USE OF PYRITE AS AN ATTENUATION STRATEGY FOR IONS MERCURY TRAPPING

W. A. Moreira[1], *B. F. Giannetti*[*2], *S. H. Bonilla*[2], *C. M. V. B. Almeida*[2], *T. Rabóczkay*[1]

[1]Instituto de Química da Universidade de São Paulo, PO BOX 26077, 05599-970, SP, Brazil
[2]Instituto de Ciências Exatas e Tecnologia da Universidade Paulista, LaFTA, R. Dr. Bacelar 1212, 04026-002, São Paulo, SP, Brazil. * e-mail: biafgian @ unip-objetivo.br

ABSTRACT

Environmental problems are generated by the output of mercury due to anthropogenic activities. In aquatic media under micro-organisms action, mercury can undergo methyl mercury, a lethal species. Facing this problem, a variety of materials as well as technical procedures have been used with the purpose of retaining heavy metals. Among these materials, the excellent trapping properties of pyrite are recognised in literature, as it presents the capability of retaining either mercury ions as well as metallic mercury. However, little information concerning the interaction between pyrite and mercury species is available, as only a few articles focused on this topic. The aim of this work is to study the spontaneous interaction between mercury and the mineral surface. For this purpose, the mineral (supplied by Morro Velho mine, Minas Gerais) was grounded, and the portion presenting less than 210 μm in size was employed to construct carbon paste electrodes. The electrodes were immersed in aerated solutions containing 10^{-3} mol/L of $Hg(NO_3)_2$, for 30 minutes at open circuit conditions. The nature and the extent of the spontaneous interaction were evaluated using voltammetric techniques. No evidence of the presence of metallic mercury was observed in the cyclic voltammograms, so the species spontaneously retained at the mineral surface present higher oxidation numbers. This study shows promising results relating the use of pyrite as a way for retain and recuperate mercury waste.

INTRODUCTION

Environmental impact and toxicity of mercury

The great risk associated with the environmental pollution due to heavy metals has motivated research work dealing with the understanding of the mechanisms controlling speciation, availability and mobility of these species in natural systems. The resulted knowledge has served as a starting point to propose solutions in order to attenuate the environmental impacts due to heavy metals.

Among the heavy metals, mercury presents a great impact due its wide use in industry (chlorine-alkali, paper) and in mining areas (gold extraction by amalgamation).

At the beginning of the 70´s, it was estimated the discharge of almost 1 kg of metallic mercury to the environment in the production of 900 kg of chlorine by sodium chloride electrolysis (National Materials Advisory Board Report). During the last thirty years and due to a most rigorous legislation, the industrial sewage processes were improved. This fact has restricted the mining area as the main responsible for mercury release to the environment.

Research groups in the country estimate a drainage of 100 tonnes of mercury into Amazonas area due to gold extraction processes (Pfeiffer and Lacerda, 1988; Lacerda and Pfeiffer, 1989). Almost 45 % of this quantity is drained directly into the river, whereas the rest goes to the atmosphere. The elementar mercury discharged into natural aquatic systems is retained in lake and river sediments. Upon anaerobic conditions the elementar mercury is converted into alkyl mercury species by the action of micro-organisms (Wood et al., 1968).

Both the organic and inorganic mercury species present toxicity. The literature cites death incidents due to methyl mercury ingestion in Minamata (Fujiki and Tajima, 1992) and Irak (Rustam, 1974). More recently, the death of a researcher as a consequence of skin contact with $(CH_3)_2Hg$ was described (Long, 1997).

Adsorbents for heavy metals

An important number of works is found in literature dealing to heavy metal adsorption on some adsorbent surfaces.

Among these, the works of Kinniburg et al (1976), Balistrieri and Murray (1982), Forbes et al.(1976) using goethite, Loganathan and Burau (1973) employing hydrous oxide gels, Farrah et al.(1980) with manganese oxides and Hara et. al. (1979) using synthetic pumice are of considerable interest.

However, only a few works concerning the use of iron sulfide minerals as adsorbent substrates are found in literature (Brown et al., 1979; Jean and Bancroft, 1986; Hiland et al., 1990; Perdicakis et al., 1999; Walcarius et al., 1999).

Brown et. al. present a comparative study describing the performance of iron sulfides and oxides as adsorbents for mercury. A discussion about the correlation between sulfide mineral adsorption and pH is also presented. This study also confirms that both pyrite and pyrrhotite are excellent adsorbent materials for heavy metals. According to the authors, mercury ions present a great affinity for sulfide surfaces. The lower value of the solubility constant (10^{-52}) confirms this fact.

The studies leading to mercury adsorption on sulfide minerals is mainly devoted to the development of a methodology to promote the remotion of this pollutant from the environment. Jean et al. (1986) and Hiland et al. (1990) made the attempt to characterise the mineral surface resulted from the interaction with heavy metals, by using ray X photoelectronic and Auger spectroscopies. These techniques failed in the species identification. Furthermore, either the combination of both atomic absorption and ray X photoelectronic spectroscopy techniques (Brown et al., 1979; Jean and Bancroft, 1986) was unable to identity the mercury species involved.

Hiland et al. (1990) affirm that more than a species are present on the mineral surface, however until now the nature of the species formed as a consequence of the interaction between sulfide minerals and Hg(II) solutions is still uncertain.

On the other hand, only a few works concerning the understanding of the mercury adsorption process on minerals present an electrochemical approach. Both of the related works found in literature were carried out in acid media and used carbon paste electrodes modified with mineral grains (Perdicakis et al., 1999; Walcarius et al., 1999). The one performed by Perdicakis et al. presents a comparative study between silver and mercury ions reactivity on pyrite. They concluded that silver ions are almost 20 times more reactive than mercury ones. Walcarius et. al., using minerals like silica, goethite and pyrite evaluated mercury adsorption in function of pH and chloride concentration. These studies have contributed to the understanding of the mineral/Hg(II) interface, although the identification of the surface species is still opened to discussion.

Objective of the work

The aim of this work is to study the spontaneous interaction between mercury species and the mineral surface. The nature and the extent of the spontaneous interaction were evaluated using electrochemical techniques.

EXPERIMENTAL PROCEDURE

A system constituted by a potentiostat/galvanostat AUTOLAB/PGSTAT 20 (Eco Chemie electrochemical instruments), connected to a computer with the GPES software was used to carry out the electrochemical measurements (open circuit measurements and cyclic voltammetry).

The electrochemical cell, a jacketed one of 100 mL of working volume, contained an acrylic cell top with a set of holes in order to place the the cell components. The working electrode was a carbon paste electrode modified with grains of natural pyrite. The comparative study of different ways of constructing mineral electrodes accomplished by Almeida, 1999, justified the use of carbon paste electrodes modified with minerals. This conclusion was based on the construction facility, and the good reproducibility of the electrochemical measurements. The natural pyrite sample is from Morro Velho Mine, Minas Gerais, Brazil. The mineral was hand ground in an agate mortar and pestle. This material was then sieved to isolate the fraction containing particles < 210 μm in size. The carbon paste electrodes consisted of 1.0 g graphite and 1.2 g paraffin containing 5 mg of the ground pyrite.

The reference electrode was a Ag/AgCl commercial one and the counter a platinum platinized wire contained in its own compartment. The fritted end of the counter electrode compartment avoid the leaching of products to the working solution.

The deaeration of the solution was carried out by using ultrapure nitrogen gas. All the solutions were prepared from treated water (obtained from a Milli Q Academic water purifier) and analytic reagents.

The working solution was a H_3CCOOH/ $H_3CCOONa$ (0,25M/0,25M) buffer, pH = 4.5. Metallic mercury (distilled and filtrated) as well as a $Hg(NO_3)_2$ 10^{-3} mol L^{-1} solution were also used.

All the voltammograms were performed at a sweep rate, $v = 20$ mV s^{-1} between the positive and negative potential limits, $E\lambda_a$ and $E\lambda_c$ indicated in each figure legend. The scans were always initiated and finished at the open circuit potential value (E_{OC}) of each interface. The interaction between mercury anions and the electrode, was carried out by the immersion of the latter in the $Hg(NO_3)_2$ solution for 30 min. The immersion of the electrode in metallic mercury for the same period of time was carried out in order to compare results. After that, the electrode was carefully washed with water and placed into the electrochemical cell.

RESULTS AND DISCUSSION

Typical potentiodinamic profiles of pyrite.

Fig. 1 shows the typical voltammograms of the pyrite electrode, comparable to those presented in the literature (Hamilton and Woods, 1981; Almeida, 1999; Giannetti et al, in press) recorded towards both positive and negative direction.

In the potential window of a_I the surface oxidation to form S, SO_4^{2-} and $Fe(OH)_3$ was proposed by Hamilton and Woods (1981).

$$FeS_2 \rightarrow Fe^{2+} + 2S + 2e^- \quad (1)$$

$$FeS_2 + 8\,H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 16H^+ + 14e^- \quad (2)$$

$$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + e^- \quad (3)$$

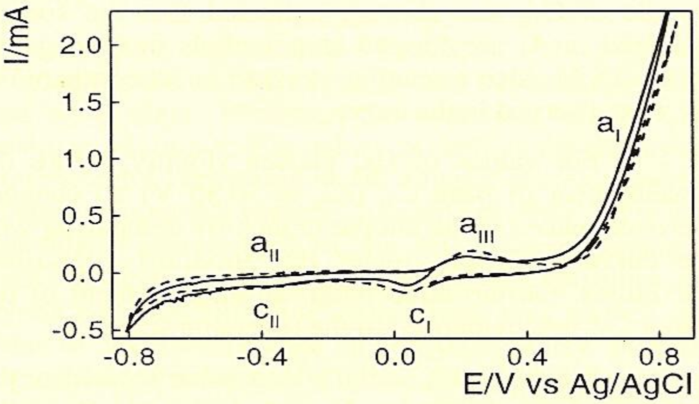

Fig.1 Cyclic voltammograms of pyrite carbon paste electrode performed towards (.....) positive and (_____) negative direction; $E_{OC} = 0.1$ V; $E\lambda_a = 0.85$ V; $E\lambda_c = -0.8$ V.

The reversal of potential scan originates two cathodic peaks c_I e c_{II}. In the potential range of peak c_I, the reduction of $Fe(OH)_3$ produced during grinding and in the course of the previous anodic incursion occurs (via inversion of reaction (3)).

Peak c_{II} is related to several reactions, among these, the reduction of sulfur (in accordance with reaction (4)) either electrochemically formed (Hamilton and Woods, 1981), or produced during grinding, as well as the mineral decomposition yielding H_2S and even H_2 (Biegler, 1976; Radyushikina et al., 1986).

$$S + 2H^+ + 2e^- \rightarrow H_2S \quad (4)$$

The subsequent scan reversal at $E\lambda_c$ towards positive direction evidences an anodic current a_{II}. Thermodynamics predicts for this potential region the oxidation of the H_2S generated at c_{II} (Hamilton and Woods, 1981). At potential near 0.22 V a step (a_{III}) is depicted in the current profile. This potential is characteristic of reaction (3).

Spontaneous interaction between mercury ions and pyrite.

It was observed for the electrodes previously immersed in the $Hg(NO_3)_2$ solution, a higher open circuit value than the typical for pyrite electrodes.

The shift towards positive direction of the open circuit potential value as a consequence of the interaction with mercury ions, evidences a more passivated surface. The presence of species sufficiently oxidized must be responsible for the higher open circuit potential value.

Figs. 2(a) and (b) exhibit a detail of the cathodic and anodic branches of the voltammogram, respectively. Peak c_I is not observed in the profile. Additionally, new current peaks appeared in the cathodic branch, C_1, C_2 and C_3.

It is possible to identify the peak a_{III} located in the middle of the new current peaks (A_1, A_2, A_3, A_4, A_5). Current a_I (not shown in the figure), remains practically unaltered after the contact between pyrite and mercury species. No evidence of the presence of peak a_{II} is observed in the figure. This high number of new processes evidences the complex nature of the pyrite/mercury (II) ions system. This fact may indicate the presence of more than a single species spontaneously formed on the electrode surface.

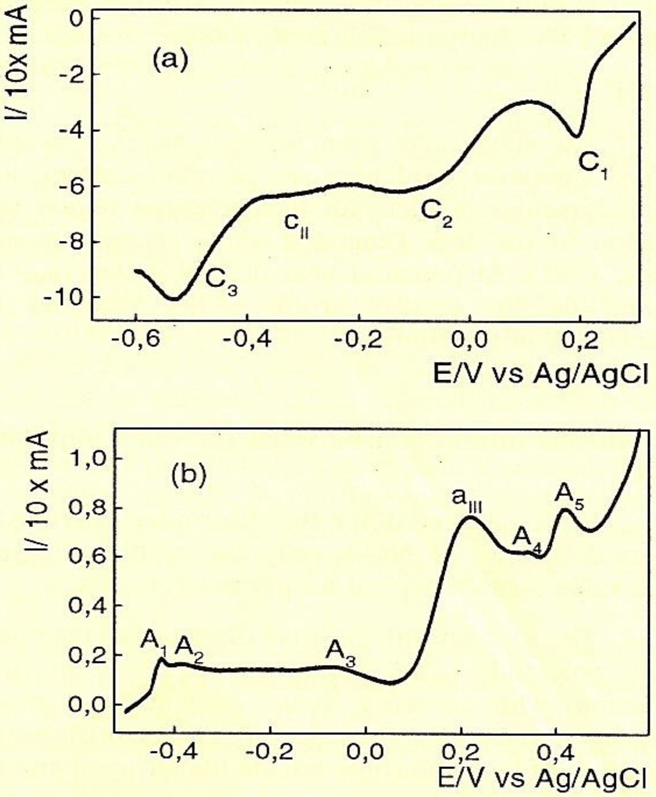

Fig.2 Cyclic voltammogram of pyrite carbon paste electrodes after interaction with Hg^{2+} solution (a) detail of the cathodic branch, (b) detail of the anodic branch. $E_{OC} = 0.3$ V; $E\lambda_a = 0.85$ V; $E\lambda_c = -0.8$ V.

In the work performed by Perdicakis et al., the potentiodynamic profile of pyrite after the interaction with mercury ions, shows two anodic current peaks located in the same potential region as peaks A_4 and A_5 of Fig. 2 (b).

These peaks were attributed to the Hg^0 oxidation process (Perdicakis et al., 1999), being the elemental mercury formed during the scan into the most negative potential region. The work also describes the presence of two cathodic peaks, each of them related to the reduction of a mercury species (Perdicakis et al., 1999). In the present study only the cathodic peak located at -0,1V , namely C_2 resembles the results obtained by Perdicakis et al.

Determination of the influence of the negative utting potential on the anodic processes.

With the purpose of determining the potential region where the species oxidized in A_4 and A_5 are formed, a set of voltammetric profiles with a fixed $E\lambda_a$ of 0.6 V and with increasing values of $E\lambda_c$ was performed. This type of assay allows the interpretation of the genesis of the anodic processes.

When $E\lambda_c$ was set in –0.6 V (Fig. 3) the disappearance of the peaks A_2 and A_3 was verified.

This fact allows to infer that the process occurring at A_2 and A_3 are related to the oxidation of species formed in a potential region more negative than –0.6 V. On the other hand, peaks A_4 e A_5 remain practically unaffected. A little hump, namely C^I_1, was depicted in the cathodic scan.

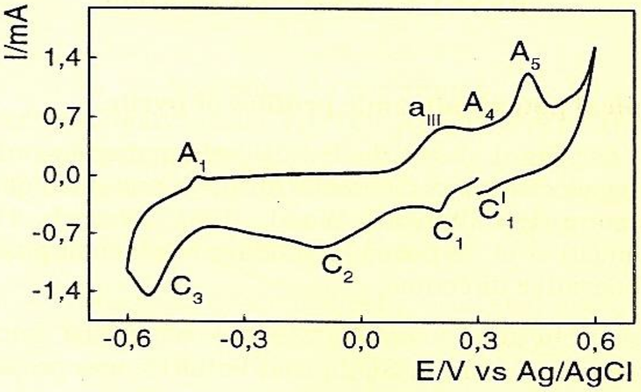

Fig.3 Cyclic voltamogramm of pyrite carbon paste electrode after the interaction with Hg^{2+} solution. $E_{OC} = 0.3$ V; $E\lambda_a = 0.6$ V; $E\lambda_c = -0.6$ V.

The lack of peak A_1 resulted in the positive scan when a value of $E\lambda_c$ = –0.5 V (located in the middle of C_3) was chosen, indicated that the species oxidized in A_1 are formed at potentials more negative than –0.5 V. Also a relative increase in A_4 compared to A_5 was observed in the curve

For values of $E\lambda_c$ chosen slightly before the development of peak C_3, ($E\lambda_c$ = –0.35 V) no changes were evidenced at the anodic branch by comparing with the curve performed under the previously described conditions. On the other hand, an enhancement of the hump C^I_1, was evidenced in the reversing scan.

When the $E\lambda_c$ = 0.09 V, a value located in the onset of C_2, only peaks A_4 and A_5 appeared in the subsequent sweep to positive direction, being the A_5 noticing diminished, Fig.4(a), solid line.

The subsequent cycles performed under the same parameters values showed the lack of A_4 and A_5 as well as C_1 after the third cycle, Fig.4(a), dashed line.

Experiments performed with stirring of the solution were carried out and were compared with those in a quiescent solution (Fig.4(b)). The disappearance of peak C_1 as well as peaks A_4 and A_5 evidenced the soluble nature of the species reduced in the former peak.

When $E\lambda_c$ = 0.24 V, potential value located before peak C_1 neither peak A_4 nor A_5 were observed.

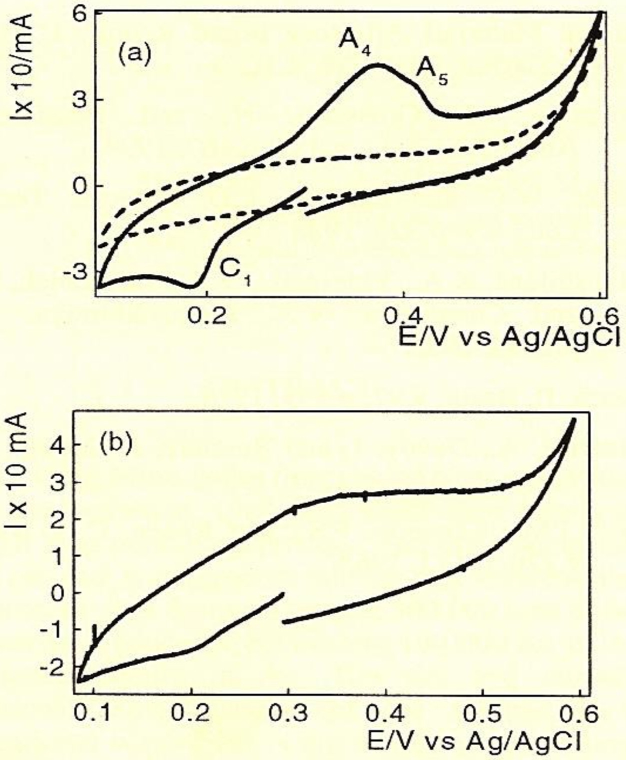

Fig.4 Cyclic voltamogramm of pyrite carbon paste electrode after the interaction with Hg^{2+}; E_{OC} = 0.3 V; $E\lambda_a$ = 0.6 V; $E\lambda_c$ = -0.09 V. (a) in a quiescent solution, (_____) first cycle; (.........) third cycle; (b) in a stirring solution.

The relationship between the processes involved in the cathodic peak C_1 and the anodic ones A_4 and A_5 is clear. However, the behaviour of the latter peaks in relation to $E\lambda_c$ values as well as the discussion presented by Perdicakis et. al. suggest the existence of another potential region, located at more negative potentials, also related to the processes occurring at peak A_4 and A_5. With the purpose of verifying this hypothesis the following experiment was carried out. First of all, three cycles in the 0.09V-0.6V potential region were performed in order to exhaust the species involved in the cathodic and anodic processes. Subsequently, a sweep scan from the E_{OC} towards negative potentials, with $E\lambda_c$ = -0.6 V, was recorded. A curve similar to that shown in Fig.3 was obtained, fact that evidences the relationship established between the processes in A_4 and A_5 and the reduction of more than a single species.

Spontaneus interaction between metallic mercury and pyrite

It was observed a lower E_{OC} value for the electrodes immersed in the metallic mercury.

This immersion led to the appearance of an anodic process, located at the same potential region as A_5, when the scan sweep was initiated towards positive potentials, Fig.5. On the contrary, peak A_5, only appeared in the second scan for the electrodes immersed in mercury ions solution..

The presence of more reduced species (probably Hg(I) species) resulting from pyrite/metallic mercury interaction accounts for the raising of peak A_5 just in the first cycle.

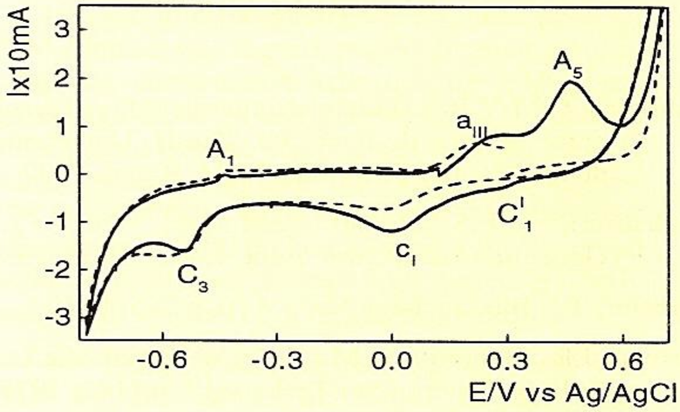

Fig.5 Cyclic voltammogram of pyrite carbon paste electrode after interaction with: (______) metallic mercury (E_{OC} = 0.11 V) and (---------) Hg^{2+} solution (E_{OC} = 0.3 V). $E_{\lambda a}$ = 0.85 V; $E_{\lambda c}$ = 0.8 V.

CONCLUSIONS

Ground pyrite exhibited an excellent performance retaining either metallic or anionic mercury species. The deposition of mercury species onto pyrite surface occurs in a spontaneous way.

Voltammetric studies showed the complex nature of pyrite/mercury ions and pyrite/metallic mercury systems. By means of the gangue character of the mineral, the use of this material as a strategy to retain mercury must be considered.

The possibility of mercury recycling by means of an ulterior oxidation, is an important advantage comparing with other adsorbents and is due to the electrical properties.

Further studies are necessary in order to evaluate the influence of experimental conditions on the mercury retaining performance.

ACKNOWLEDGEMENTS

The authors gratefully recognise the support from Vice Reitoria de Pesquisa e Pós-graduação, UNIP.

B.F. Giannetti wants to thank Fundação de Amparo à Pesquisa do Estado de São Paulo, Fapesp for the project grant (project 95/9333-2).

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