, there was a favorable electrostatic interaction between the bacterium and the mineral, which should enhance bacterial adhesion to arsenopyrite under optimal pH (1.8) conditions. However, this was not observed when FeAsS was exposed to *A. ferrooxidans* in a culture medium of acid characteristics.

By employing cyclic voltammetry and CPE containing arsenopyrite, with and without different biological and chemical treatments, these authors found that adhesion efficiency of bacteria is either low or absent due to preferential dissolution of Fe(II) from FeAsS under acid conditions, which modifies the mineral structure. In this way, it was shown that Fe(II) ions are a more available source of energy for *A. ferrooxidans* and hence it enables their oxidation to Fe(III), promoting then a non-contact dissolution of arsenopyrite.

Thus, the electrochemical response of CPE-FeAsS in a culture medium (Fig. 1**(a)**) was compared to that of realgar (As$_2$S$_2$) in the absence (Fig. 1**(b)**) and presence of Fe(II) ions (Fig. 1**(c)**). From this, it was shown that the process labelled as A, corresponds to oxidation of Fe(II) and process C1 to the corresponding reduction of Fe(III).

The acid dissolution that gives place to preferential release of Fe(II) from FeAsS and formation of a structure that is alike As$_2$S$_2$, shows why there is a better resemblance of Fig. 1**(c)** with Fig. 1(a), showing that indeed at the interface there is preferential oxidation of Fe(II) to Fe(III), when it is available.
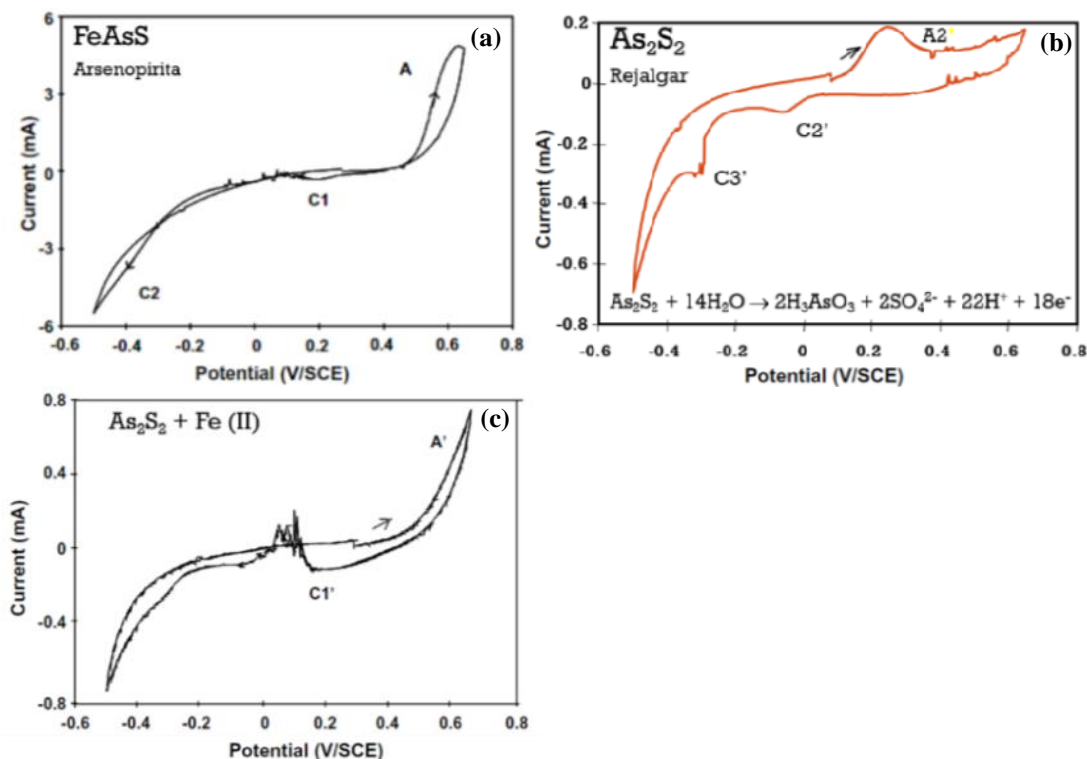

Fig. 1. Electrochemical response of CPME in a culture medium (pH=1.8) *for A. ferrooxidans*, where M = **(a)** FeAsS, **(b)** As$_2$S$_2$, **(c)** As$_2$S$_2$ and Fe(II) in solution. From reference [24]

Advances in Carbon Paste Electrodes (CPE) for Mineral Dissolution Studies

Once the capacity and versatility of carbon paste electrodes (CPE) for studying metallic minerals dissolution mechanisms were established, a series of studies on sulfide minerals of interest to Mexico were developed. Given that sulfide minerals are the primary source of base metals, and that flotation is key to their separation, it is relevant to establish many of the interfacial phenomena involved to improve the efficiency of this process. Likewise, despite the efficiency of pyrometallurgical processes, they are detrimental to the environment and that has prompted the development of hydrometallurgical processes as a greener alternative. However, a major handicap of hydrometallurgical processes is that their efficiency is limited due to issues such as elemental sulfur formation and insoluble salts that passivate the mineral surface when sulfides are involved. The following are some examples of this, where several scenarios were evaluated based on the applied mineral treatment or processing, and a systematic strategy for the application of electrochemical techniques, mainly voltammetry, chronoamperometry, and their combinations, was developed for each mineral study based on its complexity.

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Galena (PbS) Dissolution Mechanisms

Several studies were reported related to the electrochemical oxidation of galena and characterization of the species responsible for the slow dissolution kinetics of this mineral [25-27]. These studies utilized CPE-galena in a perchloric acid medium. Typical voltammograms obtained on CPE-galena without electrolyte agitation are shown in Fig. 2, with the potential sweep started in negative and positive directions from the open circuit potential (0.1 V). Other experimental conditions are described in the figure. The comparison of the voltammograms indicated that processes (B') and (C') are related to oxidative processes in (A'), while (D) and (D') correspond to the reduction of galena. The authors conducted an extensive voltammetric study on CPE-galena, varying the cathodic ($E_{\lambda-}$) and anodic ($E_{\lambda+}$) switching potentials, through which it was possible to assign the reactions corresponding to each peak or potential interval in the voltammograms. Additionally, through chronoamperometry, surface sulfur species formation was promoted and then characterized by voltammetry started in the negative direction. The authors reported that PbS oxidizes to elemental sulfur and Pb(II) in a potential range of 0.5 to 0.6 V vs. SCE, and that at potentials above 0.6 V vs. SCE, sulfur oxidizes to PbSO$_4$. It was found that the presence of elemental sulfur and PbSO$_4$ on the galena surface inhibits its dissolution, resulting in slow dissolution kinetics. This understanding is crucial for developing more efficient hydrometallurgical processes for lead extraction, based on inhibiting the stability of insoluble sulfur species.
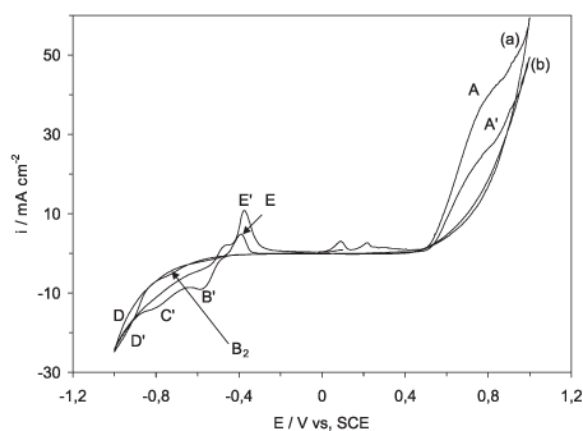

Fig. 2. Typical voltammograms obtained on CPE-galena (80:20 % weight) in 1.0 M HClO$_4$, (v = 100 mV s^{-1}). The potential scan was started in the direction: **(a)** negative and **(b)** positive. From reference [25]

Sphalerite (ZnS) Electro-Oxidation

Another mineral of economic interest is sphalerite, a zinc sulfide mineral. Cisneros et al [26] carried out a study of this sulfide mineral and reported difficulty in generating a voltammetric signal from this mineral, which was consistent with that reported by Alberg y Asbjörnsson [17]. Despite evaluating two samples of sphalerite, voltammetry did not yield significant results. Only through analysis by varying the switching potential were determined two potential regions: one at <0.5 V, where sphalerite oxidizes to form elemental sulfur and zinc cations, and the other at E>0.5 V, where the formed sulfur species were thiosulfate and sulfates (Fig. 3). However, a sequential mechanism could not be proposed. The studies were carried out in a 1.0 M NaClO$_4$ medium at pH 2, and it was observed that the iron content affects the conductivity of the sphalerite. However, the presence of pyrite in one of the samples (flotation concentrate) was not considered, therefore it was not possible to figure out the real effect of iron in solid solution with sphalerite. Hence, the main contribution of the sphalerite study was the application of anodic dissolution of sphalerite in perchloric acid and the effect of chloride ions on the oxidation of the mineral. The current recorded at different potentials versus the chloride content in the electrolyte allowed the generation of amperometric curves that defined two behaviors (Fig. 4). At potentials below 0.6 V, chloride enhances the dissolution process, which was associated with the porosity of elemental sulfur in the presence of these ions. At potentials where soluble

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sulfur species are generated, higher chloride content limits dissolution, which the authors attributed to the formation of zinc chloride precipitates.
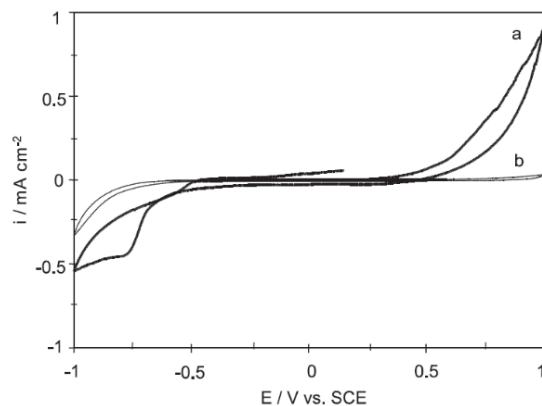

Fig. 3. Typical cyclic voltammograms obtained on CPE with different sphalerite samples (40:60 % weight) in 1.0 M NaClO$_4$ at pH 2, (v = 100 mV s^-1). The potential scan was started in the positive direction. **(a)** Sphalerite concentrate (13.8 % Fe in solid solution); **(b)** natural ZnS (0.43 % Fe in solid solution). From reference [26].
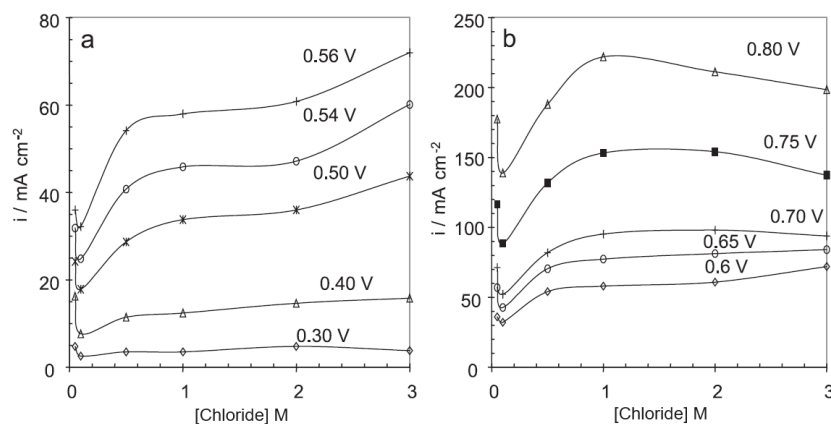

Fig. 4. Effect of chloride concentration on the voltammetric dissolution current of CPE-sphalerite (40:60 % weight), at the different potentials marked in the figure. Potentials were selected for the different oxidation stages: **(a)** when elemental sulfur is produced, **(b)** when S$_2$O$_3^{2-}$ and SO$_4^{2-}$ are produced. From reference [26]

This study was complemented by including a comparison of the electrochemical behavior of sphalerite and galena, since these minerals are generally associated in polymetallic sulfide deposits [28]. In the comparison of the voltammograms for both sulfides, a region of very low current is observed up to 0.6 V for both minerals (Fig. 5). Beyond this potential, the current increases, but it is much higher for galena. The authors concluded that the initial stage is similar for both minerals, forming elemental sulfur and dissolved cations. Subsequently, oxidized sulfur species are formed; however, the reactivity of galena in the second region is up to twice that of sphalerite, which could be due to its p-type semiconductor character, that has greater sensitivity to oxidation.
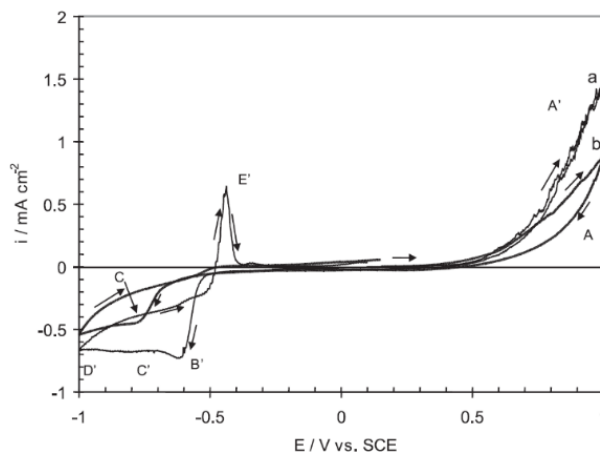
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Fig. 5. Comparison of the voltammograms of **(a)** CPE-galena (80:20 % weight) (thin line), with the corresponding voltammogram of **(b)** CPE-sphalerite (40:60 wt.%) (thick line), in 1 M NaClO₄, pH = 2. The scan was started in the positive direction, at 100 mV s⁻¹. From reference [28]

Zinc concentrate leaching

Currently, the production of a specific metal concentrate requires the application of complex flotation circuits to separate each one of the metallic sulfides present in the ore. Despite this, some mineral concentrates still contain impurities that represent drawbacks for the actual pyrometallurgical processes, either from an economic or environmental standpoint. This type of concentrates are denominated complex minerals concentrates. To establish the basis for alternative hydrometallurgical processes for complex zinc concentrates, an electrochemical study of this mineral was carried out by Nava et al [29]. The anodic dissolution mechanism of a complex zinc concentrate was studied using a more elaborated strategy combining several common electrochemical techniques with CPE-mineral. Voltammograms with CPE-complex zinc concentrate in 1.7 M H_2SO_4 electrolyte, starting the potential scan in both the negative and positive directions from the open circuit potential (Fig. 6), identified potential intervals where different components of the concentrate were activated. Chronoamperometry was applied at different constant anodic potential pulses for 180 seconds within the established potential ranges. The charge from chronoamperograms was integrated to construct an anodic charge versus electrolysis potential curve. From this data four potential zones, where the charge variations occur, were determined. Interestingly, the electro-dissolution of the concentrate is progressive and favored by increasing the applied potential. The authors attributed these trends to the oxidation of the various minerals in the concentrate.

The authors verified this by analyzing the different metals in the electrolyte and the modified surface of the CPE-zinc complex concentrate after each potential pulse. The dissolved metals in the liquor were analyzed using anodic stripping with thin-film mercury electrodes. The results identified electrochemical reactions during the oxidation of the complex zinc concentrate and how the release of Zn, Cd, Pb and Cu is dependent on the potential applied (Fig. 7). This provides a basis for selecting chemical or biological oxidizing agents that can selectively dissolve these metals sulfides from the concentrate, avoiding products that inhibit leaching.
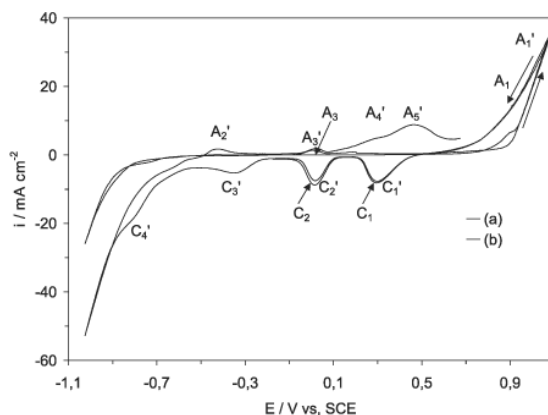
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Fig. 6. Typical voltammograms obtained on CPE-complex zinc concentrate (80:20 % weight) in 1.7 M H_2SO_4, (v = 100 mV s^{-1}). The potential scan started from the open circuit potential (- 21 mV) in the direction: **(a)** negative, **(b)** positive. From reference [29]
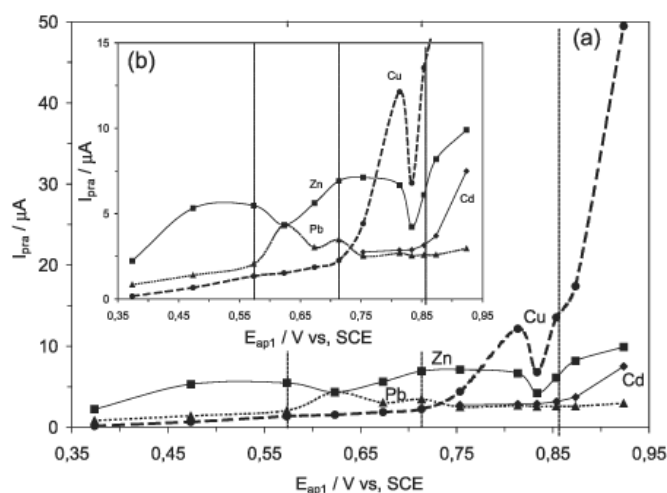

Fig. 7. (a) Anodic re-dissolution peak currents (I_{pra}), obtained in the liquor containing the different electro-dissolved metals (indicated in the figure) after the CPE-complex zinc concentrate (80:20 % weight) was oxidized at different potentials.[29]

Copper sulfide mineral reactivity

Copper sulfides are the main source of copper and among them the most relevant is chalcopyrite (CuFeS$_2$), as it is the main source worldwide. Unfortunately, CuFeS$_2$ is highly refractory in sulfate acid media under oxidizing conditions, hence, making it difficult to extract copper. Despite years of research on this mineral, for a long time there was no agreement on the cause of this unreactive behavior which was previously attributed to passivation due to formation of a sulfur layer. At the present time, it has been confirmed that it is due to a metal-deficient copper polysulfide that results from a solid-state transformation of the chalcopyrite surface during the oxidation reaction [30]. This was something that in fact, was exposed through CPE-CuFeS$_2$ in the study of Lázaro et al. [20] and it was further supported by a study of Nava and González [31,32] that coupled CPE-CuFeS$_2$ with anodic stripping voltammetry for a detailed characterization of the products formed at different potential regions. In this manner, these authors showed that the metal-deficient polysulfide was the

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main product at potentials lower than 1 V/SHE. More recently, the CPE technique has allowed electrochemical comparisons of mineral surface modification with organic agents and how this can improve dissolution of $CuFeS_2$ [33].

Likewise, the electrochemical behavior of three copper minerals, $CuFeS_2$, chalcocite (Cu_2S), and bornite (Cu_5FeS_4) in sulfuric acid has demonstrated that under similar dissolution conditions $CuFeS_2$ presents the lowest dissolution kinetics [34]. Electrochemical techniques, such as cyclic voltammetry and electrochemical impedance spectroscopy, analyzed the minerals' dissolution reactions and mechanisms. Bornite had the highest dissolution rate with less tendency for passivation, suggesting higher reactivity in sulfuric acid compared to the other minerals. Voltammetric curves indicated that chalcocite and not bornite is an intermediary product of chalcopyrite reduction and this was the result of comparing the reduction peak C2 shown in the voltammogram of Fig. 8, which is in correlation with results obtained with chalcopyrite [20].
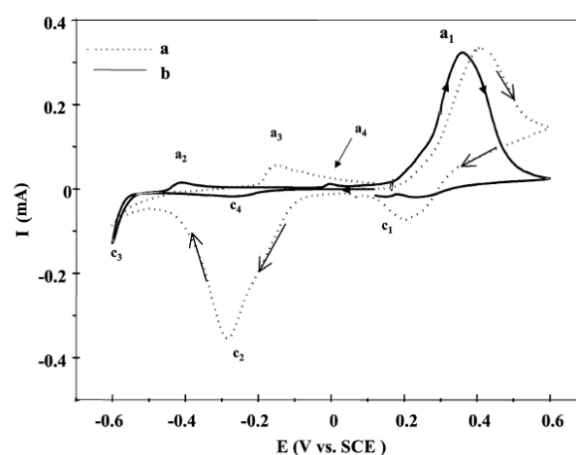

Fig. 8. Typical cyclic voltammograms obtained with chalcocite–CPE (20 wt.%, using silicon oil binder) in a 1 M H_2SO_4 solution, at v=20 mV s^{-1}. The scan potential was started in a different direction from open circuit potential (E_{OCP}=0.15 V/SCE): **(a)** positive direction; **(b)** negative direction. The arrows indicate the scan potential direction. From reference [34].

Silver minerals and cyanidation refractoriness

An interesting study compared the electrochemical behavior of silver mineral samples from different origins to study the refractoriness to cyanidation, a common leaching method [35]. Despite similar silver content, the samples differed in iron content and silver phases present. One sample contained diverse sulfosalts of silver like aguilarite, freibergite, polybasite, and hessite, while the other mainly contained acanthite. The study proved that the more complex mineral silver sample is less susceptible to electrochemical oxidation and thus more refractory to cyanidation than silver in acanthite (Fig. 9). This was demonstrated using electrochemical techniques and correlated with leaching studies, showing that silver in acanthite is more active to oxidation and easier to extract. This study provides a quick assessment of the refractory properties of silver minerals, beneficial for predicting extraction efficacy by cyanidation. In another study, the same author demonstrated that the reactivity of acanthite contained in this concentrate favors the voltammetric oxidation of pyrite due to a galvanic effect of the former on the latter [36]. This is because the rest potential (equilibrium potential) of acanthite is higher than that of pyrite. To prove this, the authors [35,36] compared the mineral sample responses before and after selectively leaching out the acanthite phase. The galvanic effect of acanthite can be observed also in comparison with Fig. 9, where the current of anodic oxidation occurs at a lower potential in Fig. 9**(a)** (with acanthite) compared to Fig. 9**(b)** (without acanthite). The galvanic effect enhances the reactivity of pyrite, which is one of the main species known as cyanicides in the cyanidation process.

About silver sulfosalts, in Mexico there are an important presence of this mineral in polymetallic ores. The unique properties of sulfosalts affect metallurgical processes like leaching and flotation. Understanding the

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reactivity and electrochemical behavior of silver sulfosalts is essential for optimizing silver recovery methods and improving metallurgical efficiency. Melendez et al [37] examined the reactivity of ruby silver minerals, proustite and pyrargyrite, using carbon-paste and paraffin-impregnated graphite electrodes. Samples were synthesized and characterized through various methods, including XRD and SEM-EDS.
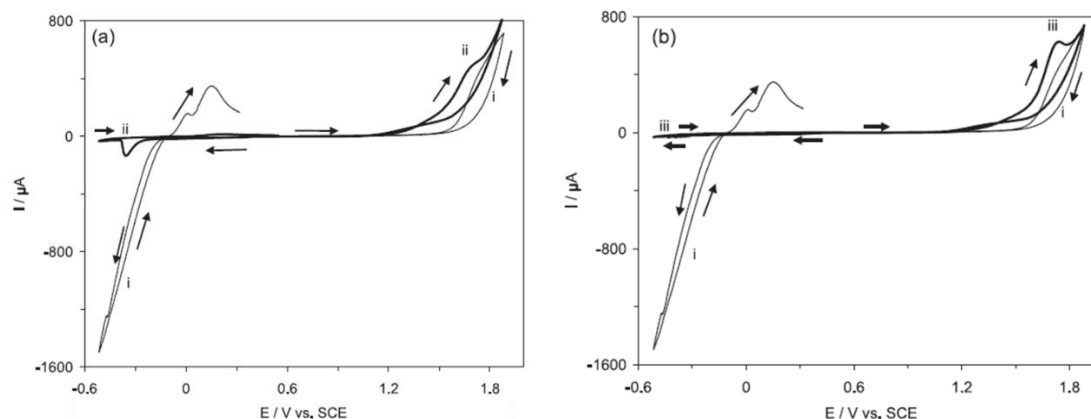

Fig. 9. Typical voltammograms obtained on CPE-mineral (70:30% weight) in 0.3 M NaCN at pH 10.60, (ν = 25 mV s^{-1}). The potential scan was started in the positive direction from the open circuit potential. **(a)** Pyrite concentrate with acanthite (ii), **(b)** Pyrite concentrate without acanthite(iii). Thin line, acanthite (i in a and b). From reference [35]

The investigation focused on the oxidation and reduction processes, influenced by the ligand-to-metal charge transfer transition. Despite differences in As and Sb content, the reactivity was similar due to the solid-state structures and oxidation states. The pnictogen (As or Sb) affected the conduction and valence band edges, modulating reactivity. Anodic dissolution and silver reduction processes were linked to specific band states, and the difficulty in dissolving these minerals in cyanide was attributed to the presence of AsS_3 and SbS_3 groups.

Assessment of sulfide mineral reactivity in mining residues

The commitment to sustainable development in mining involves the restoration and control of potential impacts during the various stages of a mining project. In precious and base metal mining from sulfides, an important aspect is assessing the environmental impact that solid waste, such as tailings or waste rock, can cause. A characteristic factor of sulfide systems is the generation of Acid Rock Drainage (ARD), which forms through the weathering of mining residues, resulting in acidic effluents with high iron and heavy metal content. With the aim of identifying the alteration processes occurring in sulfide minerals, primarily pyrite, a collaborative group of researchers from UAM-Iztapalapa, the Institute of Metallurgy at UASLP, and the University of British Columbia developed a strategy that successfully determined the factors and processes affecting the reactivity of iron sulfides from different mining sites and deposit types. This strategy yielded results comparable to those obtained using techniques defined by the relevant environmental standards.

Fig. 10 presents the voltammograms obtained for six samples of pyrite collected in different mining sites [38]. The typical response of pyrite is a low current zone followed by an abrupt increase of current associated with pyrite oxidation. It can be observed that each sample has unique features in the oxidation peak. From these responses a series of parameters were established, such as charge under the curve, current increase-to-potential ratio, and onset potential of oxidation (Table 1).

From the comparison of voltammetric response (Fig. 10) and the electrochemical parameters, it was proposed that Huckleberry pyrite was the most reactive among all the samples analyzed, and that the degree of

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reactivity of the pyrite samples decreased following the order: Huckleberry, Louvicourt 1, Zimapán, Tizapa, Louvicourt 2, and Brunswick. Therefore, since Brunswick pyrite was the least reactive, it presented the lowest I/E ratio [38].

In addition, the evolution of pyrite reactivity through alteration (weathering) process, were also evaluated from the changes in electrochemical parameters obtained for samples of pyrite with different alteration time and allowed for the determination of the effect of mineral texture and associations with other minerals on the reactivity of pyrite.
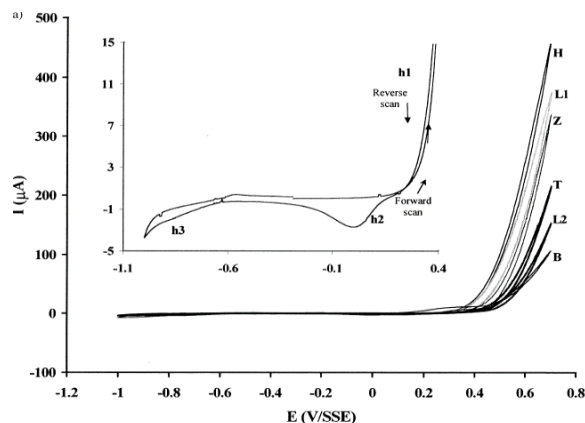

Fig. 10. Typical voltammograms obtained for pyrite samples from different origins: H, Huckleberry; L1, Louvicourt 1; L2, Louvicourt 2; T, Tizapa; Z, Zimapán; B, Brunswick. The voltammograms were obtained from a 50 % CPE-pyrite in 0.1M NaNO$_3$ at 20 mV s^{-1}. **(a)** Complete voltammetric response, **(b)** low current region of the voltammograms. From reference [38]

Table 1. Electrochemical parameters associated with the CPE-mineral voltammetric response for pyrite samples before (fresh) and after 4 and 10 weeks of weathering. The electrochemical characterization was carried out in 0.1 M NaNO$_3$. From reference [38].

Sample	OCP[a] (V)	E[b] $_{I=10 \mu A}$ (V/SSE)			I/E[c] Rate (µA/mV)			Q[d] (mC)		
		Fresh	4 weeks	10 weeks	Fresh	4 weeks	10 weeks	Fresh	4 weeks	10 weeks
Huckleberry	-0.27	0.37	0.43	0.43	1.86	1.38	1.37	5.84	3.27	3.16
Louvicourt 1	-0.27	0.40	0.46	0.49	1.54	1.20	0.71	4.52	2.79	1.57
Louvicourt 2	-0.19	0.49	0.43	0.46	0.70	1.24	0.94	1.50	3.15	2.17
Tizapa	-0.18	0.47	0.42	0.49	0.98	1.38	0.64	2.13	2.50	1.49
Zimapán	-0.17	0.44	0.46	0.47	1.47	1.22	1.25	3.47	2.79	2.18
Brunswick	-0.29	0.44	0.43	0.41	0.44	1.33	1.62	1.41	3.32	4.78

[a]OCP-Open circuit potential of CPE-fresh mineral
[b]I/E Rate - current increase as potential increase ratio
[c]E$_{(I=10mA)}$ - onset potential in forward scan for pyrite oxidation process
[d]Q – Charge evaluates from the area below the pyrite oxidation voltammograms

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The strategy previously described was also applied to pyrrhotite, another iron sulfide with common presence in Mexican mining residues [39]. For this mineral it was established that the formation of FeOOH and S^0 layers on the mineral surface was the main factor affecting reactivity. Identifying these factors would not have been possible with only knowledge of the samples mineralogical characteristics and the results from the application of kinetic tests. Finally, the strategy was validated by the study of mining residues from different sites, where it was confirmed the advantages of electrochemical techniques to determine the activity of sulfides under different mineral associations and weathering conditions [40].

Hence, knowledge of specific effects of each type of impurity on the oxidative capacity of the mineral, as well as the surface layers formed on the mineral, can be used as a basis for developing a method to assess and predict the potential for Acid Rock Drainage (ARD) from mining residues containing sulfide minerals (Fig. 11).
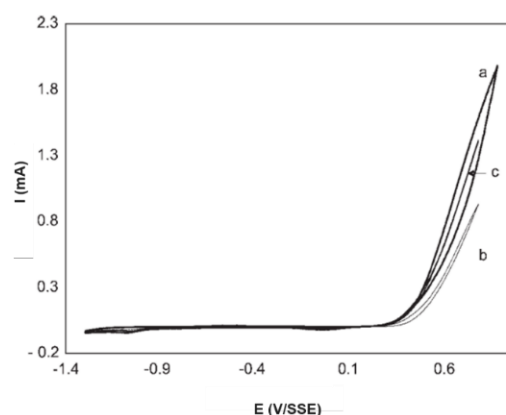

Fig. 11. Evolution of the voltammetric behavior of the mining waste sample at different alteration times: **(a)** unleached, **(b)** 2 weeks, and **(c)** 10 weeks. CPE-Mineral at 50 % in 0.1M NaNO₃. The potential scan was started in the positive direction at 20 mV s⁻¹. From reference [40]

Advancements in characterization techniques and electrochemical studies for understanding bacteria-mineral interaction in sulfide systems

Fifteen years after the initiation of electrochemical studies of minerals in Mexico, and with advancements and access to interface characterization techniques, it became possible to confirm the nature of the phases formed during the mechanisms predicted by electrochemical and thermodynamic diagram studies. With more options for spectroscopic and microscopy techniques, studies on bacteria-mineral interactions were again undertaken, which have gained interest due to the cost-effectiveness of bioleaching systems compared to other alternatives for the valorization of mining residues. Consequently, a series of electrochemical investigations on pyrite and chalcopyrite, the main minerals of interest in bioleaching, were developed and a summary of the works contributing to this are listed in Table 2 [41,42].

It must be noted that for the application of characterization techniques, it was necessary to use bulk electrodes. This was because, once the stages involved in the oxidative process were defined using CPME, the potentiostatic pulses needed to generate specific surface conditions on a bulk electrode of the mineral under study were determined. Spectroscopic and microscopic techniques permitted the definition, rather than just inference, of the mechanisms and surface products generated. Furthermore, by incorporating microbiological staining techniques, the conditions for the formation of biofilms from different bacterial strains, both on pyrite and chalcopyrite, were established.

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Influence of the surface speciation on biofilm attachment to chalcopyrite

The passivation of chalcopyrite is an industrial concern. It is considered that the redox potential of the solution must be controlled during leaching to avoid the formation of passive phases. Lara et al. [42] demonstrated that it is crucial to consider the interfacial potential rather than the bulk solution potential, as interfacial conditions include the biofilm/mineral system and its biological, chemical, physical, and electrochemical properties. Using traditional strategies in CPE-Mineral studies, four potential zones were established based on the chronoamperograms of chalcopyrite in CPE (Fig. 12).

Table 2. Summary of contributions to the understanding of Bacteria-Mineral Interaction in Sulfide Systems by Mexican researchers.

Authors	Paper title	Journal	Year/Ref
Lara et al	Influence of the sulfur species reactivity on biofilm conformation during pyrite colonization by *Acidithiobacillus thiooxidans*	Appl. Microb. Biotech	2012 [41]
Lara et al	Influence of the surface speciation on biofilm attachment to chalcopyrite by *Acidithiobacillus thiooxidans*	Appl. Microb. Biotech	2013 [42]
Saavedra et al	Interactions of mimic weathered pyrite surfaces (FeS2) with acidic culture media (0 K): An approach for (bio)leaching applications	Hydrometallurgy.	2018 [43]
Mendez-Tovar et al	Electrochemical monitoring of *Acidithiobacillus thiooxidans* biofilm formation on graphite surface with elemental sulfur	Bioelectrochemistry	2019 [44]
Saavedra et al	Attachment of *Leptospirillum sp.* to chemically modified pyrite surfaces. Fast and simple electrochemical monitoring of bacterial-mineral interactions	Hydrometallurgy.	2021[45]

Oxidative potentiostatic pulses defined for each zone were applied to massive chalcopyrite electrodes for one hour in sterile culture medium at pH 2 and Raman spectroscopy was employed to analyze superficial phases, while bacteria colonization was observed by SEM (Fig. 13). [42] In zone I, low oxidative capacity phases, such as S_n^{2-} (e.g., $Cu_{1-x}Fe_{1-y}S_2$), were obtained, where *A. thiooxidans* poorly colonized the electrode surface and did not form a biofilm. A progressive increase in cell density was observed on chalcopyrite surfaces with covellite and mainly S^0 in zones II and III. In zone IV, a well-developed and adherent biofilm with a high content of exopolysaccharides was formed. The cells of *A. thiooxidans* were embedded in the exopolysaccharides and partially covered by covellite (CuS) and S^0 aggregates. Covellite is generated as a secondary phase during chalcopyrite leaching and is then oxidized to S^0 and Cu^{2+}. The results confirmed that the activity of *A. thiooxidans* and biofilm formation in the presence of CuS and S^0 phases

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indicate that the biofilm structure results from surface speciation on chalcopyrite; this knowledge has contributed to understanding how cells interact with the surface and the environment in bioleaching systems.
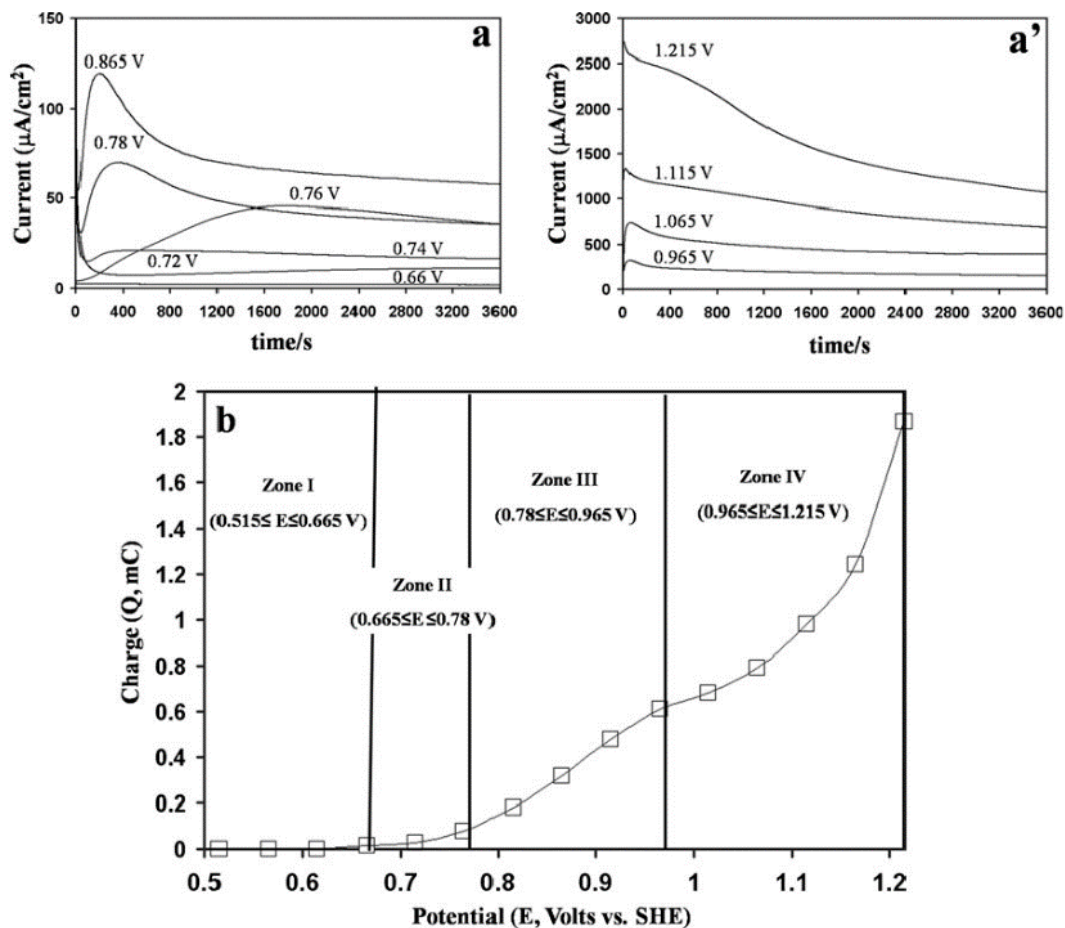

Fig. 12. Typical current transients obtained on unmodified bulk chalcopyrite electrode in ATCC-125 medium (pH 2). The applied potential pulse, E_{an}, is varied involving zones I, II, III, and IV from (a) and (a′). The applied potentials are indicated in the figure. **(b)** Charges as a function of the applied potential pulse, E_{an}. Q values were evaluated from the typical current transients obtained on unmodified MCE (a, a′). The different zones are indicated in the figure. From reference [42]
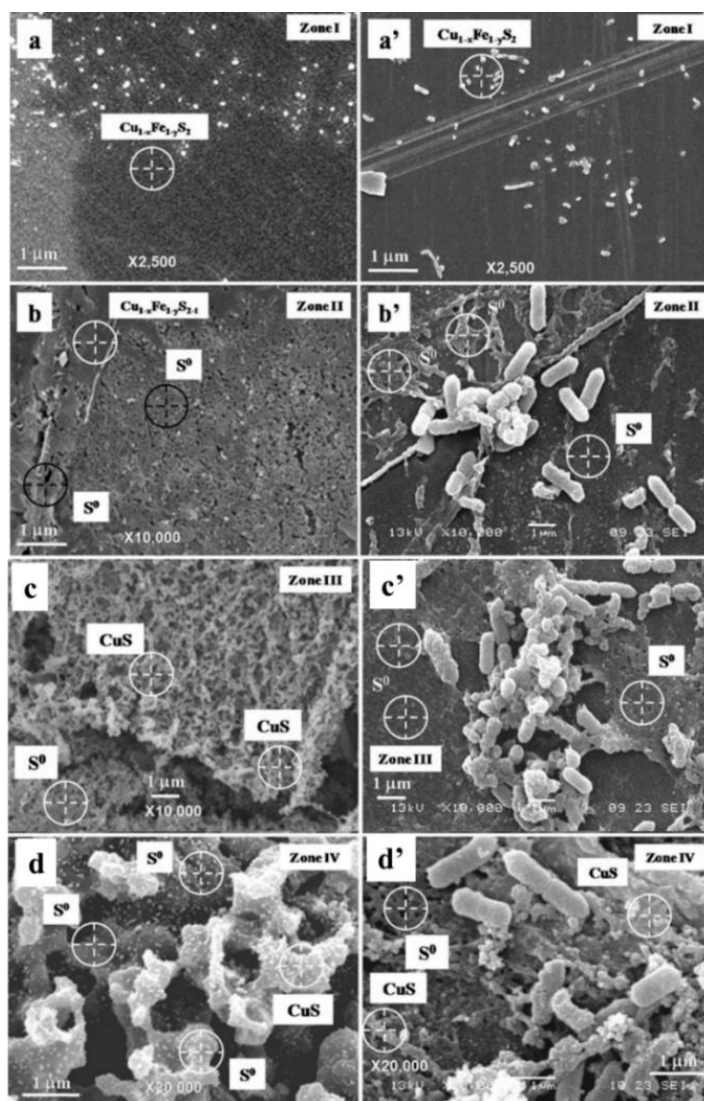
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Fig. 13. SEM images collected on abiotic leaching control samples **(a–c)** and surfaces from biotic assays (a′–b′, and c′) for electrooxidized chalcopyrite surface by application of E_{an} in each zone indicated. The main secondary phases are indicated in the figure, based on EDS analysis. From reference [42].

Electrochemical Monitoring of bacteria attachment to pyrite surfaces

　　　Despite the complexity of obtaining quality results in such a complex system as the electrolyte-bacteria-mineral, strategies were established, and electrochemical impedance spectroscopy studies were developed. These studies allowed the characterization of the properties of this triple layer interface. In a study focused on the adhesion of *Leptospirillum sp.* bacteria to modified pyrite surfaces, electrochemical impedance spectroscopy (EIS) was used to monitor this bacteria-mineral interaction. The objective was to develop a fast and simple method for evaluating bacterial adhesion to minerals, particularly in biohydrometallurgical processes [45]. The results showed significant changes in low frequencies depending on the chemical characteristics of the modified surfaces (Fig. 14). Nyquist diagrams showed varying complexities based on the chemical species at the pyrite and surface-modified pyrite interfaces. Additionally, the EIS allowed tracking of the initial steps of bacterial adhesion to pyrite electrodes, and a correlation was found between changes in phase

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angle measured by EIS and the number of adhered bacteria determined by direct counting. The spectra for pyrite and surface modified pyrite electrodes were fitted to different proposed equivalent electric circuits (Fig. 15) and in this way a quantitative relationship between the impedance spectra and surface states and the attachment of *Leptospirillum sp.* to electrode surfaces was established.

This study provided the basis for the development of sensors for rapid and multiplexed monitoring of bacterial adhesion in biohydrometallurgical processes.
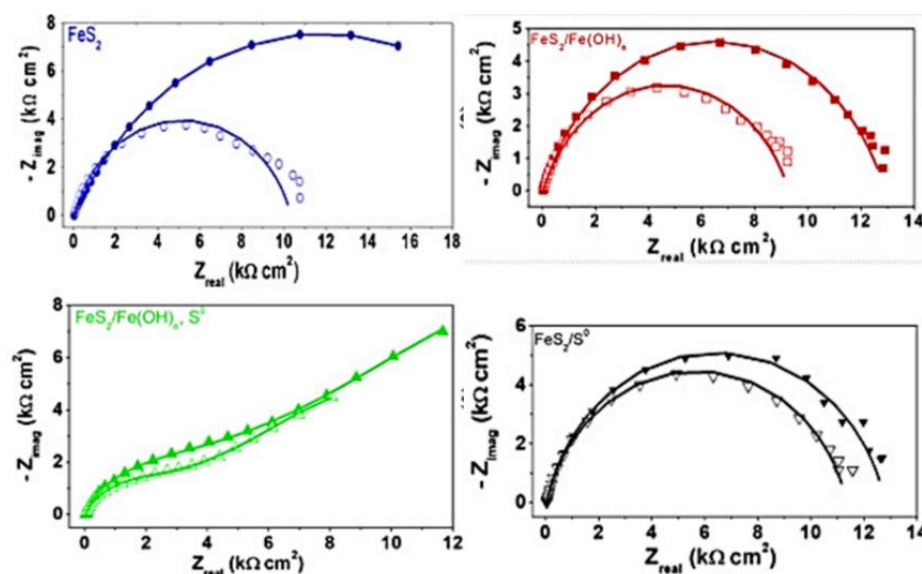
Fig. 14. Nyquist plots obtained for pyrite and pyrite modified electrodes (indicated in the figure). EIS were performed before (0 h, closed symbols) and after (6 h, open symbols) the addition of Leptospirillum sp. bacterium. Solid lines correspond to the equivalent electric circuit adjustment. 0K medium pH 1.8 was used as the electrolyte. From reference [45]
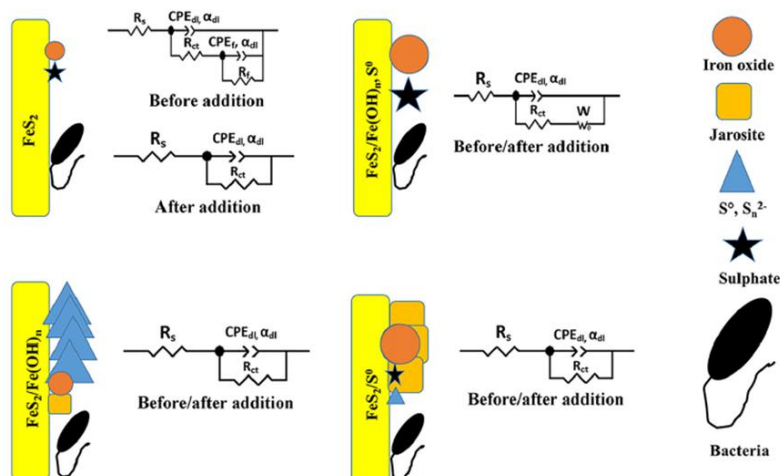

Fig. 15. Scheme describing interface conditions and their respective equivalent electric circuit assigned for the adjustment of impedance spectra shown in Fig. 14, for pyrite and surface modified pyrite electrodes. From reference [44]

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Comprehensive mexican contribution to the electrochemical study of sulfide minerals

In the earlier sections, we have highlighted the significance and main contributions to the electrochemical study of mineral sulfides by Mexican researchers. The reviewed documents are products generated during the training of some of these researchers at UAM-Iztapalapa, under projects led by Professor Ignacio González. Fig. 16 shows the historical production at UAM-Iztapalapa, as well as the output generated by researchers from Professor González's school, some still as collaborations with him but led by researchers at their respective universities. These universities include Universidad Autónoma de San Luis Potosí (UASLP), Universidad Autónoma del Estado de Hidalgo, Universidad Juárez del Estado de Durango (UJED), and outside of Mexico, Universidad Industrial de Santander in Colombia and Universidad de Buenos Aires in Argentine.

This co-generation of articles began in 2010 (Fig. 16), expanding fields of study or applying already established ones to conditions of interest in the states where the research groups in electrochemistry of metals and minerals are located. Examples include the work of a researcher at UJED on the alteration of mining residues in the calcareous environments of Mexico, and studies on the interaction of collectors and the effect of associations and water quality in flotation systems by the UASLP's mineral electrochemistry group. The production of articles in Mexico on this subject amounts to around 70 peer-reviewed articles, of which 70% have been published in JCR journals, and likewise, 70 % have been produced at UAM-Iztapalapa under the direction of Professor Ignacio González.

Although this number might seem low compared to topics developed by a larger number of research groups, it is important to note that the community dedicated to mining and extractive metallurgy is not very large and has decreased for two reasons: the migration to topics such as the synthesis and production of nanoparticles (adding value to metals and minerals) and the closure of mining companies in several developed countries, along with the belief that most research topics in this field were exhausted. However, the importance and impact of mining have been growing over the past 10 years (from 300 to almost 1300), as evidenced by the increase in the number of citations received by scientific outputs from our country (Fig. 16).
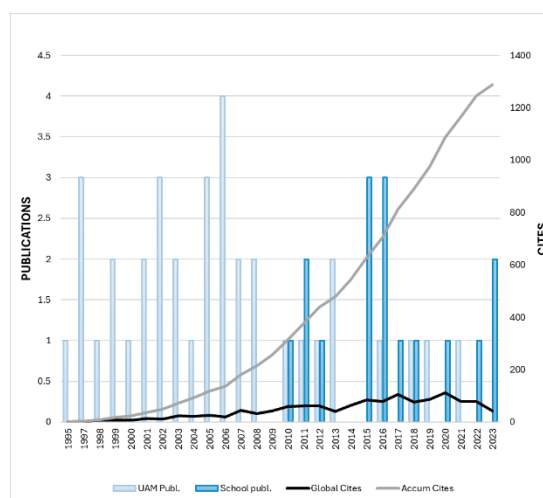

Fig. 16. Comprehensive production and citation generated from sulfide minerals electrochemistry research. Data compiled from Web of Science.

Effective strategies and methodologies have been developed to generate data essential for creating reaction models in both bio and hydrometallurgical systems at laboratory and industrial scales. The impact of water and energy conservation on the criticality of emerging metals for the energy transition requires the development of processes with low resource consumption. There are extensive opportunities for both

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fundamental and applied research in critical metal extraction processes, where chemists hold a significant advantage over other professions.

Conclusions

The brief account of the works here presented are a sample of the ways in which mineral electrochemistry research has contributed, impacted and transcended in the research field of mining operations, especially those involving mineral sulfides. It has been particularly important to highlight how some of the initial research results have matured and advanced through time because of UAM´s school and the relevance of continuing forming human resources in Mexico that are able to apply the techniques and research strategies that have been developed. The sustainability of many production processes depends on overcoming many challenges that are bound to the current complexity of valuable minerals, the demand of circular economy approaches and the more stringent environmental laws, hence mineral electrochemistry plays a key role in achieving the sustainability goal.

Acknowledgements

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