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Electrochimica Acta 50 (2005) 4160–4167

ELECTROCHIMICA Acta

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Influence of inorganic anions on electrochemical behaviour of pyrite

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Received 7 July 2004; received in revised form 17 December 2004; accepted 22 January 2005
Available online 19 February 2005

Abstract

This work gives an investigation of pyrite behaviour during anodic oxidation in solutions of four inorganic acids: sulphuric, hydrochloric, phosphoric and perichloric acid. In wider range of concentrations, the influence of acids on following parameters was investigated: rate of establishment and corrosion potential value, Tafel's slope, corrosion current and electrodic reaction order. Based on potentiodynamic and chronoamperometric investigations, it was found out that pyrite oxidation is developed in three regions conditionally named active, passive and transpassive region. It was also found out that pyrite is intensively dissolved at potentials higher than 0.75 V versus SCE and that oxidation rate of pyrite is the highest in hydrochloric acid solutions ($\geq$1 M HCl). By comparison of obtained results, it was concluded that there are no distinctive differences in pyrite behaviour during anodic oxidation in solutions of investigated acids.

Keywords: Pyrite; Anodic oxidation; Inorganic anions; Corrosion potential; Corrosion current

1. Introduction

Pyrite is one of the most spreaded sulphide mineral and one of the most spreaded mineral in general. It is present in many valuable mineral raw materials mostly as impurity that disturbs their mineral processing and treatment. Sulphide copper, lead and zinc ores contain pyrite by rule, and it is also present in oxide uranium ores and coal. Also, pyrite with arsenopyrite forms the most present gold-bearing sulphide [1].

Usual and at the same time the most efficient methods, used for pyrite separation from valuable minerals are flotation and leaching. Pyrite oxidation is an important parameter for this separation that is present everywhere and could be developed under natural conditions, due to influence of atmospheric conditions (at the open pits, tailing dumps, etc.) and during technological processes (grinding, flotation, leaching). Due to this, studying of pyrite oxidation in aqueous solutions and all the phenomena associated with this oxidation has been interesting for the scientists more than 40 years [1,2].

Pyrite oxidation in aqueous solutions is carried out by electrochemical mechanism and it could be said that the electrochemical investigations on pyrite were started by the pioneer works of Kunori and Ishii [3], Zhavoronkova et al. [4] and Peters and Majima [5]. With the thank of semiconductible characteristics of pyrite, which were known, the above mentioned authors made electrodes of natural pyrite crystals and used on them the electrochemical techniques, developed for metals. From that time until nowadays, various electrochemical investigations are carried out on pyrite with higher or lower intensity. It is certain that strong complex mechanism of pyrite oxidation in aqueous solutions had also influence on it as well as long time and lot of energy were spent on its establishment, what is confirmed in many works from this field. Hamilton and Woods [6], Mishra and Osseo-Asare [7], Mycroft et al. [8], Chander et al. [9], Ahlberg and Broo [10], Zhu et al. [11] and many other researchers gave in their works a

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doi:10.1016/j.electacta.2005.01.036

great contribution to explanation of pyrite oxidation mechanism.

One restriction could be conditionally made by analyzing the works on electrochemical investigations on pyrite. Namely, electrochemical oxidation of pyrite in base solutions is important, first of all, for understanding the electrochemical aspect of flotation until electrochemical pyrite oxidation in acidic media is important for better understanding the electrochemical aspect of dissoulution, that is pyrite leaching.

This works presents an investigation of pyrite behaviour at anodic polarization in solutions of four inorganic acids (H_2SO_4, HCl, H_3PO_4 i $HClO_4$). Investigations were carried out in large range of concentrations, from 0.1 to 2.0 M. Namely, previous investigations have some limited character due to a fact that they were often carried out in one acid (perchloric acid, sulphuric acid) and that the analyzed concentrations were often 0.5 or 1.0 M. Besides that, the majority of works discuss mechanism of electrochemical pyrite oxidation, and in the frame of this, an identification of enriched compounds on pyrite surface or in analyzed solution. Due to this, the scope of this work is evaluation of rates of anodic pyrite oxidation by the use of suitable corrosion currents. Mutual comparison of obrained results was carried out and comparison of previous obtained results on pyrite oxidation rate in mentioned acids under influence of oxidants [12–14].

2. Experimetal

Natural pyrite crystal in a form of cube from the copper mine Bor was used as electrode material. Copper wire was pasted on one side of this cube by electroconductible glue based on silver. Contact of mineral and copper conductor was realized by this. Such prepared electrode was immersed with autopolymerized methyl methacrylate to the desired height. Upon solidification, working surface of electrode was polished to the high glow on felt with impregnated diamond and then Al_2O_3 paste (0.3 μm). After that, electrode was rinsed with distilled water and alcohol, and upon drying on air immediately inserted into electrochemical cell. Fresh pyrite surface was formed by polishing on clay before each experiment. Working electrode surface was 1 cm^2 and this value was used in calculation of current density, until electrode resistance was 8 Ω.

Investigations were carried out at room temperature and atmospheric pressure with trielectrode system (FeS_2, Pt, SCE) connected to potentiostate and computer with suitable hardware–software at Technical Faculty in Bor. Reference – saturated calomel electrode (SCE) was situated into Luggin's capillary, and this was located near surface of pyrite electrode for reduction of potential drop due to electrolyte resistance between electrodes. Measurings were carried out in a glass with double bottom, volume of 150 mL where 50 mL of analyzed acid was poured.

Recording of polarization curves started from corrosion potential. Due to this, pyrite electrode was in analyzed solution for a few minutes, what was required for establishment of the stationary value of pyrite potential. Upon recording of corrosion potential, pyrite was exposed to anodic polarization in range from corrosion potential to ∼0.7 V versus SCE, at constant rate of potential change of 1 mV/s. Beside this, chronoamperometric investigations of current density change with time were carried out with correct determined potential (0.550–0.770 V). Measurings were carried out in acid solutions (H_2SO_4, HCl, H_3PO_4, $HClO_4$) without removing oxygen, in stationary conditions. Acids concentrations varied in range from 0.1 to 2.0 M. Condition of electrode surface before and after electrochemical treatment was evaluated by the use of optical microscopy.

3. Results and discussion

3.1. Corrosion potential

Change of pyrite potential was monitored in solutions of four analyzed acids at concentrations of 0.1, 0.3, 0.5, 0.7, 1.0, 2.0 M, to the establishment of stationary potential value. It was evaluated that stable potential values were realized very fast and that upon 3–4 min the pyrite potential was not changed with time (Fig. 1). This potential established on pyrite electrode that was not polarized with current from outer circuit is called corrosion potential, although it is often present in literature as open circuit potential, calm or mixed potential, depending on work character. Result have shown that corrosion potential was established a little more faster in hydrochloric and phosphoric acids, and slower in sulphuric and perchloric acids (Fig. 1). It was also noticed that the slowest establishment of corrosion potential was at acids concentrations of 0.5 and 2.0 M, and the reason for this is unclear.

Independently of a fact what acid is in question, in the investigated range of concentrations from 0.1 to 0.2 M, it was noticed that pyrite potential increases with time to the estab-

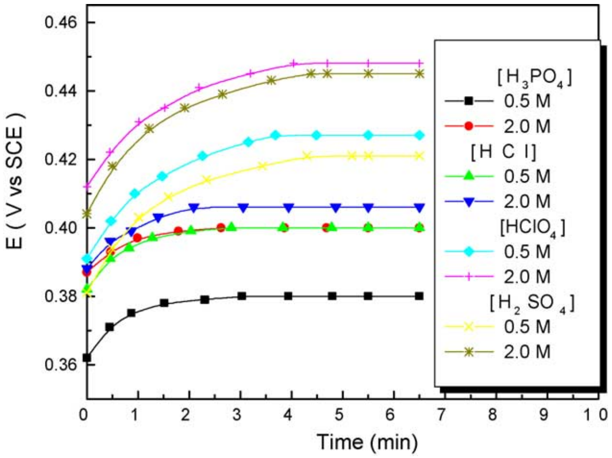

Fig. 1. Influence of analyzed acids on rate of establishment the corrosion potential for two selected acid concentrations of 0.5 and 2.0 M.