

The electrochemical study of pyrite oxidation in the presence of ozone

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ABSTRACT

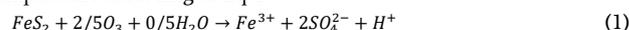
Ozone is an environment-friendly and effective oxidant in oxidizing resistant minerals. Studies show its favorable effect on pyrite leaching. However, the effect of ozone from the electrochemical perspective is not well-known. This study aims to investigate the impact of ozone on pyrite oxidation from an electrochemical perspective. OCP increased when oxidizing species were present. This increase may be attributed to a rise in the concentration of the oxidizing agent in the electrolyte. CV showed the formation of a weak anodic peak in the potential range of 0.3 to 0.5 V, indicating incomplete surface oxidation in the absence of oxidizing. Also, the increase in the intensity of anodic peaks in the pyrite oxidation condition and the presence of ozone compared to the absence of oxidizing confirmed the improvement of oxidation conditions. In the absence of ozone, the presence of two cathodic peaks C₁ and C₂ at potentials of 0.45 and -0.3 V, respectively, indicated the reduction of oxidation products, and it is expected that intermediate species, such as FeS and H₂S were formed. In the conditions of acidic solution saturated with ozone, the cathodic peak C₂ was attributed to the reduction of ozone and oxygen adsorbed on the pyrite surface. Because ozone and saturated oxygen in the solution are more prone to accept electrons compared to oxidation products and intermediate species. Finally, the morphology of the pyrite surface remaining from the electrochemical test was examined by FESEM analysis, which confirmed the effect of ozone on the corrosion of the pyrite surface.

Keywords: Ozone, Pyrite, Oxidation, Electrochemical, Cyclic voltammetry.

1. Introduction

Pyrite is the most abundant sulfide mineral and is frequently found as gangue with other sulfide minerals, such as chalcopyrite, sphalerite, galena, and cobalt. Pyrite ordinarily contains precious metals, such as gold and silver [1, 2]. Primary sulfide minerals, such as pyrite require the presence of oxidants for effective dissolution [3]. Many studies have investigated the oxidation of pyrite and observed its behavior in the presence of various oxidants. It has been appeared that the oxidation of pyrite in acidic media is related to both chemical and electrochemical properties [4, 5]. The nature and extent of the reaction between pyrite and oxidants in aqueous media are highly related to the potential and pH of the solution, and electrochemical studies can determine the surface properties and the extent of dissolution or formation of a passive layer on the surface [4]. Some researchers have reported that at a potential of less than 0.5 V (vs. SCE), the electrode surface is covered with elemental sulfur and Fe(OH)₃, which leads to limited penetration of the oxidizing agent to the surface, and by increasing the potential to 0.6 V (vs. SCE), the amorphous sulfur-rich layer on the surface is converted to S₈, which improves the oxidation conditions. Also, increasing the potential to values higher than 0.7 V (vs. SCE) leads to the formation of Fe(OH)₃ and SO₄²⁻ species, along with polysulfides and an iron-rich layer in the form of FeO and Fe₂O₃ on the surface [6, 7]. In a study, it was reported that at low anodic potentials (0.4 to 0.6 V SCE), Fe_{1-x}S₂ and Fe(OH)₃ species and a layer rich in elemental sulfur were formed on the mineral surface, which controlled the diffusion process, and by increasing the potential to over 0.7 V, sufficient potential was provided to completely oxidize pyrite and the inhibitory species that had already formed on it. At potentials higher than 0.9 V (vs SCE), extensive oxidation of pyrite also occurred [8]. Several oxidants have been

investigated to provide the potential and improve the oxidation conditions of pyrite, the most important of which is Fe III. Fe III can increase the rate of the oxidation process, on the other hand, its reaction with sulfide minerals can lead to the formation of an inhibitory layer containing polysulfides and elemental sulfur that prevents the penetration of the reactant species into the surface and slows or stops the process [2, 8, 9]. Subsequently, the utilization of an oxidant with high effectiveness, reasonable energy, and negligible environmental problems is essential. Ozone, with its unique properties, such as a potential of 2.07 V in acidic media, may be a promising oxidant in the acidic dissolution of pyrite, which can be produced in situ, has suitable kinetics, and minimal environmental impacts [3, 10]. Due to its high oxidation power, ozone is thermodynamically capable of dissolving pyrite in a sulfuric acid medium and at temperatures close to ambient temperature according to Eq. 1:



In this paper, the oxidizing behavior of ozone on the dissolution of pyrite surface is investigated using electrochemical techniques. For this purpose, the ozone utilized was present as saturated micro-nanobubbles within an aqueous solution. Cyclic voltammetry was used to detect the reduction reactions and possible products formed. In addition, Eh-pH diagrams of pyrite can predict the products formed during the oxidation-reduction process at a given temperature and pressure. To better understand the oxidation of the mineral, experiments performed with an ozone-saturated solution were compared with an oxygen-saturated solution and a blank solution. Also, to observe the changes in pyrite after oxidation, the surface of the mineral was investigated using FESEM analysis.

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2. Material and methods

2.1. Material

The samples used in this research were high-purity pyrite crystals, which were obtained from the Chah Firouze mine in Kerman. Phase identification was performed using X-ray diffraction (XRD) equipment from Philips, Netherlands, and analyzed using High Score Plus software. The XRD results in Fig. 1 indicated the high purity of the sample. The mineral content of the sample was 96.3% pyrite and 3.6% calcite. Chemical analysis was also performed using an X-ray fluorescence (XRF) device from Bruker, Germany, and the results are listed in Table 1.

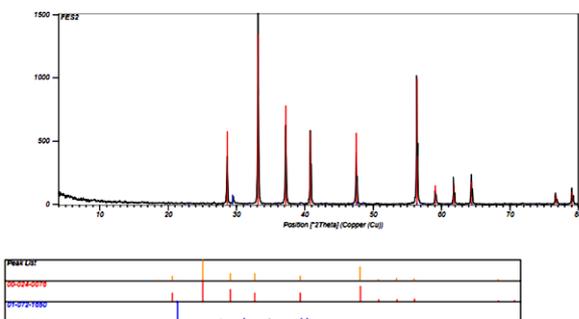


Fig. 1. The XRD pattern of the chalcopyrite electrode.

2.2. Electrode preparation

To make the working electrode (WE), intact and cubic pyrite pieces were used. According to Fig. 2, the crystal surface was smooth and free of defects. To remove impurities and further polish the pyrite surface, it was polished on a rotating disc for ten minutes. To prepare the electrode, a copper wire with silver solder at its end was connected to the pyrite by electric welding.



Fig. 2. The preparation steps of pyrite (WE) working electrode.

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rotating disc for ten minutes. To prepare the electrode, a copper wire with silver solder at its end was connected to the pyrite by electric welding.

2.3. Method

All the tests were carried out with a potentiostat (Model PARSTAT 2273, USA). This device is connected to PowerSuite. All tests were performed in a 300 ml cell containing three silver/silver chloride (Ag/AgCl) electrodes as reference electrodes, a platinum electrode with a thickness of 1 mm and a length of 10 mm as an auxiliary electrode, and a pyrite electrode as a working electrode. Two reference electrodes (RE) and a counter electrode (CE) were manufactured by Azar Electrode Co., Iran. Ozone was produced by pure oxygen with a flow rate of 2 liters per minute connected to a corona discharge ozone generator manufactured by Dantek Iran Company, and the ozone flow rate was measured at 0.2-0.3 liters per minute. The ozone produced by the two-phase vortex pump was in the form of ozone micro-nanobubbles, and after 30 minutes of water circulation, the ozone nanobubbles in the solution reached a saturated state. To perform electrochemical tests, the open circuit potential (OCP) was first recorded for 600 seconds or more until the potential reached a stable state. The tests were performed in such a way that the pyrite electrode was placed in an acid solution, an oxygen-saturated solution, and an ozone-saturated solution, and the open circuit potential and cyclic voltammetry results were recorded.

2.4. Results and discussion

2.4.1. Eh-pH diagram

The Eh-pH diagram was used for thermodynamic studies and to analyze stable species in solution or surface corrosion in and acidic or alkaline environments. Fig. 3 shows the thermodynamic stability range of iron and sulfur components in the pyrite system in solution. The diagram was drawn with the HSC V6 software. According to the diagram, pyrite is stable in a wide range of pH from 1 to 13 [11, 12]. In a highly acidic environment (pH less than 2), with a decrease in potential from 1 to 0.5 V, iron oxidation is possible. The stability potential range of pyrite is from -0.6 V to +0.3 V [13]. On the other hand, with an increase in potential to more than 0.7 V, pyrite oxidation will be accompanied by the production of Fe III and sulfate.

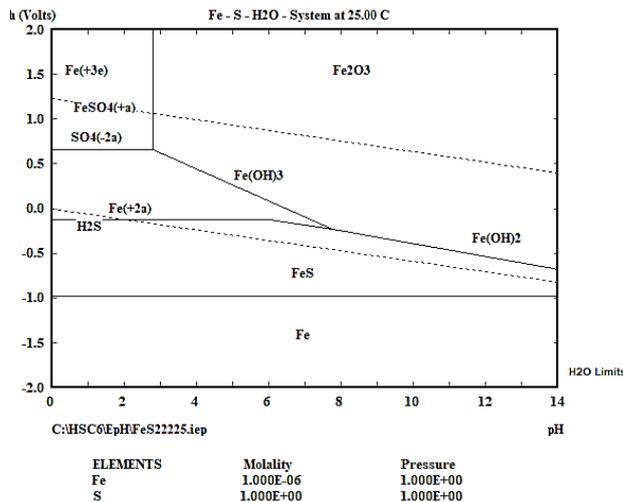


Fig. 3. The eh-pH diagram of pyrite at ambient temperature and pressure.

Table 1. The chemical analysis of the chalcopyrite sample (% wt)

Composition	SO ₃	Fe ₂ O ₃	CaO	SiO ₂	MgO	CoO	Al ₂ O ₃	CuO	NiO	LOI	Total
%wt	46.71	21.46	2.96	0.618	0.209	0.055	0.048	0.029	0.027	27.76	99.88

2.4.2. Open Circuit Potential (OCP)

Open circuit potential is a parameter that indicates a surface's resistance to corrosion. Decreasing OCP to lower values indicates that the surface of the material is more easily corroded, and an increase in OCP to higher values indicates greater resistance to surface corrosion. Fig. 4 shows that the OCP of pyrite in an acidic solution increases in the first few minutes and then reaches a steady state.

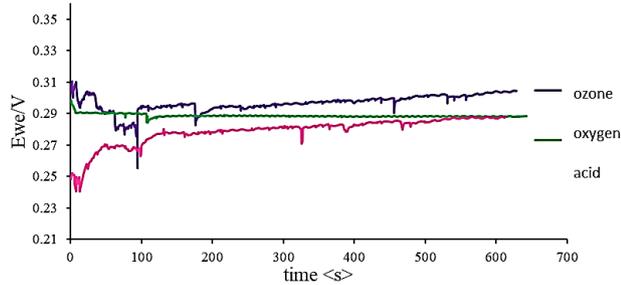


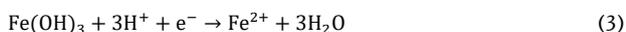
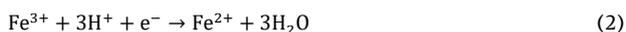
Fig. 4. The open circuit potential of pyrite electrode in a sulfuric acid solution, acid and oxygen-saturated solution, and acid and ozone-saturated solution

The open circuit potential of a surface changes when exposed to an electrolyte because, in the initial moments of contact with the solution, the surface is further protected from corrosion by the spontaneous growth of an oxide layer on the surface, and the OCP increases. Over time, the value of the potential becomes stable. The time to reach a steady-state depends on factors, such as the type of mineral and its chemical composition, and the electrolyte resistance. The control potential (sulfuric acid solution) reached a steady state of 0.28 V in 10 minutes. In the case where the electrolyte solution was saturated with nano-ozone, the steady state potential increased to 0.3 V, which could be due to the increase in the concentration of the oxidizing agent (ozone or oxygen) in the electrolyte. According to the Nernst equation, the solution potential is directly related to the concentration of the oxidizing agent [14].

2.4.3. Cyclic voltammetry (CV)

When the electrode reached a steady state, the open circuit potential was measured, and cyclic voltammetry was performed based on the open circuit potential. The voltammetric scan started from the negative side to re-identify the species that had previously formed during oxidation. Fig. 5 shows the voltammetric curve of pyrite in acidic solution and ozone-saturated acidic solution. In this study, the potential sweep was from -500 mV to +900 mV at a scan rate of 10 mV/s within the anodic current direction, and then the reverse scan was applied in the cathodic current direction. Each curve was scanned in three consecutive cycles, and finally, the results of the last scan cycle, which had less noise, were presented. As is clear from Fig. 5, three anodic peaks A₁, A₂, and A₃ were identified in the anodic (oxidation) section, and two peaks C₁ and C₂ were identified in the cathodic (reduction) section. The potential values throughout this report are expressed in terms of the silver chloride reference electrode. It should be noted that to express the potential in terms of the standard hydrogen reference electrode (SHE), the measured values are added to 222 mV. Also, the saturated electrolyte and the control electrolyte were not stirred during the process.

The cathodic peak C₁ of the curve, according to Eqs. 1 & 2 in the potential range of 0.45 V is attributed to the reduction of Fe III and Fe(OH)₃ to Fe²⁺:



In the cathode peak of C₂, according to Eq. 4 in the potential range of 0.05 to -0.35 V, it is expected to see the reduction of pyrite and the formation of FeS and H₂S species.

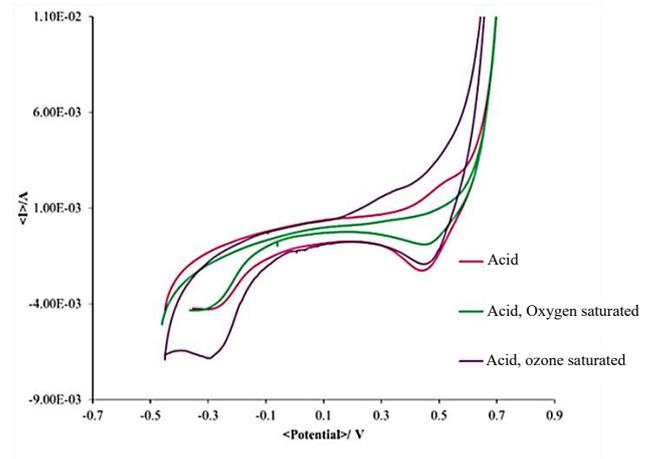


Fig. 5. The cyclic voltammetry of pyrite electrode in a sulfuric acid solution and ozone-saturated sulfuric acid solution and scan rate mV/s10.

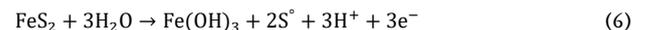


The cathodic peak C₂ is observed to be relatively wider, which could indicate multicomponent systems and multi-step charge transfer, or be associated with a combination of processes, such as the reduction of thiosulfate and metal-deficient polysulfides. In this range, the peak intensity is relatively low. According to Timoury et al., the produced H₂S gas disperses relatively quickly, resulting in a low concentration around the surface [15]. On the other hand, according to Eq. 5, the C₂ peak can be attributed to elemental sulfur, which itself leads to the formation of H₂S and is thermodynamically feasible [16]:



At the end of the cathodic scan, the curve at the potential of -0.45 V presents a reverse scan to the positive side. A mild anodic current peak is observed in region A₁. According to Liu et al., the oxidation of H₂S, which was produced in the C₂ region, probably occurs in this region [9]. In the A₂ region, oxidation of FeII occurs, and ferric hydrate is formed. According to Chen et al., peak A₂ is related to the oxidation of pyrite and the formation of a sulfur layer on the electrode surface [17]. The anodic peaks were not as prominent as the cathodic peaks, which could be due to the low concentration of the oxidized species in the solution. The range of cathodic peaks in sulfuric acid solution was between 0.2 to 0.6 V and -0.45 to -0.05 V [6].

By increasing the potential from 0.05 V, partial oxidation of pyrite can lead to the production of intermediate sulfur-rich species, such as polysulfides. The accumulation of these species on the surface of the electrode can lead to the formation of a penetration layer, which according to Eqs. 6 & 7 can only be removed at higher potentials or favorable oxidation conditions in the penetration layer [15].



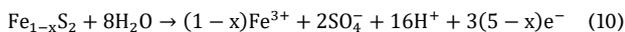
In the curve related to acid solution saturated with ozone, the cathodic peak of C₂ is attributed to the reduction reaction of ozone and oxygen absorbed on the surface of pyrite and according to Eqs. 8 & 9, ozone and saturated oxygen in solution are more prone to accept electrons compared to the products and intermediate species [2]:



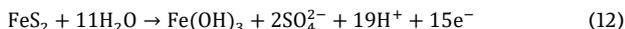
Peak C₂ for pyrite electrode in acidic solution saturated with ozone and oxygen is broader than in acidic solution without oxidant. In other

words, this peak can be attributed to the difference in the increase of ozone and dissolved oxygen concentration on pyrite surface. It has been reported that ozone and dissolved oxygen are more effective in pyrite oxidation than intermediate products[2].

Anodic current peaks A₁ and A₂ were proposed for pyrite oxidation and the activation of intermediate surface products. The current increased exponentially during anodic scanning towards the potential of 0.7 V. At higher potentials, with a slight increase in potential, the current value increased exponentially (peak A₃); according to studies and the examination of the Eh-pH diagram, complete oxidation of FeS₂ to Fe(OH)₃ and SO₄²⁻ occurs. Additionally, species, such as iron-deficient sulfides (Fe_{1-x}S₂), which were previously formed during the partial oxidation of pyrite at a potential of 0.05 V, are also extensively oxidized in this potential range according to Eqs. 10 & 11.



After several stages of CV scanning, a dark layer was visually observed on the surface of the pyrite electrode, which can be evidence of the formation of iron hydroxide Fe(OH)₃ according to Eq. 12 [6, 16].



The anodic peaks of the ozone-saturated acid curve show higher values compared to the acid curve, which could be due to the activation of intermediate products on the pyrite surface. In other words, the higher the concentration of species, the higher the voltage in the anodic direction, leading to the oxidation of intermediate products and a greater electron current exchange between the surface and the ions. Similarly, in the case of the cathodic current, due to the higher concentration of dissolved species, a greater electron current intensity is observed for the reduction of species, such as ferric ions on the pyrite surface [9].

2.4.4. Field emission scanning electron microscopy (FESEM-EDS) analysis

The morphology of the pyrite surface remaining from the electrochemical test was examined by FESEM analysis. According to Fig. 6, the pyrite surface was smooth and clean before the electrochemical test, and no roughness or species were observed on its surface. After pyrite was exposed to 0.5 M acidic solution, species were observed on its surface that can be attributed to the formation of intermediate species. As expected, it cannot be properly determined whether the formed layers are inhibitory [3]. The formed surface could be elemental sulfur or metal-free polysulfides. In the Fig. 6, roughness and small holes are observed on the pyrite surface, which could be due to surface corrosion of the electrode in the ozone-saturated solution.

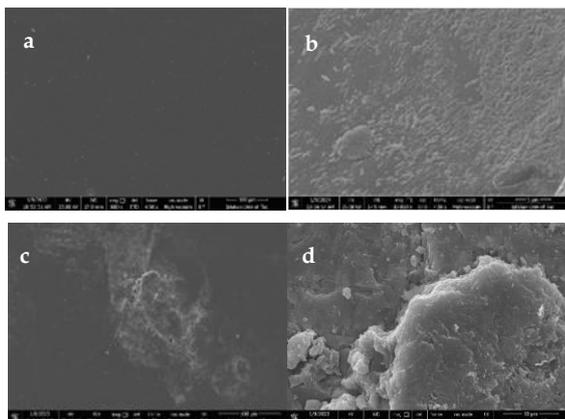


Fig. 6. The results of the FESEM analysis of pyrite surface before (a) and after exposure to sulfuric acid solution (b), ozone-saturated acidic solution (c), and (d) the explanation of D.

3. Conclusions

Ozone (O₃) appears as a strong candidate with several advantages, including fast reaction kinetics even at near-ambient temperatures, in situ generation, and minimal secondary pollution. Its ability to decompose passive layers and promote complete pyrite oxidation under mild conditions makes it especially promising for industrial hydrometallurgical applications. In this article, the effect of ozone on pyrite oxidation was investigated by electrochemical test. Due to its high oxidation power, ozone in a sulfuric acid environment and at a temperature close to ambient temperature is thermodynamically capable of proper oxidation of pyrite and proper removal of intermediate species and products on its surface. The increase in the intensity of anodic peaks in the pyrite oxidation condition and the presence of ozone compared to the absence of oxidant confirms the improvement of oxidation conditions. In the conditions of acidic solution saturated with ozone, the cathodic peak is attributed to the reduction of ozone and oxygen adsorbed on the pyrite surface. Because ozone and saturated oxygen in the solution are more prone to accept electrons compared to oxidation products and intermediate species. By comparing the curves obtained from the voltammetric and field emission scanning electron microscopy (FESEM) tests, the positive effect of ozone on the oxidation of pyrite in an acidic medium can be realized. Ozone can improve the performance of gold extraction from sulfide deposits by breaking the pyrite crystal lattice.

References

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