

Electrochemistry of marmatite – carbon paste electrode in the presence of bacterial strains

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Abstract

The electrochemical behaviors of a marmatite – carbon paste electrode with the chemical leaching of Fe^{3+} ions, or the microbial leaching using *Acidithiobacillus ferrooxidans*, were compared. The cyclic voltammograms of the electrode in the presence and absence of bacterial strains showed that the leaching process of marmatite was carried out by the different reactions occurring in the interface of the marmatite electrode – leach liquid. The polarization currents of the electrode under the differently applied potentials suggested that the microbial leaching of marmatite could be accelerated by the applied potential. The SEM observations indicated that the corrosion pits formed in the electrode surface were similar to the attached bacterial cells in shape and size, other than that by the chemical leaching of Fe^{3+} ions. The contact leaching of the attached cells on the mineral substrate played an important role on the dissolution of marmatite in addition to the chemical leaching of Fe^{3+} ions.

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1. Introduction

The bioleaching of sulfide minerals involves electrochemical and chemical reactions of the mineral with the leach liquor and the extra-cellular polysaccharide layers on the microorganisms. The electrochemical behaviors of some sulfides, such as pyrite [1], chalcopyrite [2–4], sphalerite [5] and ocean nodules [6–8], were investigated by some researchers. However, these investigations, sometimes focused on the methodology and sometimes on the process engineering, have not culminated in an understanding of the intimate mechanism involved in the oxidation of the solid substrate used, so their electrochemical behaviors still need be investigated further.

Usually, it is considered that mineral solubilization was achieved both by ‘direct (contact) leaching’ by bacteria and by ‘indirect leaching’ by ferric iron that is regenerated from

ferrous iron by bacterial oxidation [9]. Some researchers [10,11] believed that the primary attack of the sulfide mineral was a chemical ferric leach producing ferrous iron, and the role of the bacteria was to re-oxidize the ferrous iron back to the ferric form and maintain a high redox potential as well as oxidizing the elemental sulfur that was formed in some cases. Choi, et al. [12] had showed that the overall reaction of bio-oxidation of zinc sulfide involved a number of intermediate electrochemical reactions and the solubilization of ZnS was controlled by the solid - state diffusion. However, the effects between the bacterial strains and Fe^{3+} ions on the dissolution of zinc sulfides were difficult to be distinguished during the bioleaching process.

The bioleaching of marmatite flotation concentrate by *Acidithiobacillus* (formerly *Thiobacillus*) *ferrooxidans* has proven useful in mineral processing [13,14]. A major objective of the present work is to examine the electrochemical behaviors of a marmatite – carbon paste electrode in the presence and absence of bacterial strains, and to improve the understanding of the reaction mechanisms involved in the marmatite electrobioleaching. The work

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consists in relating the observations of the changes in certain electrochemical parameters, such as stable potential, open circuit potential and polarization current, to the presence of Fe^{2+} and Fe^{3+} ions in solution. The surface features of the marmatite electrodes after leaching in the differently electrolytical systems are observed by a scanning electron microscope (SEM).

2. Materials and methods

The marmatite flotation concentrate used in this study was obtained from a lead–zinc mine in Yunnan province of China. The chemical and mineral compositions of the concentrate were shown in a literature [13]. The carbon – paraffin oil mixture in the open end of the electrode was composed of 5 g graphite and 2 ml paraffin oil mixture, upon which was put a homogenized layer of 5 g marmatite, 5 g graphite power and 2 ml paraffin oil (as shown in Fig. 1). The electrode surface was compacted on a plate glass to make it flat, and its apparent active area was around 0.15 cm^2 .

The original strains of *Acidithiobacillus ferrooxidans* (*At. f.*) and a moderate thermophile (MLY) [15] were obtained from Institute of Microbiology, Chinese Academy of Science, and cultured in Leathen medium [16] with 1% (w/V) ferrous iron. The original strains were adapted in Leathen medium replacing the ferrous sulfate with the concentrate (5% w/v) as the sole energy source. The bacterial strains used in the experiments were adapted to the concentrate through being continuously subcultured over a year.

An electrochemical cell with double-wall glass, a volume of around 300 ml, was equipped with the marmatite – carbon paste working electrode, a platinum inert (counter) electrode and a saturated calomel (reference) electrode (SCE) with a salt bridge (capillary), and its temperature was controlled by a thermostat. The cell was charged with

200 ml Leathen medium (inoculated or sterile). The electrochemical measurements were performed by an electrochemical workstation (IM6e, ZAHNER Elektrik) and the experimental data was recorded by a computer.

3. Result and discussions

3.1. Polarization curve of marmatite – carbon paste electrode

Fig. 2 showed the polarization curve of the marmatite electrode in Leathen medium with 10 g/L $[\text{Fe}^{2+}]$ in the presence of bacterial strains. The curves of \overline{OABC} and \overline{ODEF} in Fig. 2 (a,b) were respectively the cathodic and anodic polarization curves, in which the curves of \overline{AB} and \overline{DE} belonged to the regions of intense polarization, i.e. Tafel curve. The stable potential (ϕ_0) and the corresponding current density (i^0), i.e. exchange current density, were also indicated in Fig. 2, their values were around 345 mV/SCE and 0.9 mA/cm^2 , respectively.

In the sterile controls, the stable potentials of the marmatite electrode were about 92 mV/SCE and the corresponding current were close to 0 in the solution with 10 g/L $[\text{Fe}^{2+}]$, about 415 mV/SCE and its corresponding current density 1.9 mA/cm^2 in the solution with 10 g/L $[\text{Fe}^{3+}]$, respectively. The stable potential and the exchange current density of the electrode in the sterile solution with 10 g/L $[\text{Fe}^{3+}]$ were highest among the three different systems. It suggested that the stable potential of the marmatite electrode was mainly determined by the concentration of Fe^{3+} ions in the leach solution. The higher value of current density (i^0) meant that the oxidation reaction rate of marmatite was higher during the leaching process, and the higher concentration of Fe^{3+} ions could play an important role for the dissolution of marmatite.

3.2. Cyclic voltammograms of marmatite – carbon paste electrode

In the leaching solution with 10 g/L $[\text{Fe}^{2+}]$ inoculating *Acidithiobacillus ferrooxidans*, the typical cyclic voltammogram curve of the marmatite electrode was shown in Fig. 3. The oxidation peaks (B, C, D) and reduction peaks (A, E) indicated respectively the different reactions occurring in the interface of the electrode and leach liquid under the different applied potentials. The cyclic voltammogram was similar to the result reported by Chio, et al. [12], in which the B' , B'' and B''' peaks indicated the reactions occurring in the electrode–liquor interface according to the redox potentials of different components as follows:

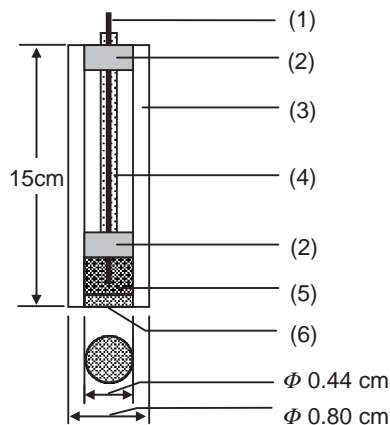
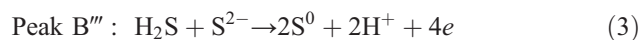
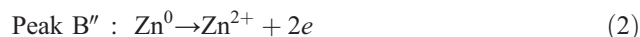


Fig. 1. (1) Copper line (2) Rubber (3) Glass tube (4) Insulating layer (5) Carbon paste (6) Marmatite (50%)+carbon paste. Diagram of a marmatite – carbon paste electrode.

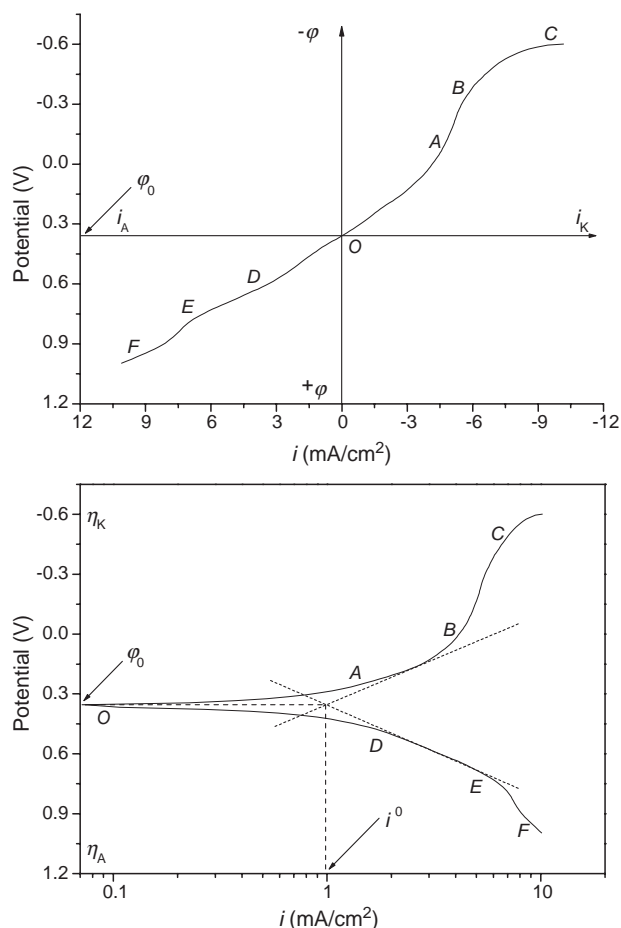


Fig. 2. Polarization curve of a marmatite-carbon paste electrode in Leathen medium with 10 g/L $[\text{Fe}^{2+}]$ inoculating *At. f* at 35 °C and applied potentials from -0.6–1.0 V.

Compared with that in the presence of bacterial strains, the peaks (B', B'' and B''') in the cyclic voltammogram of the electrode almost disappeared in the sterile solution with 10 g/L $[\text{Fe}^{3+}]$. It could be presumed that in the higher concen-

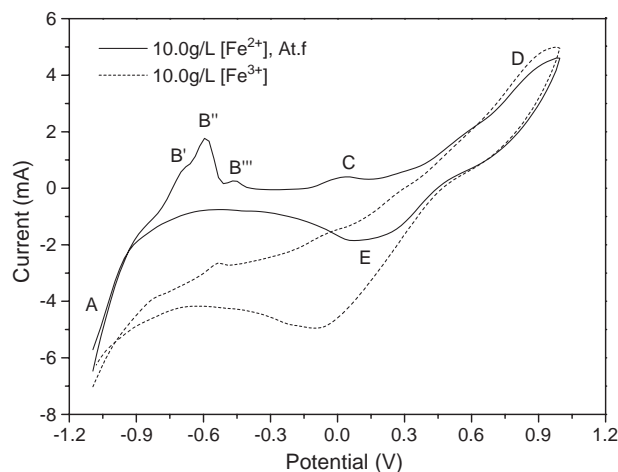


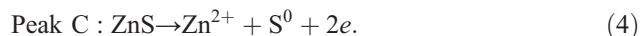
Fig. 3. Cyclic voltammograms of a marmatite-carbon paste electrode in the different leaching solutions in the presence and absence of *At. f* at 35 °C and a sweep rate of 100 mV/s.

tration of Fe^{3+} ions, the reductive products, such as Zn^0 and H_2S , were immediately oxidized by Fe^{3+} ions in the solution when the applied potential did not sweep to the suitable values, and even these reducing components were difficult to form under the higher redox potential, so led to the disappearance of peaks (B', B'' and B''') in the cyclic voltammogram. It meant that the dissolution of marmatite could be carried out by the different reactions occurring in the interface of the electrode and leach liquor in the different systems.

The effect of Fe^{3+} ion on the cyclic voltammogram of the electrode in the presence of *At. f* was shown in Fig. 4. Other than that of the peaks (A, D and E), the currents of peaks (B, C) decreased with the increase of the concentration of Fe^{3+} ions in the solution. It meant that the reactions (1–3) were difficult to occur with increasing the concentration of Fe^{3+} ions. The cyclic voltammograms in the inoculated experiments were similar to that in the sterile controls when the concentration of Fe^{3+} ions was higher. The result suggested that the chemical oxidation of Fe^{3+} ion played an important role for the dissolution of marmatite during the bioleaching process, especially in the leaching initial stage when the cell density was lower.

After 12 h of bioleaching, the peaks (B', B'' and B''') in the cyclic voltammogram of the electrode almost disappeared and the current values of peaks (C, D and E) increased markedly (as shown in Fig. 5). As the leaching time progressed, the concentration of Fe^{3+} ions increased in the presence of bacterial strains for its oxidizing action from Fe^{2+} to Fe^{3+} ions [17], which led the peaks (B', B'' and B''') to disappear as that in the sterile solution with 10 g/L $[\text{Fe}^{3+}]$.

The Peak C indicated the reaction occurring in the interface of the marmatite electrode and leach liquid as followed [12]:



The current of peak C in Fig. 5 increased markedly after 12 h of bioleaching, and one of the important reasons was

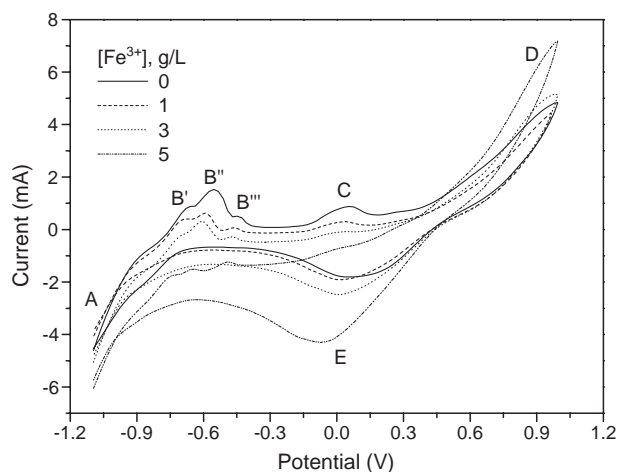


Fig. 4. The effect of Fe^{3+} ions on the cyclic voltammogram of a marmatite-carbon paste electrode in the presence of *At. f* in the solution with 10 g/L $[\text{Fe}^{2+}]$.

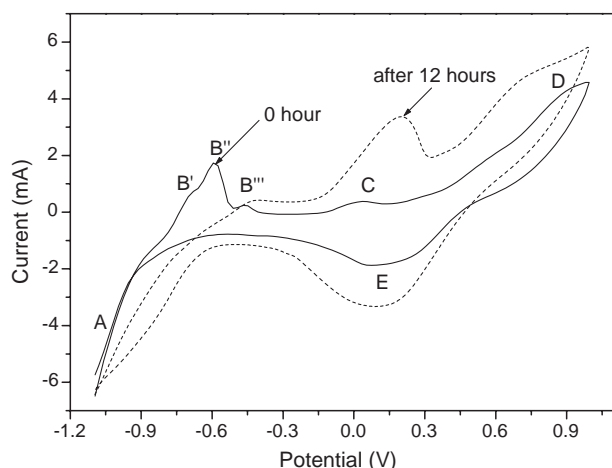


Fig. 5. Cyclic voltammograms of a marmatite – carbon paste electrode in the presence of *At. f* at 35 °C and a sweep rate of 100 mV/s: the first cycle and the one after 12 h of bioleaching.

that the cell density increased, especially in the cells by EPS [18] attached to the solid substrate surface. It could be presumed that the attached cells might accelerate the reaction (4) (Ref. [13]). The catalytic action of the attached bacteria was performed by transferring electrons from the available surface sulfur compound to the polymeric ferric ion in the EPS layer [19]. By comparison, the similar change in the cyclic voltammogram was not observed only when the concentration of Fe^{3+} ions increased. In addition, the formation of elemental sulfur on the electrode surface and the increase of the concentration of Fe^{3+} ions in the solution also resulted in the changes in the electrochemical behaviors of the electrode during the bioleaching process.

3.3. Open-circuit potentials and chronoamperometric curves of marmatite electrode

Fig. 6 showed the open-circuit potentials of the marmatite electrode in the different leaching systems. The values of the open-circuit potential (OCP) were 273.5 mV/

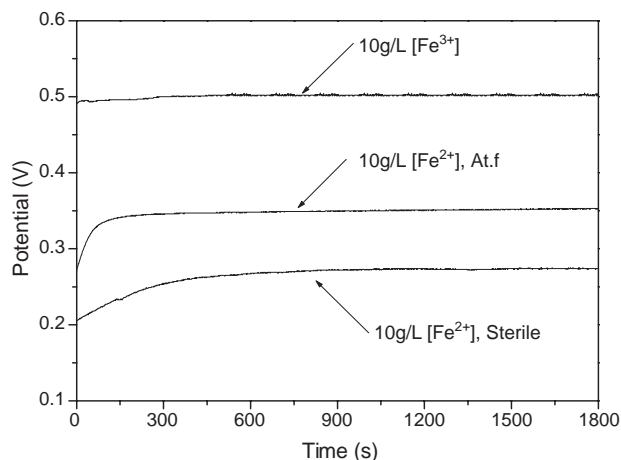


Fig. 6. Open-circuit potentials of a marmatite – carbon paste electrode in the different leaching solutions.

SCE in the solution with 10 g/L [Fe^{2+}] in the absence of bacteria, 351.5 mV/SCE in the solution with 10 g/L [Fe^{2+}] inoculating *At. f*, and 502.5 mV/SCE in the sterile solution with 10 g/L [Fe^{3+}], respectively. It was found that the values were influenced mainly by the concentration of Fe^{3+} ions and the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions in the leaching solution. The open-circuit potential in the presence of bacteria was higher than that in the absence of bacteria because a little amount of Fe^{3+} ions contained in the inoculum was added.

In the same electrolytical solution, the open-circuit potentials of the electrode were different from the stable potentials, which were indicated by the polarization curve. When the applied potential was swept from the negative to positive potentials, the concentrations of deoxidized products in the interface of the electrode and the leach solution higher than that in reality solution and the concentrations of oxidized products in the interface of the electrode and the leaching solution lower than that in reality solution, so the stable potential was lower than the open-circuit potential under the same leaching conditions. In addition, the ratio of $\text{Fe}^{3+}/\text{Fe}^{2+}$ ions in the interface of the electrode and the leaching solution was lower than that in the reality solution because the marmatite in the electrode surface could react

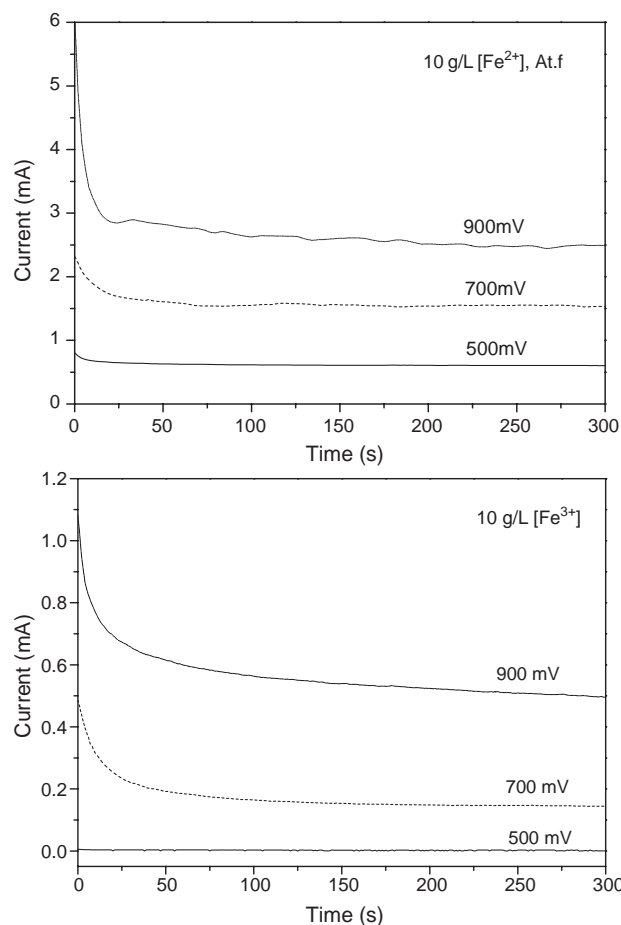


Fig. 7. Chronoamperometric curves of a marmatite – carbon paste electrode in the presence and absence of *At. f* at 35 °C and applied potentials of 500, 700 and 900 mV.

with Fe^{3+} ion, so the open-circuit potential was lower than the of the redox potential of the leaching solution.

Fig. 7 showed the chronoamperometric curves of the electrode in the presence and absence of *At. f* under the differently applied potentials. It was found that the polarization currents in all the leaching systems increased with the increase of the applied potentials, moreover, the current values were proportional to the overpotentials. The result suggested that the bacterial leaching of marmatite could be strengthened by the applied potential. Under the same applied potentials in the solution of 10 g/L $[\text{Fe}^{2+}]$, the polarization currents in the presence of bacterial strains were markedly higher than that in the sterile controls; and then the catalytic action of microorganisms on the marmatite bioleaching was shown further.

Selvi, et al. [5] reported that the dissolution rate of zinc sulfide appeared two maximums when the applied potentials were -0.5 V and $+0.4$ V during the bioleaching of sphalerite, moreover, its dissolution rate was more rapid when the applied potential was $+0.4$ V. However, when the

applied potential was too high, the growth and activity of bacterial strains could be restrained and the occurrence of the side reactions, such as the formation of oxygen and hydrogen, could lead to energy wastage.

3.4. SEM images of the surface of marmatite – carbon paste electrode

The typical SEM images of the marmatite electrode after 12 h of leaching in the differently electrolytical solutions were shown in Fig. 8. Other than that with the chemical leaching of Fe^{3+} ions, in the presence of bacterial strains the corrosion pits formed in the electrode surface were similar to the attached cells of *Acidithiobacillus ferrooxidans* and a moderate thermophilic (MLY) in shape and size, respectively. The SEM observation meant that the formation of corrosion pits in Fig. 8 (b, c) was closely related to the bacterial cells attached on the surface of solid substrate, which was also proved that the reaction (4) could be promoted by the attached cells. In addition to the chemical

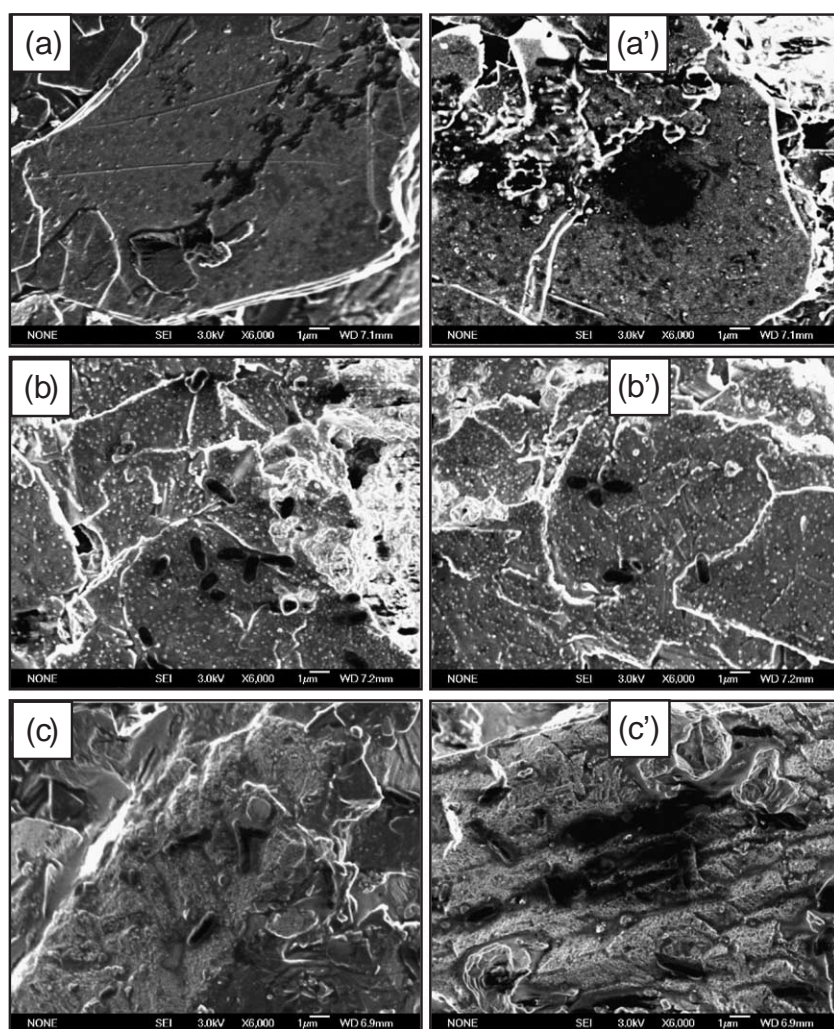


Fig. 8. Typical SEM images of the surface of a marmatite – carbon paste electrode after leaching in the different solutions: (a,a') 10 g/L Fe^{3+} ions; (b,b') *Acidithiobacillus ferrooxidans*; (c,c') moderate thermophilic (MLY).

leaching of Fe^{3+} ions, the dissolution of marmatite was influenced by the contact leaching of the attached bacterial cells during the bioleaching process of the concentrate.

4. Conclusions

The electrochemical behaviors of a marmatite – carbon paste electrode in the presence and absence of bacterial strain showed that the cyclic voltammograms of the electrode presented the different features under the different leaching conditions, which meant that the leaching of marmatite could be carried out by the different reactions. The reductive components were difficult to form or were oxidized immediately by Fe^{3+} ions in the leaching solution when the redox potential was higher. The chemical oxidation of Fe^{3+} ion played an important role for the dissolution of marmatite, especially in the initial leaching stage when the cell density was lower. It was also shown that the attached cells might accelerate the oxidation reaction of marmatite during the bioleaching process.

The polarization current of the marmatite electrode increased with the increase of applied potentials and was proportional to the overpotential, which suggested that the dissolution of marmatite could be accelerated by the applied potential. Other than that with the chemical leaching of Fe^{3+} ions, the corrosion pits formed in the electrode surface were similar to the attached bacterial cells of *Acidithiobacillus ferrooxidans* and the moderate thermophilic (MLY) in shape and size, respectively. In addition to the chemical leaching of Fe^{3+} ions, the dissolution of marmatite was influenced by the contact leaching of the attached bacterial strains during the marmatite bioleaching.

Acknowledgements

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