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Carrier-Microencapsulation for Preventing Pyrite Oxidation

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Abstract

The oxidation of pyrite causes the formation of acid mine drainage polluted by heavy metals. This paper proposes carrier-microencapsulation (CME) for preventing pyrite oxidation. In CME, an organic agent is used as an *in-situ* carrier for transporting Ti from Ti minerals to the pyrite surface through an aqueous phase. Then, the organic carrier is decomposed and $Ti(OH)_4$ or TiO_2 film is formed on the pyrite surface as a protective coating against oxidation.

To demonstrate the effect of CME on pyrite oxidation, shaking-flask leaching experiments of ground pyrite were performed at 298 K in air for 25 days, with or without anatase (TiO_2) and catechol (1,2-dihydroxybenzene) as the organic carrier. The amounts of Fe and S extracted from the pyrite were lower with TiO_2 and catechol than without TiO_2 or catechol, indicating that CME using TiO_2 and catechol is effective in suppressing pyrite oxidation. When TiO_2 and catechol coexist, the Ti concentration in the solution phase increased initially and then decreased. SEM-EDX analysis of the CME-treated pyrite showed that Ti and O are present on the pyrite surface. Cyclic voltammogram of catechol showed that catechol was oxidized on pyrite electrode. These results indicate that Ti is extracted from TiO_2 by catechol as a Ti-catechol complex and that the complex is adsorbed and oxidized on pyrite to form a $Ti(OH)_4$ or TiO_2 coating suppressing pyrite oxidation.

Keywords: Pyrite; Tailings disposal; Leaching; Acid mine drainage; Microencapsulation

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1. Introduction

Pyrite, FeS_2, is a common sulfide mineral present very widely in the earth's crust. Pyrite is stable under anaerobic conditions but is oxidized and dissolved to release soluble iron species and sulfuric acid when it comes in contact with oxygen and water. The sulfuric acid lowers the pH of the waters and enhances metal extraction from coexisting minerals. Thus pyrite dissolution causes the formation of acidic waters polluted by various metal ions, e.g. lead and arsenic, and brings about serious environmental problems. This phenomenon is called as Acid Rock Drainage or ARD. It is frequently discharged from mining sites (then referred to as Acid Mine Drainage or AMD) and underground excavation sites for subway and tunnel construction (Nagasawa et al., 2004), and also occurs naturally.

To prevent ARD formation, many methods have been proposed for suppressing pyrite oxidation and one of the promising methods is microencapsulation. In this method, a thin protective coating is formed on pyrite surface which inhibits oxygen diffusion to pyrite surface (Evangelou, 1995). It was reported that the microencapsulation using phosphate and silicate coatings was effective for preventing pyrite oxidation in column leaching experiments that lasted 1.25 years (Evangelou, 2001). The protective coatings were formed using a solution composed of hydrogen peroxide or hypochlorite as preoxidant, KH_2PO_4 or H_4SiO_4, and sodium acetate or limestone as pH buffer.

Other materials have been employed to form a protective coating on pyrite against oxidation such as organic compounds containing hydroxyl functional groups (Chander and Zhou, 1992), natural phosphate rocks and bacterial growth media (Kalin et al., 1998), and lipids having two organic hydrophobic tails and a polar hydrophilic head group (Elsetinow et al., 2003).

In the present study, the authors propose carrier-microencapsulation (CME) as a new technique for making the protective coatings. Fig. 1 is a schematic representation of CME. In CME, an organic agent is used as a carrier for Ti (9^{th} most abundant element in the earth's crust, 0.57% by mass (Taylor, 1964)), transporting it from Ti minerals to the pyrite surface through the aqueous phase. Then, the organic carrier is decomposed and TiO_2 or $Ti(OH)_4$ film is formed on the pyrite surface as a protective coating against oxidation. Because TiO_2 is very stable thermodynamically and resistant against chemical attacks by acids, alkalis, oxidant, and reductant, it may be expected that CME using TiO_2 as a protective coating can prevent pyrite oxidation over a long time. To demonstrate the effect of CME on pyrite oxidation, CME was conducted using catechol (1,2-dihydroxybenzene) as an organic carrier for forming TiO_2 or $Ti(OH)_4$ coating on pyrite surface.

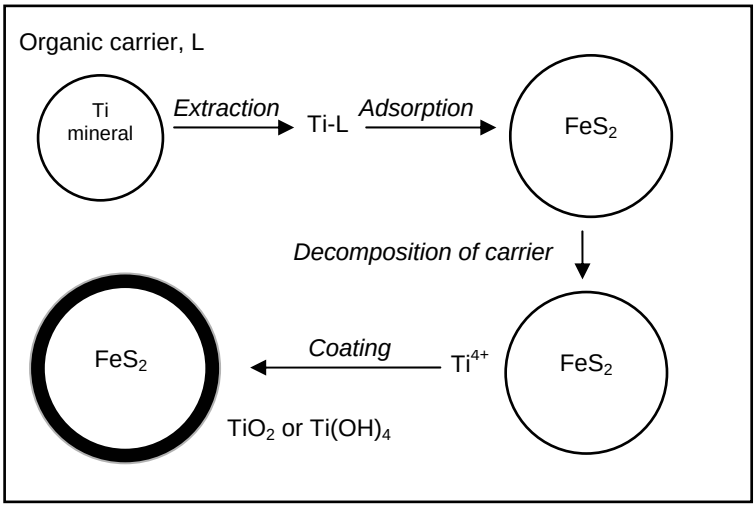


Fig. 1. Schematic illustration of carrier-microencapsulation (CME).

2. Materials and methods

Raw pyrite was obtained from Yanahara Mine, Okayama, Japan. It was ground by a ball mill and then dry-sieved to obtain +53-75 μm fraction. To remove the oxidized surface layer and to obtain a stoichiometric surface of pyrite, the washing method done by Sasaki et al. (1995) was adapted. The sieved sample was washed with ethanol in a beaker placed inside an ultrasonic vibrator for 30 s. Then, the ethanol was decanted and the pyrite was washed subsequently with 1 N HNO_3, distilled water (two times), and acetone (four times). Finally, the washed pyrite was vacuum-dried. Table 1 gives the chemical composition of the pyrite sample determined by SEIKO SPS7800 Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) after acid digestion of 0.1 g of the sample in 5 cm^3 of 60% HNO_3, 1 cm^3 of 96% $HClO_4$, and 1 cm^3 of 50% HF inside a laboratory microwave. Assuming that the particle's shape is sphere, the specific surface area of the pyrite was calculated from its mean particle diameter (64 μm) and density (5.02 g cm^{-3}), and was equal to 18.7 $m^2\ kg^{-1}$.

Reagent grade anatase and rutile TiO_2 powder (Wako Chemical Co. Ltd.) were used instead of natural Ti minerals. Specific surface area of anatase and rutile determined by BET method using N_2 were 17.6 $m^2\ g^{-1}$and 14.1 $m^2\ g^{-1}$, respectively.

As an organic carrier, reagent grade catechol (1,2-dihydroxybenzene, $C_6H_4(OH)_2$, Wako Chemical Co. Ltd.) was used. Catechol solutions were prepared by dissolving known masses of catechol in ion exchange-distilled water and pH was adjusted whenever required by addition of H_2SO_4 or NaOH.

Shaking-flask experiments were employed using a water bath shaker (shaking rate, 120 strokes min^{-1}; temperature, 25°C) to evaluate the ability of catechol to extract Ti from TiO_2, the adsorption of Ti on pyrite from aqueous phase, and the effects of CME on pyrite oxidation, as detailed in the following sections. The solutions were collected by membrane filters (pore size, 0.2 μm) and Ti, Fe, and S concentrations in the filtrates were measured by ICP-AES. In a part of the experiments, the pyrite residue was collected by filtration and vacuum-dried overnight at 50°C for Scanning Electron Microscopy and Energy Dispersion X-ray (SEM-EDX) analysis.

To investigate the oxidation of catechol on pyrite, cyclic voltammetry was carried out using pyrite working electrode, Pt counter electrode, and saturated Ag-AgCl reference electrode in 10 mol m^{-3} Na_2SO_4 solution with or without 10 mol m^{-3} catechol at 25°C and natural pH (pH 5-6) under N_2 atmosphere. Potential scan was initiated from the rest potential of pyrite electrode to anodic direction using a scan rate of 0.005 V s^{-1}.

3. Results and discussion

3.1 Extraction of Ti from TiO_2 by catechol

To confirm the ability of catechol to extract Ti from TiO_2, shaking-flask experiments were carried out for 1 day with a 50-cm^3 Erlenmeyer flask containing 1 g of TiO_2 (anatase and rutile) and 10 cm^3 of catechol solution.

Fig. 2 shows the amount of Ti extracted for 1 day as a function of catechol concentration at natural pH condition (pH 5-6). The amount increased with increasing catechol concentration, confirming that catechol acts as an extractant for Ti. The amount of Ti extracted from anatase was higher than from rutile. Maximum percentage of Ti extracted from anatase was 0.001% and from rutile was 0.0001% using 100 mol m^{-3} catechol.

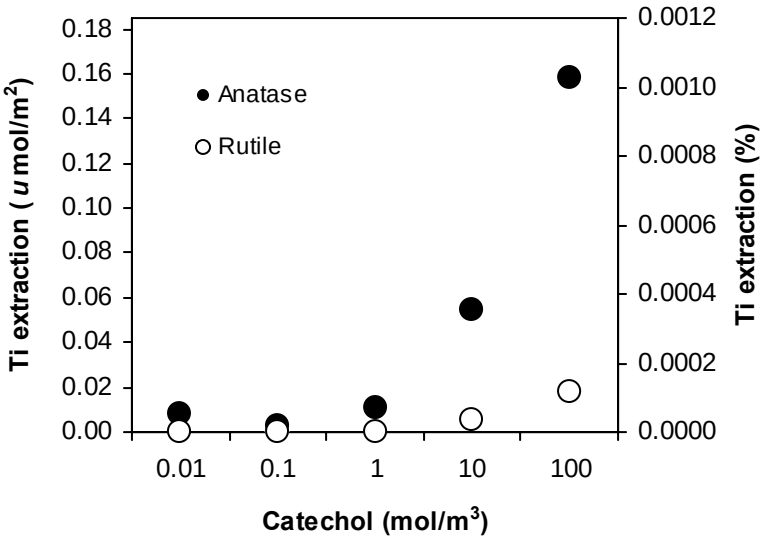


Fig. 2. Effect of catechol concentration on the amount of Ti extracted per unit surface area of TiO_2 at natural pH (pH 5-6) after 1 day.

Fig. 3 shows the effect of pH on Ti extraction from TiO_2 in the presence of 100 mol m^{-3} catechol for 1 day. In the acidic region, the amount of Ti extracted was very low but it increased with increasing pH and significant amount of Ti was extracted from TiO_2 at above pH 4 for anatase and at above pH 6 for rutile. Maximum percentage of Ti extracted from anatase was 0.03% and from rutile was 0.01% at about pH 8.

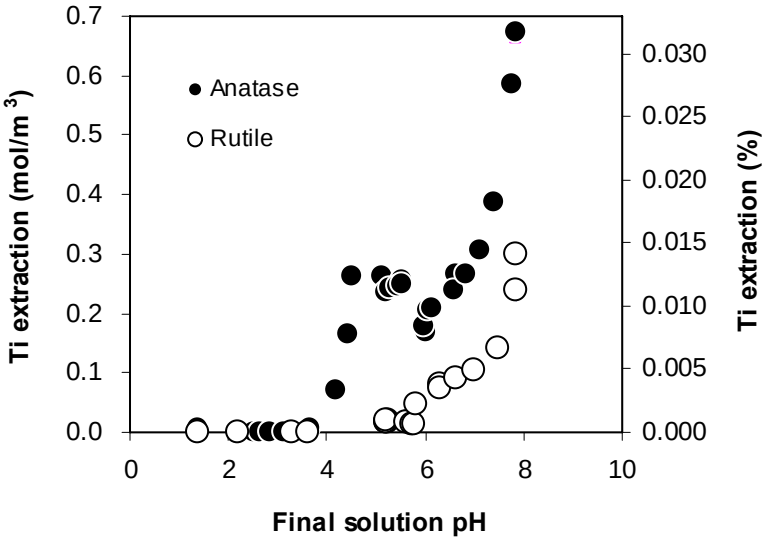
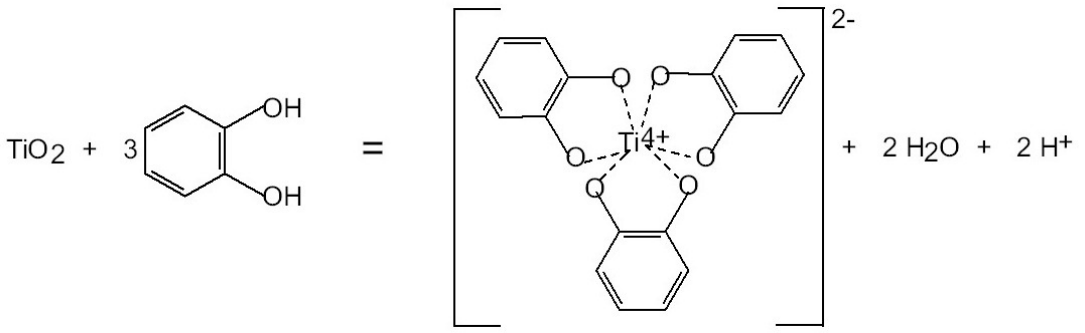


Fig. 3. Effect of pH on the amount of Ti extracted from TiO_2 in the presence of 100 mol m^{-3} catechol after 1 day.

Catechol is a weak diprotic acid (pKa_1 = 9.2, pKa_2 = 13.0) and is present in the undissociated form over a wide pH range (Rodriguez et al., 1996). It was also reported that catechol forms a tris complex with Ti, $Ti(C_6H_4O_2)_3^{2-}$, and this complex is stable from pH 6-12 (Raymond et al., 1984). The extraction of Ti from TiO_2 by catechol is assumed to be due to the following reaction:



(1)

As in the above equation, protons (H^+) are a product of the TiO_2 dissolution. This may be the reason why TiO_2 dissolution is suppressed at low pH where the H^+ concentrations are high. In support to this, pH decreased with time as Ti was extracted by catechol (separate experiment, data not shown). This agrees with Eq. 1.

3.2 Adsorption of Ti on pyrite from Ti-catechol complex solutions

The adsorption of Ti on pyrite from Ti-catechol complex solutions was next evaluated. Ti-catechol complex solutions of varying Ti concentrations but constant total catechol concentration of 100 mol m^{-3} were prepared by shaking-flask experiment of 1 g anatase TiO_2 in 10 cm^3 of 100 mol m^{-3} catechol solution (Section 3.1) and diluting the resulting Ti-catechol complex solution with 100 mol m^{-3} catechol solution.

Fifty-cm^3 Erlenmeyer flasks containing 10 cm^3 of the diluted Ti-catechol complex solution and 6 g of pyrite were shaken at 25°C for 1 day in air or in N_2 and Ti concentrations in the filtrates were determined. A preliminary experiment without pyrite confirmed that Ti does not precipitate from the solution phase. The adsorption amount of Ti on pyrite surface was calculated by subtracting the Ti concentration in the filtrate from the Ti concentration in the Ti-catechol complex solution. Following similar procedures, the adsorption of Ti ions on silica was also investigated**.**

Fig. 4 shows the amount of Ti adsorbed on 1 g of pyrite as a function of Ti concentration after 1 day shaking in air. The initial pH values of the prepared Ti-catechol complex solutions were from pH 4.5-5.0 and final pH values after mixing with pyrite were from pH 3.0-3.20. The result indicates that Ti was adsorbed on pyrite from the solution containing the Ti-catechol complex and that adsorption amounts increased with increasing Ti concentration. A rough estimate of the thickness of the TiO_2 coating on pyrite particle was obtained from the maximum amount of Ti adsorbed per unit surface area of pyrite and from the assumption that the coating is of anatase properties. The calculated thickness was 0.164 nm.

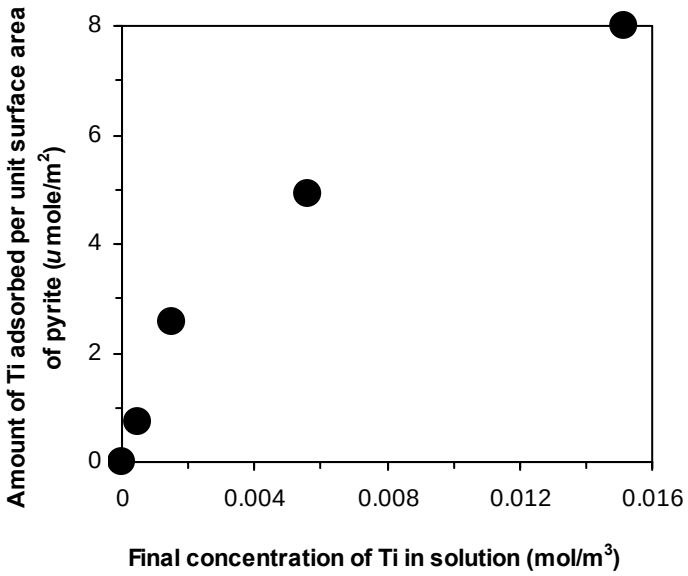


Fig. 4. Relationship between the amount of Ti adsorbed per unit surface area of pyrite and final concentration of Ti in solution after 1 day at 25°C. Initial pH, 4.5-5.0; final pH, 3.0-3.2.

Fig. 5 shows the comparison of the amounts of Ti adsorbed on pyrite and on silica in the presence or absence of O_2. Adsorption amount of Ti on silica was negligible and Ti was selectively adsorbed on pyrite. This selective adsorption is important considering that silica is more abundant in the natural environment than pyrite. If Ti-catechol complex is applied to prevent pyrite oxidation in actual situation, it can be expected that the presence of silica would have no effect on the adsorption of Ti on pyrite.

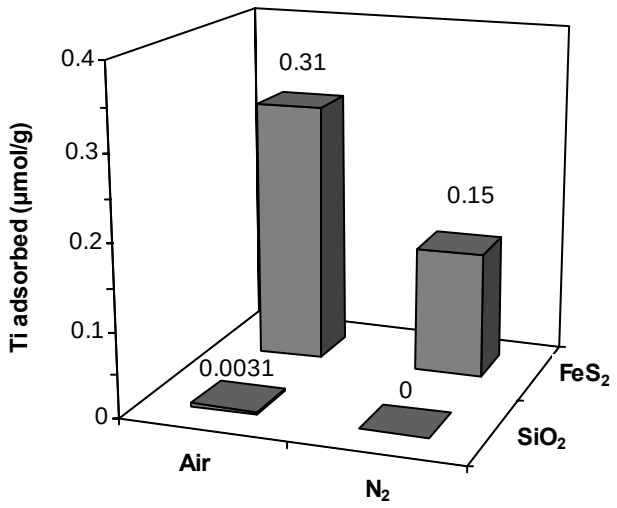
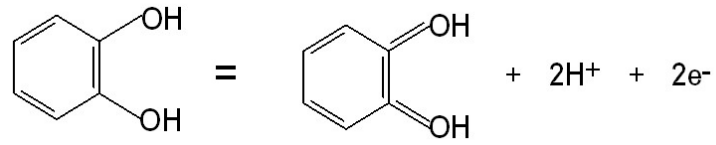


Fig. 5. Adsorption amount of Ti on pyrite and on silica with or without O_2 at 25°C after 1 day. Initial Ti concentration and pH were 0.22 mol m^{-3} and 5.8, respectively.

The result in Fig. 5 also shows that the adsorption amount of Ti on pyrite was larger in air than in N_2, indicating that O_2 enhances Ti adsorption on pyrite. Since O_2 is an oxidant, this result implies that an oxidation process plays an important role in Ti adsorption on pyrite from Ti-catechol complex solutions.

Fig. 6 shows the cyclic voltammogram for pyrite electrode in 10 mol m^{-3} Na_2SO_4 with and without 10 mol m^{-3} catechol at natural pH (pH 5-6). At redox potential greater than 0.25 V, a larger anodic current was observed in the presence of 10 mol m^{-3} catechol than without catechol. This indicates that catechol was oxidized on pyrite surface. The oxidation of catechol may be assumed to form quinone, $C_6H_4O_2$, as follows:



(2)

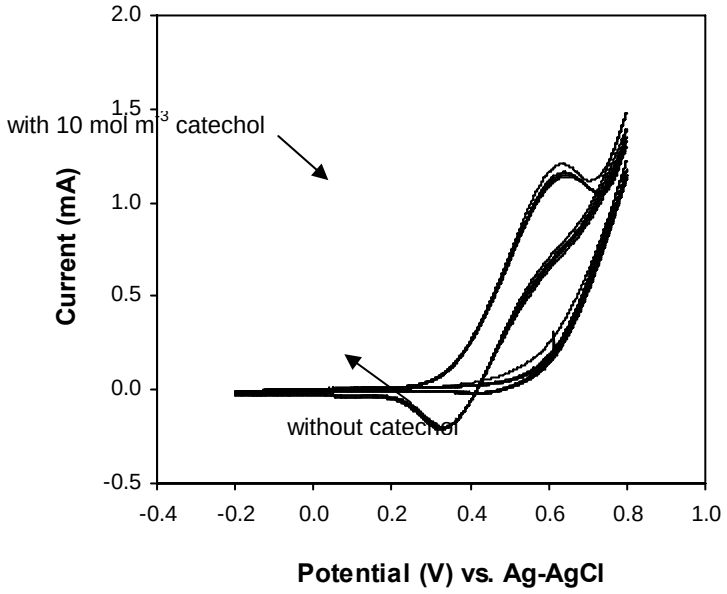
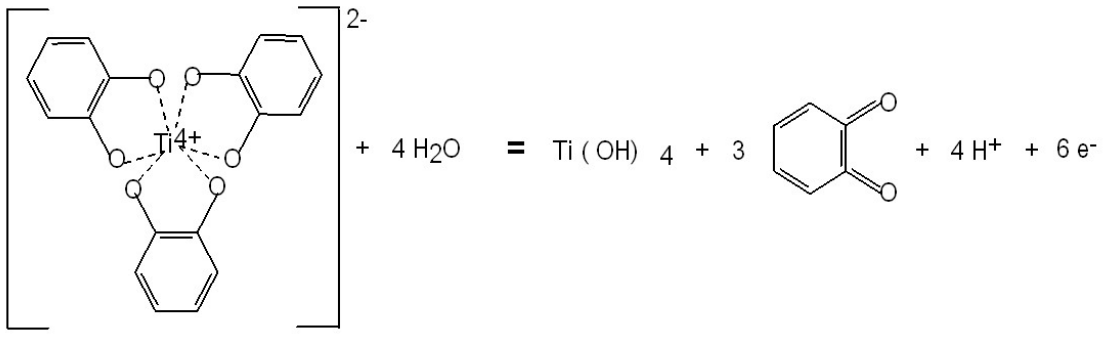
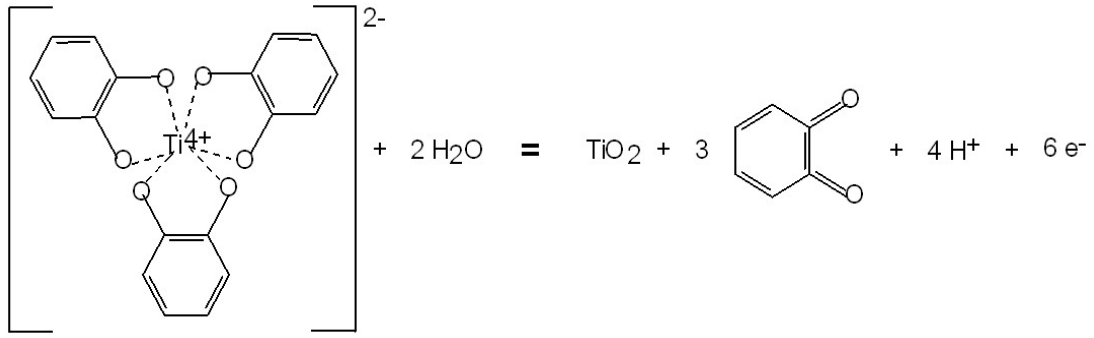


Fig. 6. Cyclic voltammogram for pyrite electrode in 10 mol m^{-3} Na_2SO_4 with and without 10 mol m^{-3} catechol at natural pH (pH 5-6).

Based on the above results, the Ti adsorption on pyrite surface from Ti-catechol complex solution is assumed to be due to the following anode reactions:



(3)

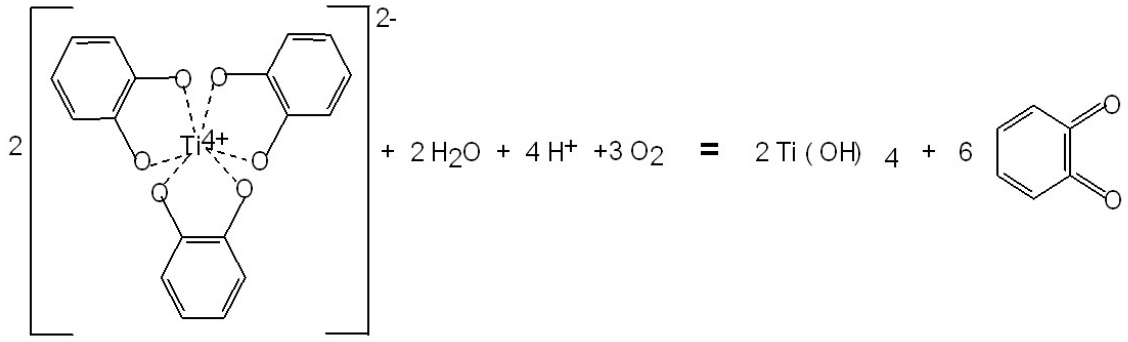


(4)

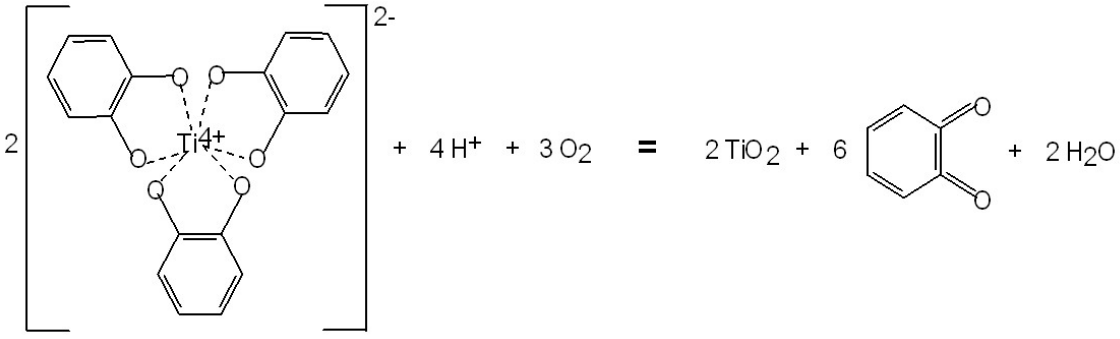
The released electrons in the above reaction may be consumed by oxygen on the cathode site of the pyrite surface as follows:

$$O_2 + 4H^+ + 4e^- = 2H_2O \tag{5}$$

Summing up the anode and cathode reactions gives the overall reactions for Ti adsorption as follows:



(6)



(7)

In the above equations, *ortho*-quinone is assumed to be a product of the reactions, but this assumption needs to be confirmed in future investigations. The oxidation mechanism may be very complex and adsorption of catechol or its oxidized product on the pyrite may occur. In this study, surface analysis like IR was not done for establishing the surface reactions between catechol and Fe and S in pyrite. Because of this, the detailed mechanism for the surface reactions cannot be discussed at the present but will be investigated in further studies.

3.3 Effects of CME on pyrite oxidation

The effects of CME using TiO_2 and catechol on pyrite oxidation were investigated by shaking-flask leaching experiment of 72 g pyrite in 120 cm^3 solution containing 100 mol m^{-3} catechol and 12 g anatase TiO_2 inside a 500-cm^3 Erlenmeyer flask for 25 days in air. For comparison, leaching experiments of pyrite with sole addition of TiO_2 or catechol and a control experiment without TiO_2 and catechol were also conducted. The results are shown in Figs. 7-10.

As shown in Fig. 7, significant amounts of Fe and S were released from pyrite in the control (without catechol and TiO_2). This would be due to pyrite oxidation by O_2 according to

$$FeS_2 + 7/2\, O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (8)$$

$$FeS_2 + 2H^+ + 1/2\, O_2 = Fe^{2+} + 2S + H_2O \quad (9)$$

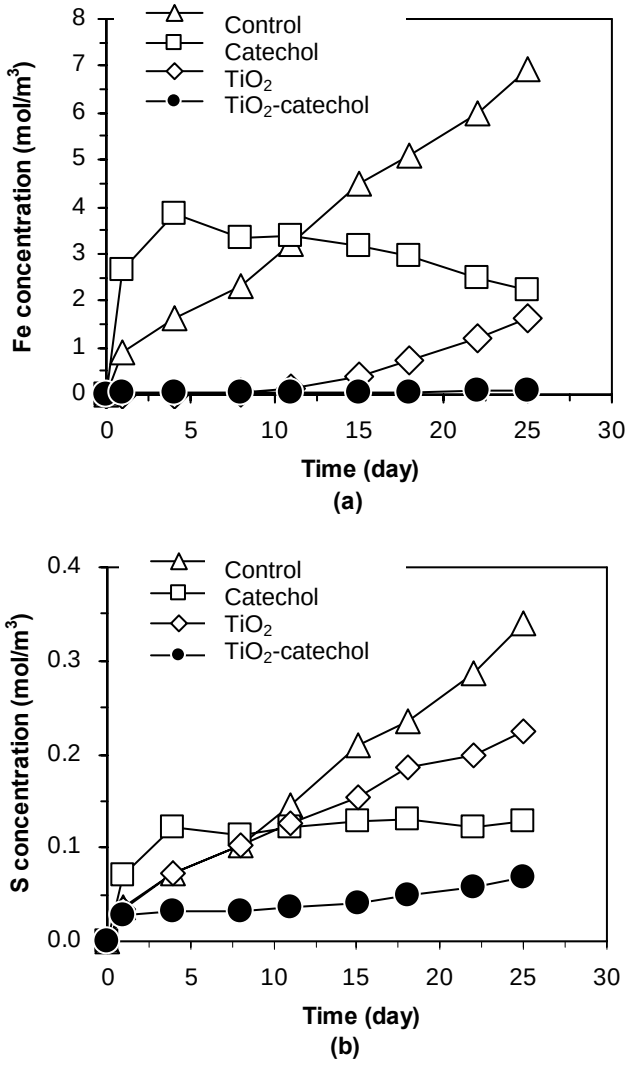


Fig. 7. Effects of anatase TiO_2 and catechol on (a) Fe and (b) S released during pyrite oxidation.

In comparison with the control, the amounts of Fe and S released were smaller with TiO_2. The amount of Fe released at the early period of the leaching with TiO_2 was almost negligible although substantial amount of S was released. The suppression in Fe release may be caused by the oxidation of Fe^{2+} to Fe^{3+} (Eq. 10) and subsequent precipitation of Fe^{3+} as a hydroxide (Eq. 11) due to the higher pH in the presence of TiO_2 at the early period (Fig. 8).

$$Fe^{2+} + H^{+} + \frac{1}{4}O_2 = Fe^{3+} + \frac{1}{2}H_2O \quad (10)$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^{+} \quad (11)$$

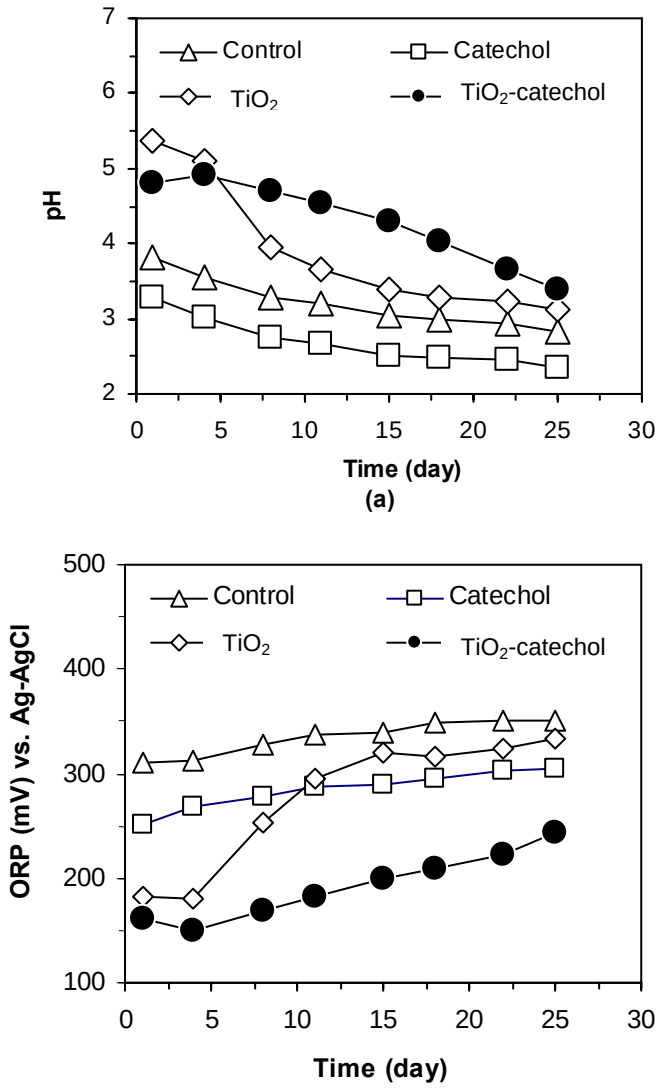


Fig. 8. Effects of anatase TiO_2 and catechol on (a) pH and (b) ORP during pyrite oxidation.

In the presence of catechol (Fig. 7), higher amounts of Fe and S were released than the control at the early period of leaching, possibly due to the enhancement of pyrite oxidation by the formation of Fe-catechol complexes (Luther et al., 1992). After 4 days, Fe concentrations decreased with time, indicating that Fe released from pyrite is precipitated according to the reaction in Eq. 11. The pH of the solution decreased gradually from pH 3.29 to pH 2.41. The concentrations of S after 4 days almost remained constant, implying that

SO_4^{2-} formation according to the pyrite oxidation in Eq. 8 has stopped. A possible explanation for this is that iron precipitate covers the pyrite surface and suppresses the oxidation in Eqs. 8 and 9. The action of catechol as a reductant might also have caused the suppression of pyrite oxidation, because O_2 and Fe^{3+}, which are oxidants to pyrite, are consumed by catechol (Pracht et al., 2001).

The release of Fe and S was significantly suppressed when TiO_2 and catechol coexisted (Fig. 7). Even with sole addition of TiO_2 or catechol, suppression in Fe and S release was recognized but the suppression was much greater with coexistence of TiO_2 and catechol. As shown in Fig. 8, pH of the TiO_2-catechol system (pH 3.5-5) was observed to be the highest after the fifth day and its ORP the lowest, supporting that oxidation of pyrite is most effectively suppressed by CME using TiO_2 and catechol. As shown in Fig. 9, when TiO_2 and catechol coexisted, significant amounts of Ti were detected in the solution phase. For the first 5 days, Ti concentration increased with time, indicating that Ti is extracted from TiO_2 in the presence of catechol. After 5 days, Ti concentration decreased with time, implying that the extracted Ti is adsorbed on the pyrite surface.

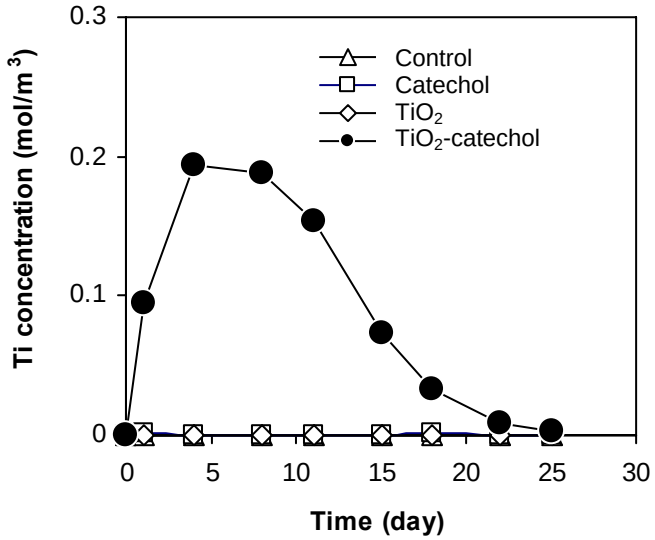


Fig. 9. Ti concentration profile with time in the leaching experiment of pyrite with anatase TiO_2 and catechol.

Fig. 10 shows the element mapping by SEM-EDX analysis of the pyrite residue leached in the presence of TiO_2 and catechol. The result shows that Ti and O are present on the pyrite surface, confirming the adsorption of Ti and also suggesting that $Ti(OH)_4$ or TiO_2 coating was formed on pyrite surface when TiO_2 and catechol coexisted. Since Fe and S signals from pyrite were also detected through the TiO_2 or $Ti(OH)_4$ coating formed on pyrite surface, it may be inferred that the thickness of the coating is very thin (possibly less than 1 μm).

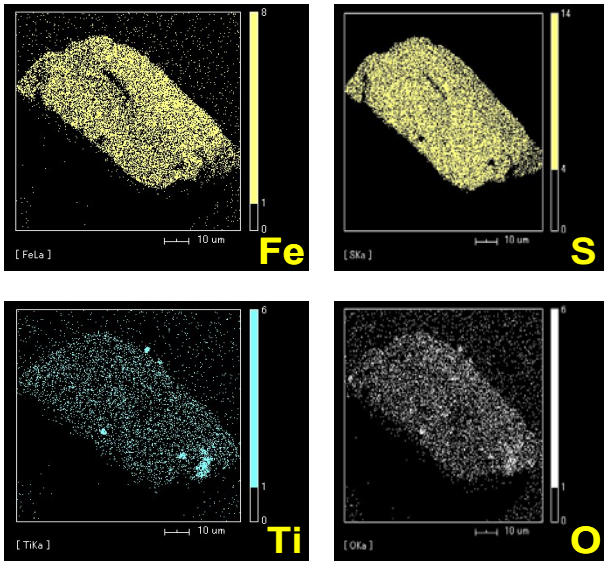


Fig. 10. Element mapping by SEM-EDX analysis of the pyrite residue leached in the presence of anatase TiO_2 and catechol.

Based on the results that indicated the presence of Ti and O on pyrite surface (Figs. 9 and 10), it may be assumed that the TiO_2 and catechol coexistence suppresses pyrite oxidation by the formation of a $Ti(OH)_4$ or TiO_2 coating on pyrite surface following the proposed redox mechanism in Section 3.2.

3.4 Factors affecting the effect of CME on pyrite oxidation

The effects of pH, concentration of catechol, amount of anatase TiO_2, and use of rutile TiO_2 instead of anatase TiO_2 on the pyrite oxidation with TiO_2 and catechol were investigated by shaking-flask leaching experiments of 6 g pyrite in 10 cm^3 of catechol solution and TiO_2 inside a 50-cm^3 Erlenmeyer flask for 7 days in air.

Fig. 11 shows the effect of pH on Fe and S released during pyrite oxidation in the presence of 100 mol m^{-3} catechol and 1 g of anatase TiO_2. The solution pH was varied by adding H_2SO_4 or NaOH to the catechol solution. The amounts of Fe and S released from pyrite were lower with anatase TiO_2 and catechol than without them (control) at pH below 5, indicating that CME with TiO_2 and catechol is effective in suppressing pyrite oxidation at the acidic region. However, at pH about 6, the suppression of pyrite oxidation by the addition of TiO_2 and catechol was not recognized. This may be explained from the overall reaction of Ti adsorption on pyrite (Eqs. 6 and 7): Ti adsorption, i.e. TiO_2 or $Ti(OH)_4$ protective coating, is suppressed when the concentration of H^+ is low, because H^+ is a reactant in Eqs. 6 and 7.

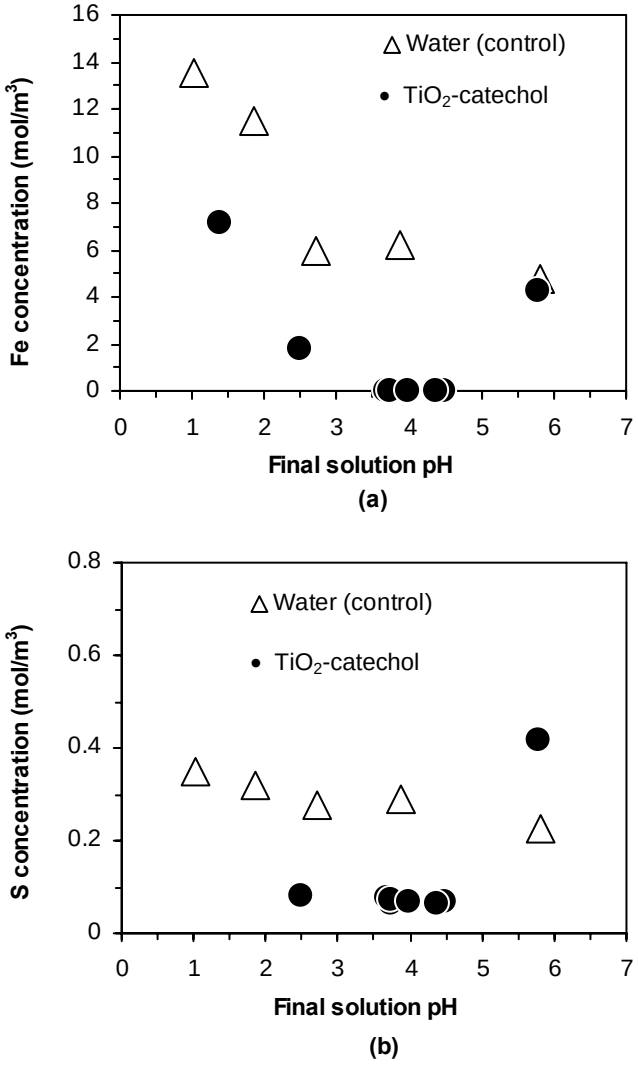


Fig. 11. Amounts of (a) Fe and (b) S released from pyrite leached with anatase TiO_2 and catechol as a function of final solution pH after 7 days.

At natural pH (pH 5-6), the effect of catechol concentration shows that decreasing the concentration of catechol from 100 to 10 mol m^{-3} still lowered the amount of Fe and S released (Fig. 12). This is a good result in terms of economic considerations in applying CME in actual situation.

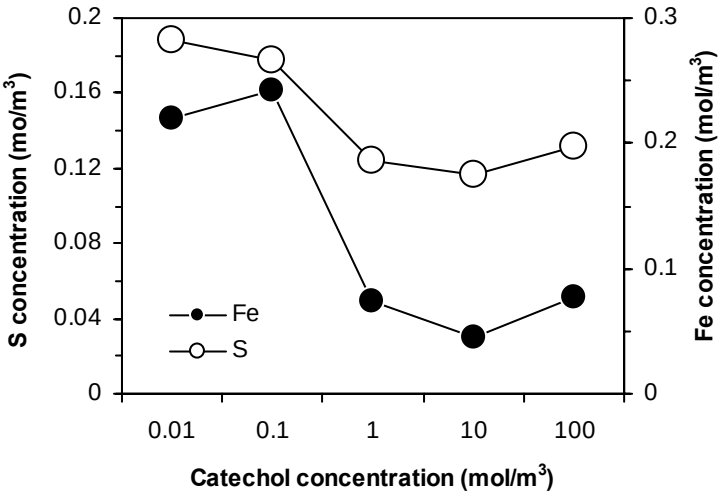


Fig. 12. Amounts of Fe and S released from pyrite leached with anatase TiO_2 and catechol as a function of catechol concentration at natural pH (pH 5-6) after 7 days.

Using 10 mol m^{-3} catechol, the amount of anatase TiO_2 was then varied. However, decreasing the amount of TiO_2 from 1 g to 0.01 g increased the amounts of Fe and S released (Fig. 13). Therefore, 10 cm^3 of 10 mol m^{-3} catechol and 1 g of TiO_2 are found to be optimum for suppressing pyrite oxidation.

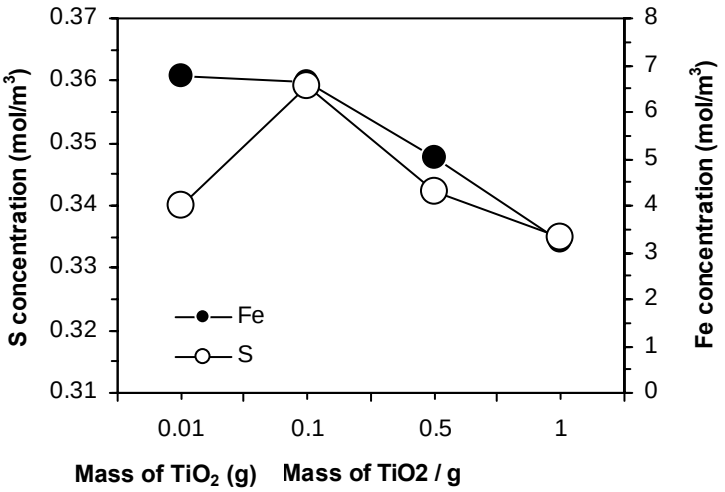


Fig. 13. Amounts of Fe and S released from pyrite leached with anatase TiO_2 and 10 mol m^{-3} catechol as a function of mass of anatase TiO_2 at natural pH (pH 5-6) after 7 days.

The effect of CME using rutile TiO_2 instead of anatase TiO_2 in the pyrite leaching with 1 g of TiO_2 and 100 mol m^{-3} catechol at natural pH (pH 5-6) was investigated. Anatase was used in the adsorption and leaching experiments of pyrite but in the natural environment, rutile is the more common form of TiO_2. Fig. 14 shows that pyrite oxidation in terms of Fe and S released was also suppressed with using rutile TiO_2, although to a lesser extent than with using anatase TiO_2. The significance of this result is that pyrite oxidation can be expected to be suppressed in actual application of CME (using catechol as organic carrier) for pyrite or sulfide minerals containing Ti minerals which could most probably exist as rutile TiO_2.

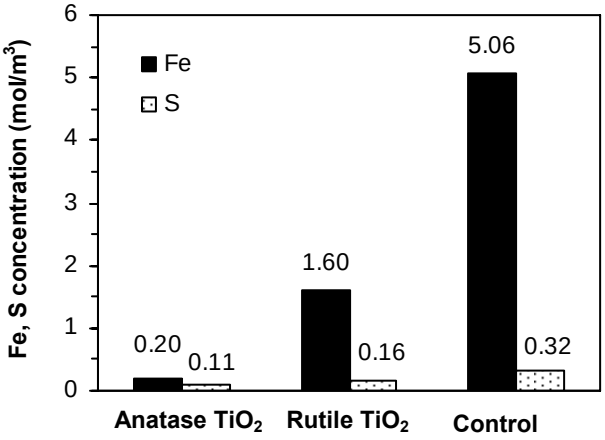


Fig. 14. Amounts of Fe and S released from pyrite leached with 1 g of anatase TiO_2 or rutile TiO_2 and 100 mol m^{-3} catechol at natural pH (pH 5-6) after 7 days.

With respect to the use of catechol and its by-products, catechol is readily biodegradable and has no potential to bioaccumulate in the environment (Speciality Chemicals Magazine, 2002; Gericke and Ficher, 1979). Catechol is not classified as dangerous for the environment according to Annex 1 of CEE/67/548 directive by the Council of European Community (Speciality Chemicals Magazine, 2002). It can be degraded by air (Hathway and Seakins, 1957) and by ferric ions (Pracht et al., 2001). Microorganisms such as methanogenic bacteria (Healy and Young, 1978), yeast (Margesin et al., 2005), and fungi (Krastanov et al., 2006) can also degrade catechol and related compounds. However, the effect of these degradation products on the environment still needs to be confirmed.

Catechol and related phenolic compounds can also be found naturally in aquatic and humic materials (Christman and Chassemi, 1966; Christman et al., 1978; Schnitzer and Khan, 1972) and are produced from wood-decaying fungi (Goodell et al., 1997). However, in actual application of CME, higher amount of catechol than what is naturally present will be needed. Its environmental effect should be investigated in the future.

4. Conclusions

In this study, carrier-microencapsulation (CME) was proposed for preventing pyrite oxidation and was demonstrated using catechol and TiO_2. Titanium ions were extracted from TiO_2 by catechol and were adsorbed on pyrite, indicating that catechol can act as an organic carrier agent for Ti ions from TiO_2 to pyrite. Pyrite oxidation was significantly suppressed by addition of both TiO_2 and catechol in pyrite leaching experiments. Sole addition of TiO_2 or catechol also suppressed pyrite oxidation but to a lesser extent than addition of both TiO_2 and catechol. The formation of $Ti(OH)_4$ or TiO_2 coating on pyrite surface is assumed to be the cause of the suppression of pyrite oxidation by TiO_2 and catechol.

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