การยับยั้งปฏิกิริยาการออกซิเดชันที่ผิวของอาร์เซโนไพไรต์โดยการเคลือบผิวด้วยฟิล์มโซลเจล MTMOS : การศึกษาทางไฟฟ้าเคมี

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บทคัดย่อ

ปัญหาการกระจายของสารหนูบริเวณเหมืองแร่ ส่วนหนึ่งเกิดจากการออกซิเดชันของแร่อาร์เซโนไพไรต์ (FeAsS) แบคทีเรียชนิด chemolithotropes โดยเฉพาะอย่างยิ่ง แบคทีเรียชนิด *Acidithiobacillus ferrooxidans* จะเร่งอัตราการออกซิเดชันของแร่โดยผ่านการดูดซับที่ผิวแร่ การเคลือบฟิล์มที่ผิวแบบบางที่ผิวแร่ด้วยการสร้างชั้นป้องกันไม่ให้แบคทีเรียเข้าไปเกาะ เป็นวิธีที่ได้ผลที่สุดในการป้องกันการออกซิเดชันแร่อาร์เซโนไพไรต์ไม่ให้สารหนูแพร่กระจายออกไป ในการศึกษาเบื้องต้นนี้ ได้ใช้สารเคลือบชนิด methyltrimethoxysilane (MTMOS) เคลือบผิวแร่อาร์เซโนไพไรต์ จากการทดลองการออกซิเดชันทางชีวภาพและทางเคมี พบว่าสามารถยับยั้งการออกซิเดชันของแร่อาร์เซโนไพไรต์ได้เป็นอย่างดี นอกจากนี้ การทดลองทางไฟฟ้าเคมีเพื่อหาความต้านทานของฟิล์มโดยการจุ่มในสารละลายอิเล็กโตรไลต์โซเดียมคลอไรด์ร้อยละ 3 เพื่อหา Electrochemical Impedance Spectroscopy (EIS) พบว่า ความต้านทานเท่ากับ 10^8 โอห์มต่อตารางเซนติเมตร และเมื่อเวลาผ่านไป 3 วัน พบว่า ค่ามีลดลงเล็กน้อยเท่ากับ 10^7 โอห์มต่อตารางเซนติเมตร ซึ่งแสดงให้เห็นว่า ฟิล์มมีความต้านทานสูงและมีความเสถียร

คำสำคัญ : อาร์เซโนไพไรต์ / โซลเจล / *Acidithiobacillus ferrooxidans* / Electrochemical Impedance Spectroscopy (EIS) / Methyltrimethoxysilane (MTMOS)

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Suppression of Arsenopyrite Surface Oxidation by Coating with MTMOS Sol-Gel Film: An Electrochemical Characterization

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Received 18 October 2004 ; accepted 14 March 2005

Abstract

Oxidation of arsenopyrite (FeAsS) in mine tailings is considered as the major cause of arsenic releasing in groundwater around mine sites. The oxidation rate is accelerated by the biooxidation of chemolithotropes bacteria, such as *Acidithiobacillus ferrooxidans* via the adsorption mechanism. Hence, coating with thin films as a physical barrier for oxidants approaching the mineral surface is one of the effective abatement strategies. In preliminary work, we confirmed the effectiveness of methyltrimethoxysilane (MTMOS) coating by biochemical and chemical oxidations. In this work, we examined the effectiveness by the technique of the resistance of MTMOS film coated on arsenopyrite rod under immersion in 3 wt% NaCl electrolyte with electrochemical impedance spectroscopy (EIS). The coating resistance was 10^8 ohm/cm^2 and slightly decreased to a steady state value around 10^7 ohm/cm^2 after 3 d immersion.

Keywords : Arsenopyrite / Sol-Gel / *Acidithiobacillus ferrooxidans* / Electrochemical Impedance Spectroscopy (EIS) / Methyltrimethoxysilane (MTMOS)

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1. Introduction

The arsenic contamination of soils and surface waters or groundwater represents a great threat to human health due to its high potential to enter into the food chain.

Today, millions of people in the world are suffering from arsenic related diseases due to consumption of arsenic contaminated underground water. Arsenic pollution in ground water has been found in many countries in different parts of the world. High concentration of arsenic in water has caused symptoms of chronic arsenic poisoning in local populations of many countries: New Zealand [1], Spain [2], Rocky mountain, United States [3], Canada [4], South California, United States [5], Bangladesh [6, 7], Saskatchewan, Canada [8], Prebuz mine, Czech Republic [9], France [10] and Thailand [11].

Arsenic is presented in the environment in a number of different inorganic and organic chemical forms due to its participation in complex biological and chemical processes. Some of the most important arsenic species from a toxicological perspective include the two oxidation states: As (III), As (V), monomethylarsonic acid (MMA), dimethylarsinic acid (DMA), arsenobetaine and arsenocholine.

Arsenic is widely distributed as a trace constituent in rocks and soils, natural waters and organisms. It can be mobilized by natural processes, mainly by weathering and microbial activity. However, its natural contamination potential by geochemical processes on the widespread natural occurrences is not very well known. The main natural occurrences of arsenic are ore deposits with sulphide minerals, which can contain very high amounts of As, and some rock types such as shales, sandstones and phosphate rocks, which can contain up to some hundreds of mg/kg [12].

More than 320 minerals [13] contain arsenic, the most common ones being arsenopyrite (FeAsS) [11, 14, 15], orpiment (As_2S_3), realgar (As_2S_2), and solid solution in pyrite (FeS_2) [16]. Arsenic-rich mine drainage usually originates from the weathering of arsenical pyrite or arsenopyrite. These effluents, which are acidic and also contain high levels of metals, discharge into the surrounding environment and are toxic to biota [17].

In Thailand, arsenic contamination of domestic water supplies in Ron Phibun District, Nakhon Si Thammarat Province, the south of Thailand was first recognized in 1987. The arsenic concentration was up to 5,000 mg/kg [18]. The contamination of arsenic in the area came from the arsenopyrite from the mining process abandoned around the area. The bacteria present in the area, *Acidithiobacillus ferrooxidans*, a chemolithoautotroph bacteria, has played an important role in the arsenic releasing mechanism [19].

Acidophilic bacterial genera species are presented in acid mine drainage environments [20] and play an important role on the behavior of metals in surface waters. Well known microbial processes are involved in the S cycle [21, 22]: oxidation of Fe sulfide by acidophilic bacteria produces H_2SO_4 and metal ions or AMD (Acid Mine Drainage), a reaction which is mainly utilized in the microbial leaching of low grade sulfide ores to extracted metals [23].

Acidithiobacillus ferrooxidans (formerly known as *Thiobacillus ferrooxidans* [24]). *A. ferrooxidans* is found in drainage waters associated with many AMD environments and is known to accelerate the rate of sulfide-containing mineral oxidation [25]. Microbial activity is essential for the rapid production of AMD in tailings piles and natural acidic systems [26]. Ehrlich [27] reported that *Acidithiobacillus* increased the rate of oxidation of arsenopyrite, which resulted in precipitates of iron arsenite and arsenate. The oxidation is explained by two different mechanisms: direct and indirect which are simultaneously developed [28]. Through the direct mechanism, the bacterium *Acidithiobacillus ferrooxidans* adheres to the mineral surface, promoting bio-oxidation. The bacteria adhered to the surface of the ore tend to change the surface oxidation potential and to depolarize it via the oxidation of S and Fe [29]. Through the indirect mechanism, chemical leaching of the sulphide occurs via reduction of the ferric ion in solution, which is re-oxidized by *Acidihiobacillus*.

Solidification/stabilization (S/S), also known as encapsulation or fixation, is usually a technology used to transform potentially hazardous solid wastes into less hazardous or nonhazardous solids, thus preventing the waste from entering the environment [30]. However, the cost for solidification/stabilization is considered high. For protection of arsenic leaching, many techniques were applied to use encapsulation or fixation; i.e., creating impermeable barrier for prevent either O_2 or Fe^{3+} from further oxidizing such as phosphate or silica coating [31], limestone [31], lipid coating [32]. Nevertheless, limestone, phosphate or silica coating requires the surface oxidation to create the coating barrier that may produce some arsenic releasing.

Creating the impermeable barrier for preventing either O_2 or Fe^{3+} from further oxidizing was the point of origin treatment solution. The coating by sol-gel as the protective films is proposed. The reagents used for coating are mainly alkoxides; methyltrimethoxysilane (MTMOS) or tetraethoxysilane (TEOS). So far, alkoxide coating has been used for conservation of stone via consolidation since 1925. The application of alkoxide as an stone conservation has been used widely [33-35] owing to its strengthness, durability and corrosion resistance. Also sol-gel coating has been widely used on metal to improve the corrosion resistance or to modify the surface properties. However, there are no papers published that examined sol-gel application to mineral surface coatings [36-38].

In this research, the at-source preventing strategy is adopted for the abatement of arsenic contamination problem. Surface modification by alkoxysilane coatings on arsenopyrite particles are investigated by varying H_2O/Si molar ratio. The effectiveness of the coating is investigated by both biological and chemical oxidation. The coating resistance is verified by electrochemical impedance spectroscopy (EIS).

2. Experimental procedures and methods

2.1 Sol preparation

Alkoxysilane sol was synthesized by using methyltrimethoxysilane (MTMOS, Merck, purity 98%). HCl (1 N) was used as the acid catalyst. The molar ratio of H_2O:Si:MeOH:HCl is $2:1:3:7x10^{-5}$. The solution was stirred for 2 h at 60°C.

2.2 Chemical and biological assessment

Arsenopyrite minerals The arsenopyrite used in this study was a natural mineral obtained from Geoprime Minerals & Earth Materials Company, California. The samples were crushed and finely grounded in a ball mill. The grounded minerals were sieved to obtain the size fraction of 300-425 μm in diameter. The mineral powder was washed with distilled water, air dried at 50°C for 24 h and stored in desiccators.

The principal components of arsenopyrite from X-ray Fluorescence (Philips, PW-2404) analysis are Fe 33.75 wt% As 3.5 wt% and S 0.4 wt%.

Microorganisms Autochemotropes, *Acidithiobacillus-like* isolated from Mae Moh coal mine in Northern Thailand was used in this study. The cells were maintained on the 9K medium (0.4 g/L $(NH_4)_2SO_4$, 0.4 g/L $MgSO_4 \cdot 7H_2O$, 0.4 g/L KH_2PO_4, 33 g/L $FeSO_4 \cdot 7H_2O$ and pH of 2.0) given by Silvermann and Lundgren [39]. Precultures were grown in 500 mL Erlenmeyer flask with 200 mL medium shaking at 200 rpm with a rotary shaker (INNOVA 4335 refrigerated incubator shaker) for 3 d. Cultures were inoculated from precultures to an initial optical density of 0.05. Cells were grown at the same condition as precultures but were harvested after being incubated for 2 d. The cell broth was centrifuged (HITACHI himac CR 21 centrifuge) at 4.67×10^3g for 15 min at 50°C and then washed twice with deionized water and resuspended in 9K medium to the predetermined cell concentrations.

Coating procedures The coating procedure is as follows: (i) pour 10 ml of MTMOS to a beaker and add water at pH 2 (adjusted with 1 M HCl) to the precursor at a selected H_2O/Si molar ratio of 2; (ii) allow the mixture of the precursor and water to stand for 10 min at 50°C; (iii) add 8.6 ml of methanol (99.5%) into the mixture; and stand for 120 min at 50°C.

Arsenopyrite particles (10 g; 300-425 μm in diameter) were dispersed ultrasonically in the mixture and intensively stirred for 30 min at room temperature. Then the coated arsenopyrite particles were separated from the reaction medium by centrifugation and dried at 50°C for 72 h.

Biological resistance assessment Five hundreds milligrams of coated arsenopyrite (300-425 μm in diameter) were added into 200 mL *Acidithiobacillus-like* cell solution. The mixture was shaken at 200 rpm at 35°C for 120 h. The solution sample was taken for the analysis of arsenic during the experiment.

Chemical oxidation resistance assessment We adapted the leaching procedure from Evangelou [40] for the assessment of chemical oxidation resistance. One gram of arsenopyrite particles coated with MTMOS film was leached in 200 mL solution containing 0.145 M hydrogen peroxide (H_2O_2). All leaching solution was adjusted to pH 3.0 by conc. H_2SO_4. The leaching solution with coated arsenopyrite particles was shaken at 200 rpm for 45 h. The solution was sampled for the analysis of arsenic concentration during the experiment.

Analytical methods The components of Fe, As and S in the arsenopyrite were determined by X-ray fluorescence analysis (PW-2404, Philips; Eindhoven, The Netherlands). Arsenic concentration in solution was determined by atomic absorption spectroscopy (Hitachi Z-8270 Polarized Zeeman; Hitachi, Tokyo). The surface morphology of the coating was observed by SEM (Leica S260; Cambridge, UK, operated at 15 kV accelerating voltage).

2.3 Electrochemical Impedance Spectroscopy (EIS)

Preparation of material Arsenopyrite minerals were cut into rod-bars (4 mm in diameter, 15 mm in length) degreased and cleaned in an ultrasonic bath, followed with rinsing in ethanol. The surface was polished with 1.0 μm and 0.05 μm alumina slurry and then washed with distilled water, air dried at 50°C for 24 h and stored at 25°C in desiccators.

Dip-coating of arsenopyrite rod with MTMOS was done by immersing the rod in the MTMOS sol and withdrew at constant speed 1 cm/min. The gel films were dried at 60°C overnight.

EIS measurement EIS measurements for the MTMOS coated on arsenopyrite were performed in 3 wt% NaCl using three electrodes, with a saturated calomel electrode as a reference electrode and a platinum as a counter electrode. EIS tests were carried out using an ACM instrument (Gill AC). The data were obtained using a signal of 10 mV amplitude applied over a bandwidth from 10 kHz to 10 mHz. Modeling of EIS spectra was made with Equivalent Circuit 4.55 software (B.A. Boukamp, 1997).

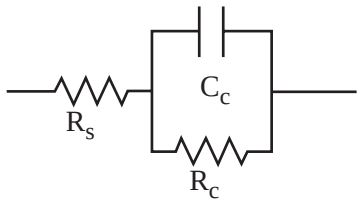


Fig. 1 The equivalent circuit of MTMOS coated on arsenopyrite at the beginning time of immersion.

During the initial period of immersion, a perfect coating often has excellent barrier performance, resulting in a large impedance of mineral/coating system. The MTMOS coating is equivalent to a barrier layer with a high-value coating resistance parallel to a low-value coating capacitance. In this case, the equivalent electrical circuit (EEC) shown in Fig. 1 is used to fit the impedance data. The total impedance, Z, is defined by Eq. (1):

$$\begin{aligned} Z &= R_s + \frac{R_c}{1 + j\omega C_c R_c} \\ &= R_s + \frac{R_c}{1 + \omega^2 C_c^2 R_c^2} - \frac{j\omega C_c R_c^2}{1 + \omega^2 C_c^2 R_c^2} \end{aligned} \quad \textbf{(1)}$$

where R_s is the solution resistance,

C_c is the coating capacitance,

R_c is the coating resistance,

ω is the angular frequency ($\omega = 2\pi f$, f is the frequency),

and $j = \sqrt{-1}$.

3. Results and discussion

3.1 Chemical and biological oxidation

We coated the arsenopyrite particles with the MTMOS at the molar ratio H_2O/Si of 2. The resistance to chemical and biological oxidation of arsenopyrite coated by MTMOS film was shown in Fig. 2(a) and (b).The concentrations of arsenic ion concentration released during the oxidations of arsenopyrite particles coated by MTMOS (O). MTMOS demonstrated a great value of resistance in both cases of chemical and biological oxidations. MTMOS coating suppressed arsenic oxidation to the concentration 0.4-0.5 mg/L in both biological and chemical oxidations over the duration of the experiment Fig. 2 (a) and (b). Compared with intact arsenopyrite minerals without coating, a rapid increase of arsenic dissolution was detected. An increasing of the arsenic in the solution of the biological oxidation experiment was attributed to the bacteria adhering to the mineral surfaces and the startup of biological oxidation [41].

SEM micrographs in Fig. 3a, 3b show the morphology of intact arsenopyrite and arsenopyrite after coating with MTMOS respectively. Compared with intact arsenopyrite, the surface of arsenopyrite coated with MTMOS coating was smooth and crack-free throughout the whole particle.

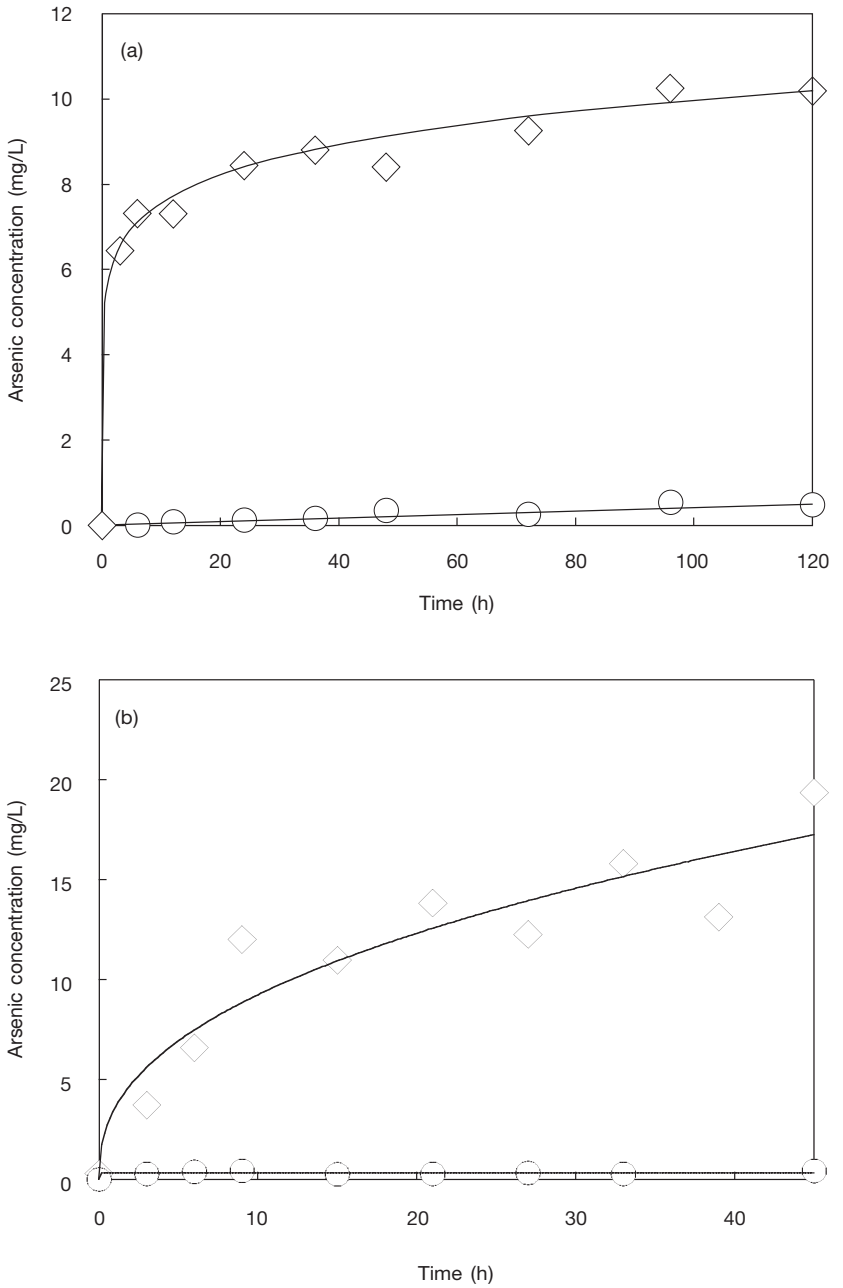
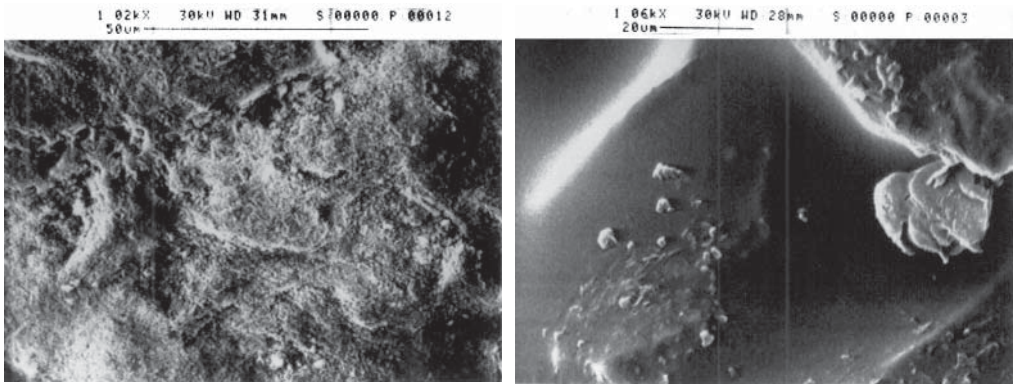


Fig. 2 Time profiles of the arsenic ion concentrations released from the oxidations of arsenopyrite particles coating with MTMOS (○) and control (◇) compared to
(a) for biological oxidation with *Acidithiobacillus-like*
(b) chemical oxidation with 0.145 M H_2O_2.



(a) (b)

Fig. 3 SEM micrographs of the (a) intact arsenopyrite and (b) after coating by MTMOS.

3.2 EIS measurement

EIS measurement of MTMOS coated on arsenopyrite was carried out with 3 wt% NaCl solution. The results were presented as Bode plots that comprised with the impedance modulus measured over a frequencies range. The high frequency range reflects the coating defects including the capacitance of the coating and the electrolyte resistance, while the low frequency range reflects the processes occurring at the mineral surface [42, 43].

As shown in Fig. 4, we found that the impedance modulus ($|Z|_{0.1Hz}$) of arsenopyrite sample was significantly increased to the order of 10^7-10^8 ohm/cm^2 when coated with MTMOS particularly in the range of low frequency (0.1-10 Hz). Moreover there is no indication of the coating degradation during the immersion under 3 wt% NaCl solution. However, the intact arsenopyrite sample demonstrates a lower value of impedance modulus (10^6-10^7 ohm/cm^2). In addition, the Table 1 verifies that the $|Z|_{0.1Hz}$ of arsenopyrite with MTMOS coating almost unchanged and slightly decreased with immersion time, whereas the impedance modulus of intact arsenopyrite decreased to 10^5 ohm/cm^2 and increased to 10^6 ohm/cm^2 after 3 and 5 d of immersion respectively. The decrease of the impedance modulus in the first stage could be ascribed to the high rate of surface oxidation of the intact arsenopyrite at the beginning of immersion. An increase of the impedance modulus after 5 d was attributed to the formation of corrosion products or the oxide layer at the mineral/electrolyte interface [44, 45]. A comparison of the EIS results obtained from the arsenopyrite with and without MTMOS coating reveals that MTMOS coating enhanced the impedance modulus and induced a stable protective layer, which protected the arsenopyrite surface from oxidative media.

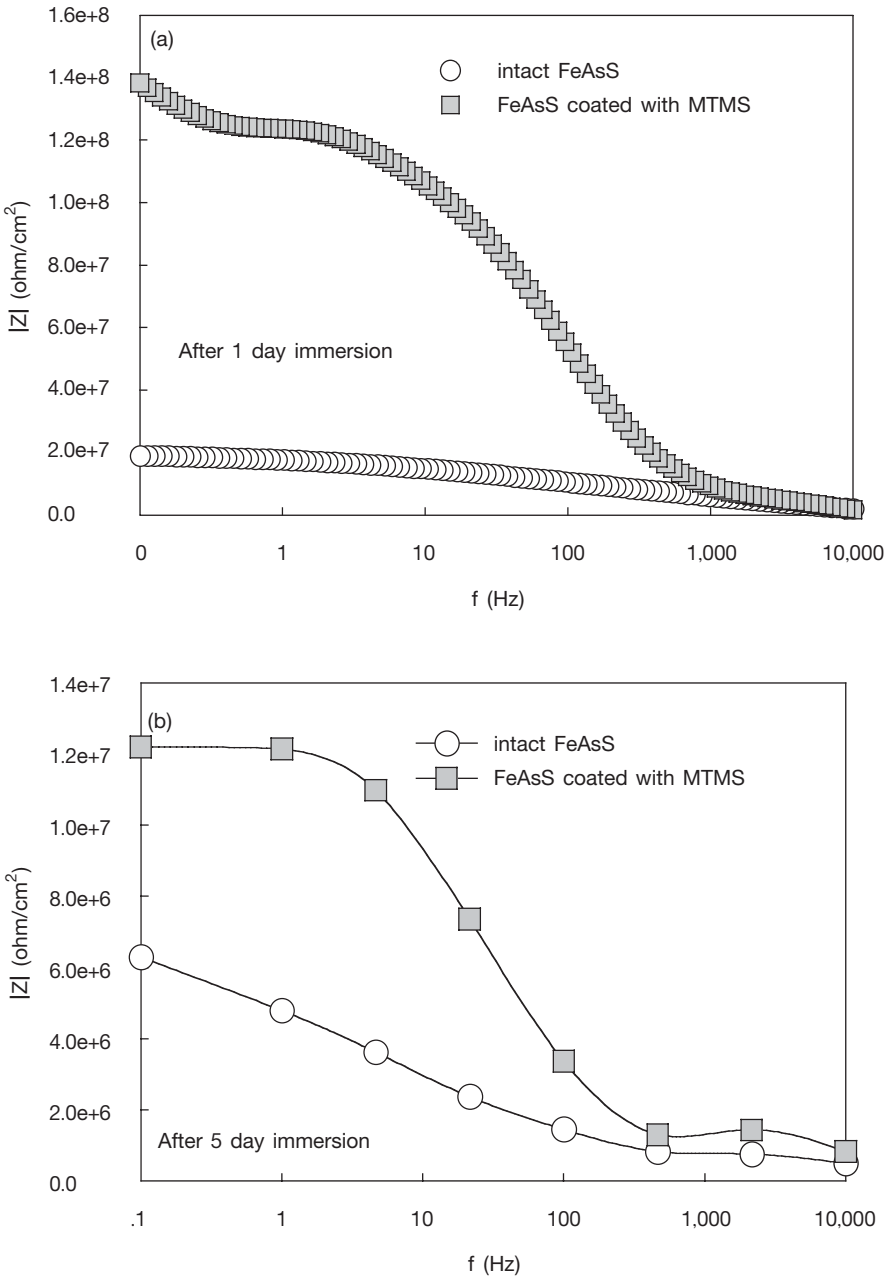


Fig. 4 Bode plot of intact arsenopyrite and arsenopyrite with MTMOS coating in 3 wt% NaCl (a) at 1 d immersion (b) at 5 d immersion

Table 1 The impedance modulus of arsenopyrite with and without MTMOS coating at different immersion times

Sample	$\|Z\|_{0.1Hz}$ (ohm/cm^2)			
	15 min	1 d	3 d	5 d
without MTMS	1.89E+07	1.17E+07	6.99E+05	5.79.E+06
with MTMS	2.10E+08	1.38E+08	3.67E+07	1.21E+07

4. Conclusion

The results show that MTMOS coating inhibits the arsenopyrite surface oxidation and suppress both biological oxidation by *Acidithiobacillus ferrooxidans* and chemical oxidation. The EIS measurement reveals that the impedance modulus decrease with immersion time because of the water permeation into the surface and the resulting in a large impedance of mineral/MTMOS coating system demonstrates a high performance protective layer from oxidative environment.

5. Acknowledgement

We acknowledge professor Bernard A. Boukamp at the University of Twente (Department of Science and Technology), the Netherlands, for kindly providing the Equivalent Circuit 4.55 software for this study. This study was financially supported by the Joint Graduate School of Energy and Environment, King Mongkut's University of Technology Thonburi.

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