



RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

In Situ Characterization of the Locked Particle Behavior of Sulfide Minerals Using Non-Destructive Electrochemical Measurements

Sülfür Minerallerinde Bağlı Tane Davranışının Tahribatsız Elektrokimyasal Ölçümler Kullanılarak Yerinde Tayini

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Abstract

The flotation of sulfide minerals mostly depends on electrochemical reactions occurring on the mineral surfaces. Understanding the interaction mechanisms in the pulp is crucial for explaining the effects of different flotation chemicals on flotation performance. For this purpose, electrochemical techniques are used in the flotation of sulfide minerals by utilizing the semiconductor properties of these minerals. In this study, three non-destructive electrochemical measurements - open circuit potential (OCP), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) - were used to assess the electrochemical reactivity of the locked and liberated sulfide particles. Various combinations of mineral electrodes - Galena/Pyrite (0.52 cm²), Galena/Sphalerite (0.35 cm²), pure Galena (0.20 cm²), pure Sphalerite (0.80 cm²) and pure Pyrite (0.18 cm²) - were tested. A three-electrode electrochemical cell configuration was set up to investigate the electrochemical responses of the prepared electrodes. The changes in the surface chemistry of the mineral electrodes, in the presence (1×10⁻⁴ M NaEX) and absence of a collector were compared in detail. During the process, charge transitions occurred between the minerals in the locked particle mineral electrode due to galvanic interactions regardless of the surface area. Thus, the flotation behavior of the minerals changed by reducing and oxidizing each other. The present study suggests that the electrochemical methods may be an alternative technique to the conventional batch scale flotation tests as they can easily monitor the effect of any flotation reagents in the system causing possible reactions that may occur on sulfide mineral surfaces.

Keywords: Sulfide Minerals, Surface Chemistry, NaEX, Cyclic Voltammetry, Electrochemical Impedance Spectroscopy

Öz

Sülfürlü cevher flotasyonu çoğunlukla, mineral yüzeyinde oluşan elektrokimyasal tepkimelere bağlıdır. Çeşitli flotasyon kimyasallarının flotasyon verimine etkisini anlamak açısından, palp içerisindeki karşılıklı tepki mekanizmalarını açıklayabilmek önemlidir. Sülfürlü minerallerin yarı iletken özelliklerinden yararlanılarak kullanılan elektrokimyasal yöntemler ile flotasyon uygulamalarında bu mekanizmalar ortaya konabilmektedir. Yapılan bu çalışmada, üç farklı tahribatsız elektrokimyasal yöntem - Açık Devre Potansiyeli (OCP), Dönüşümlü Voltametri (CV) ve Elektriksel Empedans Spektroskopisi (EIS) - kullanılarak bağlı ve serbest tanelerin elektrokimyasal tepkiselliğini ortaya koymak hedeflenmiştir. Deneysel çalışmalarda kullanılmak üzere çeşitli mineral elektrotları - Galen/Pirit (0,52 cm²), Galen/Sfalerit (0,35 cm²), saf Galen (0,20 cm²), saf Sfalerit (0,80 cm²) ve saf Pirit (0,18 cm²) - hazırlanmıştır. Üç elektrotlu elektrokimyasal hücre düzeni kurularak, hazırlanan mineral elektrotlarıyla deneysel çalışmalar yapılmıştır. Mineral elektrotların yüzey kimyasındaki değişimler toplayıcı (1×10⁻⁴ M NaEX) ve toplayıcısız ortamda denenerak kıyaslanmıştır. Bağlı tane mineral elektrotundaki ölçümler sırasında ortaya çıkan galvanik etkileşim sebebiyle, minerallerin yüzey alanından bağımsız olarak yük geçişlerinin olduğu tespit edilmiştir. Minerallerin birbirlerini indirgeyip yükseltgemeleri, flotasyon davranışlarının da değişmesine sebep olmuştur. Mevcut çalışmada kullanılan yöntemler, ortamdaki herhangi bir flotasyon reaktifinin sülfürlü mineral yüzeyinde meydana gelebilecek olası tepkimelere neden olan etkisini kolayca ölçülebilmektedir. Bu sebeple elektrokimyasal ölçümlerin, kesikli laboratuvar flotasyon testlerine alternatif bir yöntem olabileceği düşünülmektedir.

Anahtar Kelimeler: Sülfürlü Mineraller, Yüzey Kimyası, NaEX, Dönüşümlü Voltametri, Elektriksel Empedans Spektroskopisi

1. Introduction

Electrochemistry is one of the tools used for the surface characterization of sulfide minerals and the assessment of the adsorption mechanisms of flotation reagents on sulfide minerals. Most sulfide minerals have semiconducting properties. Thus, surface changes and reagent adsorption occur mainly through electrochemical mechanisms [1]. The electrochemical properties of these minerals enable their use as electrodes [2]; therefore,

electrochemical techniques can easily be applied to these minerals.

A comprehensive understanding of mineral surface chemistry is crucial for explaining the flotation processes. Various factors, including reagent types (collectors, depressants, and activators), pH levels, and dissolved oxygen content, can significantly influence the surface reactions of minerals. To explain these reactions, several techniques have been employed, such as

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contact angle measurements, surface analytical techniques such as X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), Raman Spectroscopy, Fourier Transform Infrared Spectroscopy (FTIR), and electrochemical techniques [3–5]. While XPS provides valuable information about changes in the oxidation state of chemical elements on mineral surfaces, it is a costly and complex technique that requires extensive data processing. Simpler surface characterization methods, such as zeta potential and contact angle measurements, are also utilized for studying surface chemistry. However, it is essential to combine these techniques with other surface analytical methods to understand the interactions and species present on mineral surfaces in detail. Therefore, many researchers prefer electrochemical tools for the surface characterization of sulfide minerals, as they offer sensitivity, reproducibility, and high accuracy, enabling the in situ detection of surface layer formation on mineral electrodes. Surface responses of the minerals and problems in processes can be identified faster with electrochemical methods, which are also low cost compared to other techniques.

Some of the most common electrochemical techniques used in sulfide minerals are open circuit potential (OCP), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) [4,6]. The most beneficial part of the electrochemical method is being an alternative technique to the conventional batch-scale flotation tests for pre-screening of various flotation reagents.

OCP is an electrochemical technique often used to evaluate the resting potential of a system. This technique involves cathodic reduction of dissolved oxygen and oxidation of sulfide minerals [7]. In sulfide mineral flotation, OCP measurements are useful for monitoring changes either in the liquid phase or at the mineral/solution interface.

Electrochemical reactions at sulfide mineral surfaces are frequently investigated because the potential of a mineral is not always at an equilibrium state. In order to study such a dynamic state, it is necessary to follow the changes occurring when a certain amount of anodic or cathodic current has passed through the system. CV is a commonly used electrochemical technique to determine the reactions on the surface of sulfide minerals. In this technique, the potential of the mineral electrode is varied linearly at the desired rate using a potentiostat. When a current peak is observed during potential scanning, it can be used to identify the undergoing reaction.

EIS is based on the measurement of resistance and capacitance at the electrode surface and can be used to determine the species formed on mineral surfaces, regardless of the reaction type [8]. This analysis provides quantitative information about the conductance, dielectric coefficient, static properties of the interfaces of a system, and its dynamic change due to the adsorption mechanism, leading to the characterization of solid/liquid interfaces. As the formation of a non-conductive layer of oxides, hydroxides, elemental sulfur, or collector reagents causes an increase in resistance, EIS can be combined with the floatability of sulfide minerals.

Since the mineral-collector interaction is electrochemical, a sulfide mineral can be measured using the above-mentioned electrochemical techniques. Electrochemical methods can only be used successfully if there is measurable electron transfer due to the adsorption of collector molecules at the mineral electrode surface. EIS can be successfully used to measure the adsorption of different types of collectors on mineral electrode surfaces.

The effects of locked particles on flotation are thought to depend on the surface area of the mineral to be recovered [9]. However, galvanic interactions between minerals are observed in locked particles, regardless of the area [10]. Due to galvanic interactions, charge transitions between minerals have been observed [11]. Therefore, they reduce and oxidize each other, resulting in a change in the flotation behavior [12]. Investigation of the galvanic interactions of sulfide minerals by electrochemical techniques has been well documented by many researchers [13–15]. However, studies on the in situ electrochemical characteristics of sulfide minerals during galvanic reactions are limited, and further studies are required [7]. To our knowledge, the effect of the collector (NaEX) on frequently used sulfide minerals (pure Galena, pure Sphalerite, and pure Pyrite) and their locked particle (Galena/Pyrite, Galena/Sphalerite) behavior by simple, in situ process has not been presented by using electrochemical measurements so far.

The present study suggests a simple in situ method to understand the possible reactions occurring on the surface of sulfide minerals interacting with a collector using non-destructive electrochemical techniques. In this study, OCP, CV, and EIS techniques were performed in an alkaline solution (pH 9.2), where Galena, Pyrite, and Sphalerite electrodes were used to simulate free particles. Galvanic interactions occurring between the minerals and their effects on the surface chemistry were also investigated by simulating locked particle behavior. For this purpose, Galena/Pyrite and Galena/Sphalerite mineral pieces were paired to be in contact with each other and prepared binary-bounded mineral electrodes. The effects of sodium ethyl xanthate (NaEX) on the possible surface reactions were also studied.

A previous study [16] reported the surface changes in galena and pyrite minerals using electrochemical methods. In this work, in addition to these minerals, a pure sphalerite mineral and a binary bounded sphalerite mineral with galena were studied. The information gathered was then used to predict the equivalent circuit model.

2. Materials and Methods

According to their natural semiconductor properties, sulfide ores are adequate for obtaining reasonable electrochemical responses. For better electrochemical responses, the sulfide content of a mineral sample should be high. For this purpose, mineral electrodes composed of high purity sulfide ore samples (pure Galena, pure Sphalerite, and pure Pyrite) were tested to investigate the surface characteristics in this study.

Mineral electrodes were prepared as working electrodes by cutting a rectangular cross-section of the minerals (0.18-0.80 cm² geometric surface area) from a massive mineral specimen, mounting the mineral piece into an electrochemically inert epoxy resin, and placing it in a glass tube. The connection of the mineral electrode to the potentiostat/galvanostat was achieved using a copper wire.

In addition to the single use of mineral pieces in a mineral electrode, two sulfide minerals were also adhered to one another to simulate the locked particle behavior. For this purpose, Galena/Sphalerite and Galena/Pyrite mineral electrodes were also prepared. The mineral percentages present in the mineral electrodes are listed in Table 1.

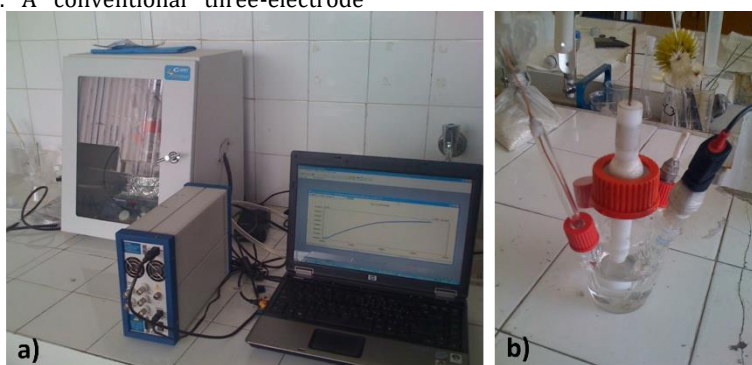
After each experiment, the surfaces of the mineral electrodes were polished with alumina paste to remove any contaminants for the next electrochemical process. After polishing the surface, the electrode was rinsed with distilled water and immediately transferred to a cell.

Table 1. Mineral content and geometric surface areas of the mineral electrodes.

Electrodes	Galena (%)	Pyrite (%)	Sphalerite (%)	Surface Areas (cm ²)
Galena	100	-	-	0.20
Pyrite	-	100	-	0.18
Sphalerite	-	-	100	0.80
Galena/Pyrite	50	50	-	0.52
Galena/Sphalerite	50	-	50	0.35

Gamry Reference 600 model potentiostat/galvanostat was preferred to perform electrochemical techniques in this work. To isolate the system from external noise, the potentiostat was placed in a Faraday cage. A conventional three-electrode

electrochemical cell was used for electrochemical measurements. The experimental setup of the electrochemical studies is shown in Figure 1.

**Figure 1.** Experimental set-up of the studies (a); a conventional three-electrode cell (b)

A saturated calomel electrode (SCE) as a reference electrode, a platinum plate electrode with a 1 cm² area as the counter electrode, and mineral electrodes (Galena, Sphalerite, Pyrite, Galena/Pyrite, Galena/Sphalerite) were used in the electrochemical cell.

The choice of pH for the buffer solution in electrochemical processes involving sulfide minerals is typically determined based on the collecting ability of the chemical, surface chemistry of the minerals, and stability of the collectors. Adjusting the solution pH to a specific range can also help control the activation or depression of unwanted minerals or impurities. For NaEX and other xanthate collectors commonly used for sulfide minerals, a pH of approximately 9-10 is often preferred. In this pH range, the collector molecules are ionized, and their hydrophobic properties are enhanced, allowing them to adsorb onto the sulfide mineral surfaces more effectively [17]. Thus, sulfide minerals exhibit maximum floatability or optimal charge conditions. In this investigation, a buffer solution (pH 9.2) of sodium tetraborate decahydrate (0.05 M Na₂B₄O₇·10H₂O, Merck ≥ 99.5%) at room temperature (~25 °C) was used to maintain the pH value at the same level during the measurements and to prevent possible pH changes as a result of the reactions between the minerals and the solution. The pH of the buffer solution was determined to be 9.2, and all electrochemical experiments were performed only at this pH.

Before each run for 15 minutes, high-purity nitrogen gas was introduced into the cell for intensive bubbling through the buffer solution to eliminate fluctuations during measurements due to oxygen present in the system. During the electrochemical measurements, the nitrogen flow was stopped, and the cell was completely sealed to prevent the diffusion of atmospheric oxygen into the system.

Xanthate collectors have found widespread application in the flotation processes of valuable minerals, particularly in the recovery of base metal sulfides [18]. It has been reported in the literature that xanthates have the highest rate of adsorption on pyrite samples compared to other types of collectors [19]. In electrochemical techniques, NaEX is commonly preferred for sulfide minerals because of its selectivity, stability, and low cost [20]. In this study, NaEX (CH₃CH₂OCS₂Na, Metsop ≥ 90%) was selected as the collector to gain insight into the specific reactions that may occur on the surface of sulfide minerals during their interaction with the collector.

To investigate the possible electrochemical reactions upon adsorption and oxidation of the collector on the mineral surfaces, electrochemical methods were studied in the absence and presence of a certain amount of collector. The NaEX concentration was adjusted to 1×10⁻⁴ M since this concentration has been commonly employed in flotation studies and has widespread applications in the literature [21–23].

In this study, electrochemical techniques such as OCP, CV, and EIS methods were performed to investigate the changes in the surface characteristics of the locked and liberated particles. The OCP values of the mineral electrodes were recorded continuously for 30 min at pH 9.2. The CV was scanned through three cycles at a scan rate of 20 mV/s. EIS experiments were performed in the frequency range of 1×10⁵ to 1×10⁻² Hz. The obtained EIS data of the prepared mineral electrodes in the absence and presence of NaEX were fitted to an equivalent electrical circuit model using Gamry Echem Analyst software. The design of each mineral electrode is illustrated together with the fitted equivalent circuit model given in Figure 2.

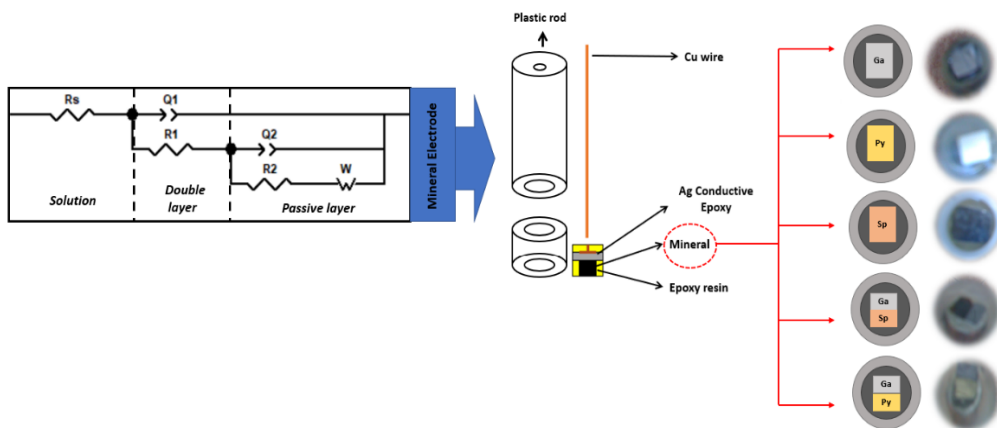


Figure 2. The equivalent circuit model for modeling the EIS data of the mineral electrodes and schematic representation of the mineral electrodes

3. Results and Discussion

The electrochemical responses of the mineral electrodes (Galena, Pyrite, Sphalerite) were studied in the absence and presence of 1×10^{-4} M NaEX using three methods: OCP, CV, and EIS measurements. To observe oxidation/reduction reactions between the locked particles and their possible galvanic interactions, two mineral pieces were glued together to produce two more electrodes (Galena/Pyrite and Galena/Sphalerite). The adsorption of the 1×10^{-4} M NaEX collector was also investigated in all the above-mentioned mineral electrodes using the same electrochemical techniques.

3.1. Electrochemical responses of the mineral electrodes in terms of the OCP technique

The OCP values of the mineral electrodes (Galena, Pyrite, and Sphalerite) and those coupled with the galena electrodes (Galena/Pyrite, Galena/Sphalerite) were recorded as a function of time, as shown in Figure 3. The OCP measurements of the samples were performed to compare their electrochemical reactivities in the absence (Figure 3a) and presence (Figure 3b) of the collector. The absence of a collector during the experiments is denoted as "Nil" in the figures.

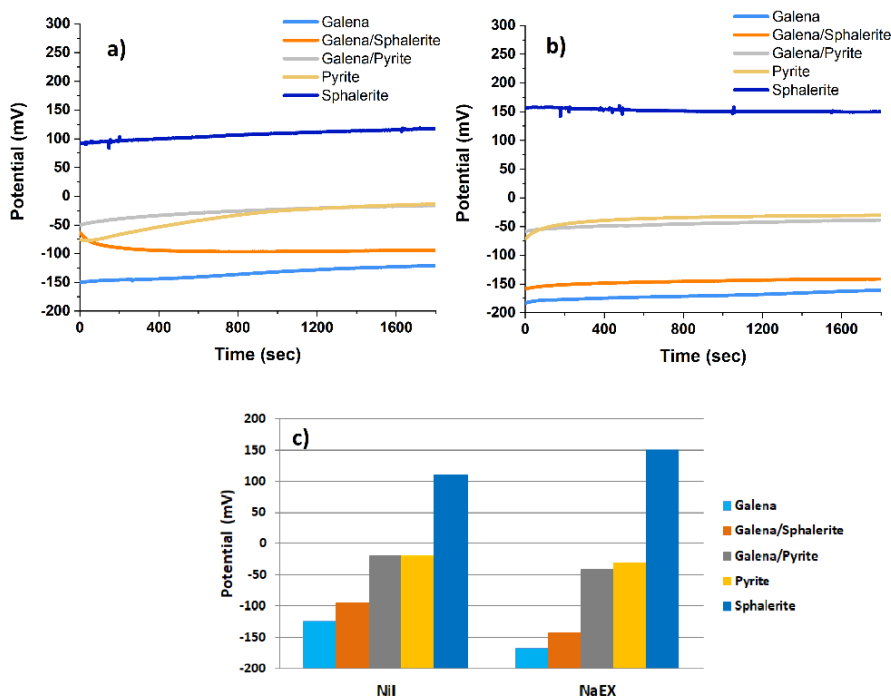


Figure 3. Open Circuit Potential measurements of the mineral electrodes in the absence (a), presence of the collector (NaEX) (b), and graphical comparison of the OCP results (c); Nil: absence of collector; NaEX: presence of collector

According to the OCP results, all mineral electrodes showed less variation in potential value after initiation for approximately ten minutes. This indicates that a passive film spontaneously formed on its surface. Galena electrodes had lower OCP values than other mineral electrodes under both collector adsorption and collectorless conditions. When the Galena electrode was coupled

with Pyrite and Sphalerite electrodes, the OCP values were between those of Galena and their coupled electrodes. The obtained results are in good agreement with the mixed potential theory. Liu et al. (2018) have obtained a similar potential time profile when the chalcopyrite electrode was coupled with the pyrite electrode [7]. However, the voltage values decreased

regardless of the mineral type when a collector was present in the system (Figure 3c). However, the Sphalerite electrode showed a different response. Additionally, this electrode had much higher voltage values than any other mineral electrode in both experiments. This indicates that the Sphalerite electrode is more electrochemically reactive than the other tested mineral electrodes, thus eliminating the individual usage of Sphalerite in the upcoming tests. Instead, only those locked with galena were chosen for further study. Further tests to reveal the surface characteristics of the other mineral electrodes were performed based on the CV and EIS test results.

3.2. Electrochemical responses of the mineral electrodes in terms of the CV technique

Comparative voltammetric studies were performed to identify galvanic interactions. All CV measurements were taken in three cycles, and the scan rate was determined to be 20 mV/s. All potential values reported in this study were converted to the

standard hydrogen electrode (SHE) scale by adding 245 mV to the saturated calomel electrode (SCE) readings [24]. Figure 4 represents the voltammograms of the mineral electrodes in the absence of any collector and in the presence of 1×10^{-4} M NaEX. In the cyclic voltammogram obtained without collector addition, Galena (collectorless) had a very narrow response interval in terms of current density over the whole potential range (-0.80 V to +0.40 V vs SHE).

When the scanning potential was initiated in the positive direction in the presence of the collector, an oxidation process where one small peak that begins near 0.20 V was observed (Figure 4a). This indicates the oxidation of Galena to form PbX. In the cyclic voltammograms of the Pyrite electrode, as the scanning potential became negative, a reduction peak was observed at nearly -0.450 V both in the presence and absence of a collector. A more apparent peak in the oxidation phase was observed at -0.365 V in the presence of the collector (Figure 4b).

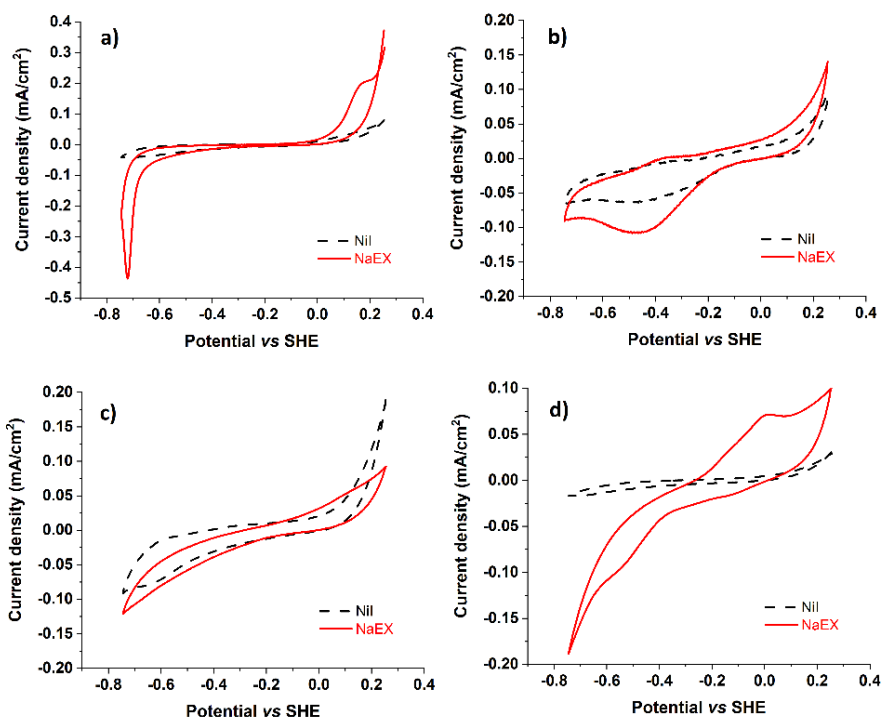
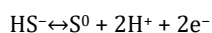
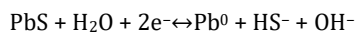


Figure 4. Cyclic voltammograms of Galena (a), Pyrite (b), Galena/Pyrite (c), and Galena/Sphalerite (d) minerals in the presence and absence of the collector (NaEX); Nil: absence of collector; NaEX: presence of collector

It is known that galena is thermodynamically unstable, and it reduces to the metallic form according to the galvanic interaction model shown in Figure 5. The reactions are as follows:



Therefore, the peak of the oxidation reaction almost disappeared and was barely detectable. In addition, S^0 is not stable at high potential values, and oxidation causes the formation of porous thiosulfate and sulfates [25].

To identify the different processes in the locked particles involved in galena oxidation, voltammetric studies were carried out using Galena/Pyrite and Galena/Sphalerite mineral electrodes. Typical voltammograms of the positive scans on these electrodes are shown in Figure 4c and 5d. Peaks in the Galena/Pyrite and Galena/Sphalerite electrodes are related to the formation of PbX on the electrode surface by anodic oxidation

of the galena surface in the presence of the collector. The analysis of the voltammograms obtained in those conditions showed that the galena oxidation was associated with peaks at 0.20 V, 1.20 V, and 0 V in the mineral electrodes of Galena, Galena/Pyrite, and Galena/Sphalerite, respectively.

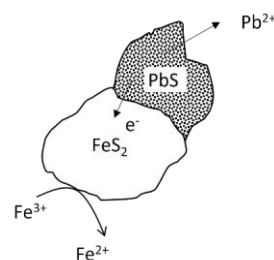


Figure 5. The galvanic interaction model for the pyrite-galena locked particle during flotation

3.3. Electrochemical responses of the mineral electrodes in terms of the EIS technique

The differences between the surface characteristics of the studied mineral electrodes were also indicated by EIS measurements. The EIS test results for the different mineral samples are presented as Bode diagrams (in the form of Bode-Magnitude and Bode-Phase Angle) and Nyquist plots in the presence and absence of the collector, as shown in Figure 6. When the Bode diagrams were evaluated at the lowest frequency (0.01 Hz), the Galena electrode exhibited the highest Z_{mod} value among the other electrodes, indicating the lowest rate of adsorption. The Nyquist plot in Figure 6 exhibits a semicircular shape that is not fully formed. This incomplete semicircle suggests that the processes of mineral electrode oxidation and NaEX adsorption are primarily influenced by the charge transfer mechanism [26]. This EIS result is also compatible with the obtained OCP and CV results and shows a slightly inferior electrochemical reactivity compared to the other mineral electrodes.

There were significant differences when the collector was absent or present in the system, especially in the Galena and

Galena/Sphalerite electrodes. The results also help interpret the collector adsorption mechanisms, as at low frequencies, high phase angle values imply that the adsorption rates are low and diffusion-controlled [19]. This effect is more evident in the Nyquist plot for the Galena/Sphalerite electrode, where the radius of the semicircle curve of the electrode is notably greater in the presence of NaEX than in its absence.

The adsorption mechanisms of various reagents on sulfide minerals via electrochemical techniques have been investigated by many researchers [27–31]. To explain the surface characteristics of mineral electrodes, different equivalent circuit models can be used to describe the processes occurring on the electrode surfaces (mineral/collector/electrolyte junction). The Z_{mod} values at higher frequencies were typically low and mostly constant, reflecting the solution resistance. At medium frequencies, the relationships between Z_{mod} and the frequencies were linear. This explains the capacitive behavior caused by the electrical double layer at the mineral/solution interface and adsorption of NaEX [32].

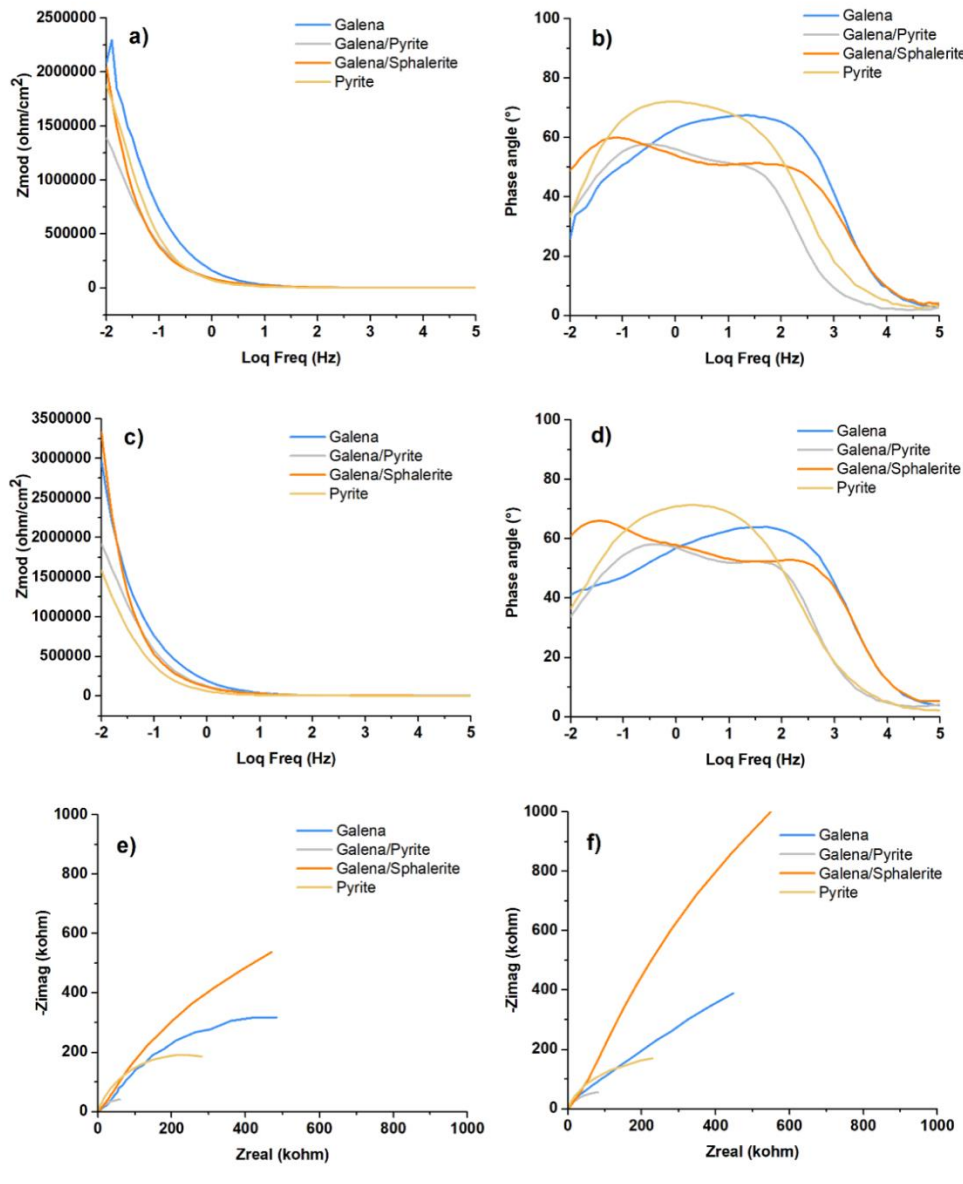


Figure 6. EIS results of all the studied minerals in the absence (a, b) and presence (c, d) of NaEX as Bode diagrams and in the absence (e) and presence (f) of NaEX as Nyquist diagrams

In this study, the equivalent electrical circuit model (Figure 2) with the smallest chi-square (χ^2) value ($\leq 1.09 \times 10^{-3}$) was chosen, as given in Table 2. Hence, the minimum errors of each element parameter were obtained. This equivalent model consists of a solution resistance (R_s), double-layer capacitance ($Q_{1,2}$), charge transfer resistance ($R_{1,2}$), and Warburg (W) element. Q is represented in terms of a constant phase element (CPE) that indicates a nonhomogeneous surface [4]. The charge transfer reactions are related to the electrochemical process, which occurs on the electrode surface and helps explain the adsorption of the collector. This is represented by R_{ct} , which explains the formation of the collector layer.

To compare the collector adsorption behavior of the prepared electrodes, the EIS spectrum of each experiment was fitted to the equivalent electrical circuit model, and their fitted electrochemical impedance element parameters are summarized in Table 2. The net rates of the electrochemical reactions on the electrode surfaces are represented by R_{ct} and are inversely proportional to the adsorption capacity of the collector [33]. The calculated R_{ct} values, which were compared to explain the mineral behavior in the absence and presence of the collector, are given in Figure 7.

Table 2. Fitted electrochemical impedance element parameters for the prepared mineral electrodes. (The equivalent electrical circuits used for modelling the EIS data are presented in Figure 2.)

Electrodes	R_s	R_1	Q_1	n_1	Q_2	n_2	R_2	W	Chi-squared/ χ^2
	$\Omega \cdot \text{cm}^2$	$\Omega \cdot \text{cm}^2$	$S \cdot \text{cm}^{-2} \cdot s^{-n}$		$S \cdot \text{cm}^{-2} \cdot s^{-n}$		$\Omega \cdot \text{cm}^2$	$\Omega \cdot s^{-1/2} \cdot \text{cm}^{-2}$	
<i>Collectorless</i>									
Galena	2.52×10^1	6.67×10^2	1.81×10^{-5}	0.86	2.54×10^{-5}	0.57	1.57×10^5	3.93×10^{-3}	5.26×10^{-4}
Galena/Sphalerite	1.15×10^2	6.41×10^3	1.31×10^{-5}	0.72	9.29×10^{-6}	0.81	5.43×10^3	7.43×10^{-6}	2.21×10^{-3}
Galena/Pyrite	8.77×10^1	1.22×10^3	4.52×10^{-5}	0.82	7.94×10^{-5}	0.69	6.24×10^4	2.06×10^{-3}	2.18×10^{-4}
Pyrite	2.39×10^1	2.57×10^1	9.22×10^{-5}	0.81	2.55×10^{-10}	0.98	9.92×10^4	5.14×10^{-2}	1.09×10^{-3}
<i>$1 \times 10^{-4} M NaEX$</i>									
Galena	2.99×10^1	2.10×10^4	2.50×10^{-5}	0.77	3.21×10^{-12}	0.86	5.25×10^{-1}	3.05×10^{-5}	2.22×10^{-3}
Galena/Sphalerite	1.02×10^2	2.72×10^3	6.43×10^{-6}	0.78	2.32×10^{-5}	0.61	2.42×10^3	9.03×10^{-6}	1.39×10^{-3}
Galena/Pyrite	6.91×10^1	1.46×10^3	3.08×10^{-5}	0.80	5.40×10^{-5}	0.70	7.80×10^4	4.21×10^{-4}	4.33×10^{-4}
Pyrite	2.12×10^1	2.51×10^1	6.94×10^{-5}	0.80	3.93×10^{-5}	0.83	7.04×10^4	5.89×10^{-4}	2.08×10^{-4}

According to the R_{ct} values calculated in Figure 7a, the interaction between the Galena/Sphalerite mineral electrode and NaEX has the lowest R_{ct} , which indicates a higher rate of adsorption of the collector. In other words, it was less resistive and more capacitive than the other mineral electrodes. The EIS analysis results are compatible with the results of OCP and CV, which confirm that NaEX adsorption occurred at a much faster rate with the

Galena/Sphalerite mineral electrode. In addition, the R_{ct} values of the pure Galena and Pyrite electrodes decreased with the addition of NaEX, indicating the occurrence of collector adsorption. However, the Galena/Pyrite electrode showed a completely different adsorption behavior in the presence of NaEX.

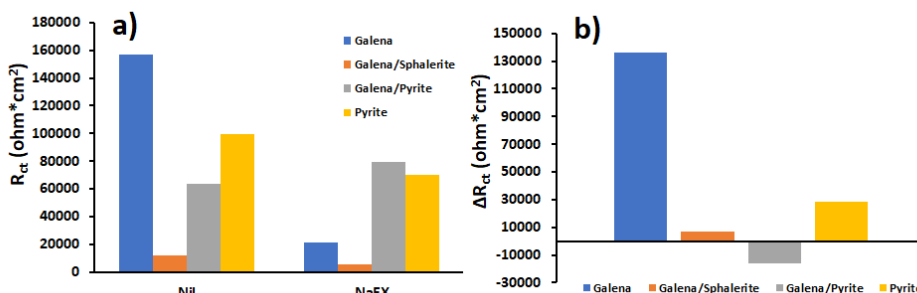


Figure 7. Comparison of the total resistance (R_{ct}) values (a) and their differences in R_{ct} (ΔR_{ct}) values (b) of the collector (NaEX) tested with the different mineral electrodes at pH 9.2; Nil: absence of collector; NaEX: presence of collector

The difference in R_{ct} of “Nil” and “NaEX” (ΔR_{ct}) was calculated to better comparison of the rate of adsorption of NaEX, given in Figure 7b. It can be seen that the ΔR_{ct} of the prepared electrodes

has a positive value, except for the Galena/Pyrite electrode. This also shows that the collector molecules could adsorb onto the surface. The reason for the different behavior of the

Galena/Pyrite electrode may be the galvanic effect. Liu et al. (2018) demonstrated that galvanic interaction occurs when pyrite and galena are present together, and galena with a lower OCP value dissolves anodically [10]. On the other hand, better adsorption of NaEX on galena together with sphalerite can be attributed to the galvanic protection offered by sphalerite on galena, thereby avoiding its free oxidation [12]. It could be concluded that higher adsorption of NaEX is reached in the presence of the Galena/Sphalerite electrode, while Galena/Pyrite shows less adsorption behavior due to the galvanic interaction.

4. Discussion

Electrochemical methods are important for controlling the flotation kinetics of sulfide minerals. Methods such as OCP, CV, and EIS help to gain an understanding of the relevance of galvanic interactions between locked particles, as it is an extensive consideration in assessing interactions between different sulfide minerals.

The presence of minerals, mineral associations, or chemicals in the process can change the electrochemical conditions in the pulp, which affects the flotation kinetics.

For example, the presence of galena in the system allows the observation of sphalerite oxidation, which cannot be observed with pure sphalerite alone.

It was revealed that the electrochemical reactivity of sulfide minerals and galvanic interactions favor the oxidation of electrochemically reactive minerals over other minerals in sulfide mineral flotation. The electrode potentials also indicate a decrease or increase in the reactivity of the minerals.

The use of electrochemical measurements in sulfide flotation can be described as a simple and feasible way to present the change in surface properties while changing the chemical conditions in the pulp.

5. Conclusions

The surface changes of the pure mineral electrodes (Galena, Pyrite, Sphalerite) and locked-particle electrodes (Galena/Pyrite, Galena/Sphalerite) were observed using OCP, CV, and EIS methods.

Galvanic interactions play a major role in the locked-particle electrode surfaces and completely change the surface properties. When two sulfide minerals interacted with each other in the bulk solution as locked-particle electrodes, it was observed from the measured electrochemical techniques that their responses changed compared to the liberated pure mineral electrode responses.

The collector (NaEX) adsorption efficiencies and adsorption rates on the electrode surfaces were evaluated as a result of the electrochemical responses obtained from the measurement techniques. Despite the higher adsorption rate of NaEX on the Galena/Sphalerite electrode, less collector adsorption behavior was observed on the Galena/Pyrite electrode surface. This behavior indicates that the presence of pyrite in the system caused a decrease in galena reactivity. This was attributed to galvanic interactions on the mineral surfaces, thereby avoiding free oxidation.

Consequently, this study showed that EIS is a very promising technique to understand the possible reactions occurring on the surface of sulfide minerals interacting with flotation reagents. This method can be used as an alternative to conventional batch-scale flotation tests for monitoring instant changes at the mineral/solution interface. Further in situ electrochemical studies can be performed using various flotation reagents

(collectors, activators, depressants, and/or their mixtures) on different sulfide mineral electrodes.

Ethics committee approval and conflict of interest statement

This article does not require ethics committee approval.

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Author Contribution Statement

Damla Izerdem (1): Material preparation, laboratory studies, writing the first draft of the manuscript.

Zeliha Ertekin (2): Writing the latter version of the manuscript, fitting the EIS parameters using the software.

All authors read and approved the final manuscript.

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