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12	
13	Abstract
14	Mineral processing, pyro- and hydrometallurgical processes of auriferous sulfide ores and porphyry copper

14 15 deposits (PCDs) generate arsenopyrite-rich wastes. These wastes are disposed of into the tailings storage facilities 16 (TSF) in which toxic arsenic (As) is leached out and acid mine drainage (AMD) is generated due to the oxidation 17 of arsenopyrite (FeAsS). To suppress arsenopyrite oxidation, this study investigated the passivation of 18 arsenopyrite by forming ferric phosphate (FePO<sub>4</sub>) coating on its surface using ferric-catecholate complexes and 19 phosphate simultaneously. Ferric iron (Fe<sup>3+</sup>) and catechol form three types of complexes (mono-, bis-, and tris-20 catecholate complexes) depending on the pH, but mono-catecholate complex (i.e., [Fe(cat)]<sup>+</sup>) became unstable in the presence of phosphate because the chemical affinity of  $Fe^{3+}$ —PO<sub>4</sub><sup>3-</sup> is most probably stronger than that of 21 22  $Fe^{3+}$ —catechol in  $[Fe(cat)]^+$ . When two or more catechol molecules were coordinated with  $Fe^{3+}$  (i.e.,  $[Fe(cat)_2]^-$ 23 and [Fe(cat)<sub>3</sub>]<sup>3-</sup>), however, these complexes were stable irrespective of the presence of phosphate. The treatment 24 of arsenopyrite with  $[Fe(cat)_2]^-$  and phosphate could suppress its oxidation due to the formation of FePO<sub>4</sub> coating, 25 evidenced by SEM-EDX and XPS analyses. The mechanism of FePO<sub>4</sub> coating formation by [Fe(cat)<sub>2</sub>]<sup>-</sup> and 26 phosphate was confirmed by linear sweep voltammetry (LSV): (1) [Fe(cat)<sub>2</sub>]<sup>-</sup> was oxidatively decomposed and

- 27 (2) the resultant product (i.e., [Fe(cat)]<sup>+</sup>) reacts with phosphate, resulting in the formation of FePO<sub>4</sub>.
- 28 Keywords: arsenopyrite, passivation, ferric-catecholate complexes, phosphate, ferric phosphate coating
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# 30 1. Introduction

31 Arsenopyrite (FeAsS), the most common arsenic (As)-bearing sulfide mineral in nature, is often found in 32 auriferous sulfide ores. Due to the fact that arsenopyrite is one of the most common hosts of invisible gold (Au), 33 which is optically undetectable Au particles because of its incorporation into the structure of host minerals, 34 auriferous sulfide ores are typically processed by flotation to recover the bulk of gold-bearing arsenopyrite, and 35 then flotation concentrates are processed via pretreatment (e.g., acidic pressure oxidation (Gudyanga et al., 1999), 36 alkaline pretreatment (Espitia and Lapidus, 2015), biooxidation (Ciftci and Akcil, 2010), pyrolysis (Dunn and 37 Chamberlain, 1997), ultra-fine grinding (Corrans and Angove, 1991)) to expose Au particles encapsulated in host 38 minerals followed by cyanidation—a conventional hydrometallurgical technique for the selective leaching of gold 39 (Asamoaha et al., 2018; Deol et al., 2012; Pokrovski et al., 2019; Tabelin et al., 2020a). Because arsenopyrite is 40 not dissolved during cyanidation, it ends up with the leaching residues typically disposed of into tailings storage 41 facilities (TSF). In addition, arsenopyrite is also found in porphyry copper deposits (PCDs)-the world's most 42 important source of copper (Cu) accounting for more than 60% of the annual world copper production (John et 43 al., 2010; John and Taylor, 2016). Michiquillay (Peru), Potrerillos (Chile), and Río Blanco-Los Bronces (Chile) 44 are the examples of PCDs containing arsenopyrite (Berger et al., 2008). In the flotation of PCDs, however, the 45 recovery of arsenopyrite is unfavorable because Cu concentrates with high contents of As are highly penalized by 46 smelters. Because of strict emission standards for As, smelters in recent years will only treat Cu concentrates with 47 < 0.5% As, and penalties of around US\$3 per 0.1 wt% is charged above 0.2 wt% As (Bruckard et al., 2010; Lane 48 et al., 2016; Nazari et al., 2017). Because of this, almost all arsenopyrite is removed during bulk flotation of PCDs, 49 and the generated As-rich tailings are discarded.

50 When arsenopyrite is exposed to oxygen and water, it is readily oxidized and releases toxic As into the 51 surrounding environment (Eqs. (1)–(3)).

$$52 4FeAsS_{(s)} + 11O_{2(aq)} + 6H_2O \rightarrow 4Fe^{2+}_{(aq)} + 4H_3AsO_{3(aq)} + 4SO_4^{2-}_{(aq)} (1)$$

53 
$$4Fe^{2+}_{(aq)} + O_{2(aq)} + 4H^{+}_{(aq)} \rightarrow 4Fe^{3+}_{(aq)} + 2H_2O$$
 (2)

54 
$$\text{FeAsS}_{(s)} + 13\text{Fe}^{3+}_{(aq)} + 8\text{H}_2\text{O} \rightarrow 14\text{Fe}^{2+}_{(aq)} + \text{H}_3\text{AsO}_{4(aq)} + \text{SO}_4^{2-}_{(aq)} + 13\text{H}^+_{(aq)}$$
 (3)

55 Arsenic and its compounds are strictly regulated substances because they have been reported to cause 56 numerous diseases like hyperpigmentation, keratosis, anemia, and neuropathy (Mohan and Pittman, 2007; Tabelin 57 et al., 2017a, 2017b). When ingested continuously for prolonged periods of time via contaminated drinking water, 58 for example, the risk of developing several types of cancers is greatly increased (Boddu et al., 2008; Huyen et al., 59 2019a, 2019b; Tabelin et al., 2018, 2020b). Because of this, the maximum contaminant level (MCL) for As in 60 drinking water has been set at 10 µg/L (USEPA, 2001). Aside from being a substantial source of As, arsenopyrite 61 also has an acidification potential (AP) about three times higher than pyrite, which means that its oxidation 62 together with that of pyrite is the primary cause of acid mine drainage (AMD) formation (Chopard et al., 2017; 63 Park et al., 2019; Tabelin et al., 2017c, 2017d). AMD is the acidic leachate (pH < 3) generated in old TSFs, 64 abandoned underground mine sites and pyrite-bearing waste rock dumps polluted with heavy metals and toxic 65 metalloids (Igarashi et al., 2020; Tabelin et al., 2009, 2013; Tatsuhara et al., 2012; Tomiyama et al., 2019, 2020).

66 Arsenopyrite dissolves electrochemically in the presence of oxidants and water, so the suppression of their 67 interactions with mineral is a key point for limiting the release of As and AMD formation resulting from 68 arsenopyrite oxidation. One promising approach is the direct passivation of this problematic mineral via 69 microencapsulation. Evangelou (1995) introduced a microencapsulation technique using hydrogen peroxide 70  $(H_2O_2)$  and dipotassium hydrogen phosphate  $(K_2HPO_4)$  to passivate pyrite with ferric phosphate (FePO<sub>4</sub>) coating. 71 In this technique, pyrite passivation was achieved via the following steps: (1) H<sub>2</sub>O<sub>2</sub> oxidizes pyrite and generates 72  $Fe^{3+}$  near the pyrite surface, and (2)  $Fe^{3+}$  reacts with phosphate and precipitates as  $FePO_4$  on the pyrite surface. 73 Although effective, there are some serious drawbacks of this technique; for example, (1) the use of H<sub>2</sub>O<sub>2</sub> to pre-74 oxidize sulfide minerals and generate Fe<sup>3+</sup> is problematic because handling and storage of this compound, 75 especially in large quantities, are very challenging (Barreiro et al., 2007; Ouyang et al., 2015), (2) the technique 76 cannot target sulfide minerals in complex wastes like tailings, which typically contain < 10% sulfide minerals 77 (Blowes et al., 1998), resulting in unwanted large consumption of this expensive reagents, and (3) high 78 concentration of As is most likely leached out during treatment due to the strong oxidizing ability of  $H_2O_2$ .

79

To overcome the limitations of using  $H_2O_2$ , many alternative techniques have been recently developed: (1)

80 formation of organic coatings using sodium oleate (Jiang et al., 2000), humic acid (Ačai et al., 2009), 81 phospholipids (Elsetinow et al., 2003), (2) formation of silane-based coatings using alkoxysilanes (Dong et al., 82 2020; Liu et al., 2017), and (3) carrier-microencapsulation (CME) using metal-organic complexes (e.g., 83  $[Ti(cat)_3]^{2-}$ ,  $[Al(cat)_n]^{3-2n}$ ,  $[Fe(cat)_n]^{3-2n}$ ; where "cat" is catechol (1,2-dihydroxybenzene, C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>) and "n" is 84 the number of catechol molecules in the range of 1–3) (Li et al., 2019; Park et al., 2018a, 2018b, 2020a). All these 85 techniques are effective in suppressing arsenopyrite/pyrite oxidations, but each of them has apparent drawbacks. 86 For example, organic coatings would be stable for a relatively short period of time because in nature, there are 87 various types of microorganisms that can degrade even very complex organic compounds. Meanwhile, silane-88 based coatings have a better durability than that of organic coatings, but the lack of ability of alkoxysilanes to 89 selectively target the problematic minerals like arsenopyrite and pyrite would be one of the problems in its 90 application to real mine wastes. In the case of CME, inorganic coatings (e.g., metal-oxyhydroxides) could be 91 selectively formed on the surfaces of arsenopyrite and pyrite; however, the stability of metal-oxyhydroxide 92 coatings is lower than that of FePO<sub>4</sub> coating under strongly acidic conditions (< pH 3). Thus, an improved 93 microencapsulation technique having abilities to not only target arsenopyrite as well as other problematic minerals 94 but also create stable coatings is required to be developed.

95 The above-mentioned limitations of Evangelou's technique forming FePO<sub>4</sub> coating using K<sub>2</sub>HPO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> could be addressed by adopting alternative ways of supplying Fe<sup>3+</sup> to facilitate microencapsulation of sulfide 96 97 minerals. For example, in CME, a technique that forms a surface protective coating on the surface of sulfide 98 minerals like arsenopyrite and pyrite, metal-organic complexes are used to deliver metal ions to the 99 arsenopyrite/pyrite surfaces (Li et al., 2019; Park et al., 2018a, 2018b, 2020a). Metal ion is released from the 100 complex via its oxidative decomposition taking place only on the surface of semi-conducting minerals. Therefore, 101 the use of Fe<sup>III</sup>-catecholate complexes can be a promising alternative to the use of H<sub>2</sub>O<sub>2</sub> because of its ability to 102 selectively supply  $Fe^{3+}$  to the surface of arsenopyrite. In this study, a new passivation approach via simultaneous 103 use of Fe-catecholate complexes and phosphate to create FePO<sub>4</sub> coating on arsenopyrite was investigated. 104 Specifically, the objectives of this study are as follows: (1) to evaluate the stability and oxidative decomposition 105 behavior of Fe-catecholate complexes without and with phosphate by linear sweep voltammetry (LSV), (2) to 106 elucidate the passivation of arsenopyrite using leaching tests under various conditions, and (3) to determine 107 important suppression or passivation mechanisms using surface-sensitive characterization techniques like 108 scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray photoelectron 109 spectroscopy (XPS).

110

# 111 2. Materials and methods

# 112 *2.1. Arsenopyrite sample*

113 The arsenopyrite sample used in this study was obtained from Toroku mine, Miyazaki, Japan. It was crushed 114 by a jaw crusher (BB 51, Retsch Inc., Germany), ground in a vibratory disc mill (RS 100, Retsch Inc., Germany), 115 and then screened to obtain a size fraction of  $100-150 \mu m$ . This sample is mainly composed of arsenopyrite (67%) 116 with pyrite (13%) and quartz (15%) as minor mineral impurities (Park et al., 2018a). Details of sample 117 characterizations are provided as supplementary information (Fig. S1 and Tables S1). Prior to the leaching 118 experiments, the sample  $(100-150 \,\mu\text{m})$  was washed to remove slime coating and any oxidized layer formed during 119 preparation and storage by the method of McKibben et al. (2008): (i) ultrasonic desliming in methanol, (ii) 120 washing with 1.8 M HNO<sub>3</sub>, (iii) rinsing with deionized (DI) water, (iv) dewatering with acetone, and (v) drying 121 in a vacuum desiccator.

122

# 123 2.2. Stability of Fe-catecholate complexes in the absence and presence of phosphate

124 For passivation of arsenopyrite to be selective, the complex should be oxidatively decomposed only on the 125 mineral's surface and not in the bulk solution. To evaluate the stability of Fe-catecholate complexes in a system 126 containing phosphate, solutions containing 1 mM FeCl<sub>3</sub>·6H<sub>2</sub>O with (i) none, (ii) 1 mM NaH<sub>2</sub>PO<sub>4</sub>, (iii) 3 mM 127 pyrocatechol, and (iv) 3 mM pyrocatechol and 1 mM NaH<sub>2</sub>PO<sub>4</sub> were prepared, and its pH was adjusted from 2 to 128 11 using 0.1 and 1.0 M HCl and NaOH. All chemicals used in this study were of reagent grade (Wako Pure 129 Chemical Industries, Ltd., Japan). Once the solution pH reached predetermined values, it was allowed to stabilize 130 for 10 min. Afterward, the solutions were filtered through 0.2 µm syringe-driven membrane filters (LMS Co. Ltd., 131 Japan) to remove precipitates and polymerized organic molecules, and the filtrates were analyzed by an 132 inductively coupled plasma atomic emission spectrometer (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan) 133 to measure the concentration of dissolved Fe. Similarly, control experiments were conducted using solutions 134 consisting of 1 mM Fe<sup>3+</sup> with and without 1 mM NaH<sub>2</sub>PO<sub>4</sub> to check the solubility of each precipitate as a function 135 of pH. The precipitates formed during the experiments were collected and analyzed by attenuated total reflectance Fourier transform infrared (ATR–FTIR) spectroscopy (FT/IR-6200 HFV and ATR Pro One attachment equipped with a diamond prism, Jasco Analytical Instruments, Japan) under the following conditions: 1000 scans at a resolution of 4 cm<sup>-1</sup> and in the range of 400–4000 cm<sup>-1</sup>. As a reference, iron(III) phosphate n-hydrate (FePO<sub>4</sub>·nH<sub>2</sub>O) (Wako Pure Chemical Industries, Ltd., Japan) was also analyzed by ATR-FTIR.

140

# 141 2.3. Oxidative decomposition of Fe-catecholate complexes in the absence and presence of phosphate

142 Oxidative decomposition of bis-catecholate complex (i.e.,  $[Fe(cat)_2]$ ) in the presence of phosphate was 143 investigated by linear sweep voltammetry (LSV). For this, an electrochemical measurement unit (SI 1280B, 144 Solartron Instruments, UK) with a conventional three-electrode system consisting of a platinum (Pt) electrode, a 145 Pt wire, and an Ag/AgCl electrode (filled with 3.3 M NaCl solution) was used as working, counter, and reference 146 electrodes, respectively. The LSV measurement was conducted in the solution containing 1 mM FeCl<sub>2</sub>·6H<sub>2</sub>O, 2 147 mM pyrocatechol (denoted as H<sub>2</sub>cat), and 1 mM NaH<sub>2</sub>PO<sub>4</sub>, the pH of which was adjusted to 7 where bis-148 catecholate complex is dominant. Prior to LSV measurement, the solution was filtered through a 0.2 µm syringe-149 driven membrane filter, deoxygenated by N<sub>2</sub> purging, and equilibrated at 25°C for 30 min. Afterward, the working 150 electrode was equilibrated at open circuit potential (OCP) and then anodically polarized up to +1.0 V vs. SHE at 151 a scan rate of 5 mV/s. For the comparison, LSV measurements of mono-catecholate complex ( $[Fe^{3+}]$ , 1 mM; 152 [H<sub>2</sub>cat], 1 mM; pH, 5), bis-catecholate complex (([Fe<sup>3+</sup>], 1 mM; [H<sub>2</sub>cat], 2 mM; pH, 7), and catechol ([H<sub>2</sub>cat], 2 153 mM; pH, 7) were also conducted via an identical procedure as mentioned above. All solutions contain 0.1 M NaCl 154 (Wako Pure Chemical Industries, Ltd., Japan) as a supporting electrolyte.

155

156 2.4. Passivation of arsenopyrite by microencapsulation using Fe-catecholate complex with and without

157 *phosphate* 

To check the passivation of arsenopyrite by microencapsulation using Fe-catecholate complex with and without phosphate, three types of solutions (e.g., DI water (control), 5 mM  $[Fe(cat)_2]^-$  only, and 5 mM  $[Fe(cat)_2]^$ with 5 mM PO<sub>4</sub><sup>3-</sup>), all of which were adjusted to pH 7, were prepared. One gram of washed arsenopyrite was mixed with 10 mL of prepared solution in a 50-mL Erlenmeyer flask and shaken at 120 min<sup>-1</sup> in a constant temperature water bath shaker (25 °C) for 3 days. At predetermined time intervals, samples were filtered through

163	0.2 µm syringe-driven membrane filters, and the filtrates were analyzed by ICP-AES. Some experiments were
164	done in triplicates. Meanwhile, the residues were thoroughly washed with DI water, dried in a vacuum oven at
165	40°C for 24 h, and analyzed by SEM-EDX (JSM-IT200, JEOL Ltd., Japan) and XPS (JPS-9200, JEOL Ltd.,
166	Japan). The XPS analysis was conducted using a monochromatized Al Ka X-ray source (1486.7 eV) operated at
167	300 W (Voltage, 12 kV; Current, 25 mA) with charge neutralization under ultrahigh vacuum conditions
168	(approximately $10^{-7}$ Pa). Narrow scan spectra of Fe $2p_{3/2}$ , As $3d_{5/2}$ , S $2p_{3/2}$ , and P $2p_{3/2}$ were obtained and calibrated
169	using the binding energy of adventitious carbon (C 1s) (285.0 eV) for charge correction. For deconvolutions of
170	the spectra, XPSPEAK version 4.1 was used with an 80% Gaussian-20% Lorentzian peak model and a true Shirley
171	background (Nesbitt and Muir, 1994; Shirley, 1972).

#### 173 *2.5. Leachability tests of treated-arsenopyrite*

After 3-day treatments of arsenopyrite by control, Fe-catecholate complex with and without phosphate, the stability of coating and leachabilities of Fe and As from treated samples were investigated. For this, one gram of treated arsenopyrite and 10 mL of DI water were put in a 50-mL Erlenmeyer flask and shaken at 120 min<sup>-1</sup> and  $25 \,^{\circ}$ C for 24 h. After this, the suspension pH was measured, and the filtrates collected after filtration using 0.2 µm syringe-driven membrane filters were analyzed by ICP-AES to measure the concentrations of Fe and As released from untreated and treated samples. All tests were done in triplicates.

180

# 181 2.6. Chronoamperometry measurements

182 Chronoamperometry was adopted to evaluate the anodic half-cell reactions of untreated arsenopyrite and the 183 one treated with  $[Fe(cat)_2]^-$  and phosphate. For this, a mineral working electrode was prepared as follows: (i) 184 arsenopyrite sample was cut using a diamond cutter, (ii) connected to a copper wire with silver conducting paste 185 (DOTITE, Fujikura Kasei Co., Ltd., Japan), and (iii) fixed inside a plastic holder with Technovit® non-conductive 186 resin (Heraeus Kulzer GmbH, Germany). Afterward, the prepared mineral electrode was polished using a 187 polishing machine (SAPHIR 250 M1, ATM GmbH, Germany) with a series of silicon carbide papers (P320, P600, 188 and P1200) and diamond suspensions (3 and 1 µm) to expose a new and unreacted surface. Two-set of 189 experiments were conducted using untreated mineral electrode and the one treated with 5 mM [Fe(cat)<sub>2</sub>]<sup>-</sup> with 5

mM  $PO_4^{3-}$  for 3 days. Untreated or treated mineral working electrode, Pt counter electrode, and Ag/AgCl (filled with saturated KCl) reference electrode were immersed into the electrolyte solution (0.1 M Na<sub>2</sub>SO<sub>4</sub>) and connected to potentiostat/galvanostat (SP-300, BioLogic, France). After measuring OCP under N<sub>2</sub> atmosphere, a fixed potential of 0.7 V vs. SHE was applied to the working electrode for 1 h with magnetic stirring at 250 rpm. This applied potential was chosen based on typical redox conditions where AMD has been formed (i.e., about 0.64– 0.68 V) (Yamaguchi et al., 2015).

196

#### 197 **3. Results and discussion**

# 198 *3.1. Stability of Fe-catecholate complexes in the absence and presence of phosphate*

199 Catechol is known to form three types of complexes with Fe<sup>3+</sup> depending on the pH; that is, mono-catecholate 200  $([Fe(cat)]^+)$ , bis-catecholate  $([Fe(cat)_2]^-)$ , and tris-catecholate  $(Fe(cat)_3]^{3-})$  complexes are dominant at pH 3.0–5.5, 201 5.5-9.0, and >9.0, respectively (Li et al., 2019). The formation of Fe-catecholate complexes was also 202 experimentally confirmed in this study. In the absence of any chelators,  $Fe^{3+}$  starts precipitating at above pH 3, 203 most of which are precipitated when pH is greater than 4. However, the addition of catechol dramatically changes 204 the solubility of Fe<sup>3+</sup> (Fig. 1a). From pH 3 to 5, dissolved Fe concentration decreased from about 1.0 to 0.8 mM, 205 then it increased as the pH increased above 5.0. This change in the solubility of  $Fe^{3+}$  could be achieved due to the formation of three types of Fe-catecholate complexes (i.e., [Fe(cat)]<sup>+</sup>, [Fe(cat)<sub>2</sub>]<sup>-</sup>, and Fe(cat)<sub>3</sub>]<sup>3-</sup>). When 206 207 phosphate is present in the Fe-catechol system, dissolved Fe concentration was considerably changed in the pH 208 range of 4.0-6.0; that is, dissolved Fe concentration was lower compared to that without phosphate. In this pH 209 range, the dominant species of Fe-catecholate complex is  $[Fe(cat)]^+$ , which became unstable in the presence of 210 phosphate. This implies that the chemical affinity of  $Fe^{3+}$ —catechol in  $[Fe(cat)]^+$  is weaker than that of  $Fe^{3+}$  phosphate, and thereby catechol molecule coordinated with Fe<sup>3+</sup> is replaced with phosphate as illustrated in the 211 212 following equation:

213 
$$[Fe(cat)]^+ + H_2PO_4^- \rightarrow FePO_4 \downarrow + H_2cat$$
(4)

This deduction on the formation of FePO<sub>4</sub> is supported by ATR-FTIR analysis of the precipitate formed in solution containing  $[Fe(cat)]^+$  and phosphate at pH 5 (Fig. 1b). As shown in the FTIR spectrum of precipitate, the absorption bands detected in 3500–3000 and 1700–1600 cm<sup>-1</sup> regions are the stretching and bending vibrations of water molecules, respectively (Boonchom and Puttawong, 2010; Zaghib and Julien, 2005). The symmetric ( $v_1$ )

and antisymmetric stretching ( $v_3$ ) modes of the P–O bonds are observed in 1200–900 cm<sup>-1</sup> region (Fig. 1b) while IR absorption bands observed at 610, 583, and 542 cm<sup>-1</sup> are attributed to antisymmetric bending mode ( $v_4$ ) of O– P–O (Fig. 1b-1) (Boonchom and Puttawong, 2010; Zaghib and Julien, 2005). These IR signatures of precipitate are almost the same as that of FePO<sub>4</sub> reagent (Fig. 1b-2), indicating that the precipitate formed between [Fe(cat)]<sup>+</sup> and phosphate is most likely FePO<sub>4</sub> as illustrated in Eq. (4).

223 The stability of complex(es) is of importance because it is directly related to its selectivity for acid-generating 224 minerals like sulfide minerals in a complex system (e.g., TSF in which sulfide contents are < 10%; Blowes et al., 225 1998). For the selective passivation of sulfide minerals by Fe-catecholate complexes and phosphate, the former 226 should be oxidatively decomposed only on the mineral surface, not precipitated in the bulk solution. Based on 227 this, pH >7.0 at which Fe-catecholate complexes (e.g.,  $[Fe(cat)_2]^-$  and  $[Fe(cat)_3]^{3-}$ ) are stable in the presence of 228 phosphate could be considered as suitable conditions for selective passivation of arsenopyrite; however, in this 229 study, all the experiments were conducted at pH 7.0 to synthesize [Fe(cat)<sub>2</sub>]<sup>-</sup> because the oxidative decomposition 230 of  $[Fe(cat)_3]^{3-}$  was reported to be sluggish compared to  $[Fe(cat)_2]^-$  (Li et al., 2019).



# 231

Fig. 1. (a) Solubility of Fe with pH in Fe only, Fe-catechol and Fe-catechol-phosphate systems ( $[Fe^{3+}] = 1 \text{ mM}$ ,

[H<sub>2</sub>cat] = 3 mM, [PO<sub>4</sub><sup>3-</sup>] = 1 mM), (b) ATR-FTIR spectra of FePO<sub>4</sub> reagent and the precipitate formed in solution containing Fe<sup>3+</sup>, H<sub>2</sub>cat , and PO<sub>4</sub><sup>3-</sup> at pH 5, and deconvoluted spectra between 645 and 485 cm<sup>-1</sup> of the precipitate (b-1) and FePO<sub>4</sub> reagent (b-2).

236

# 237 3.2. Effects of phosphate on the oxidative decomposition of Fe-catecholate complexes

Linear sweep voltammetry (LSV) was conducted to understand the mechanisms of how Fe-catecholate complexes are oxidatively decomposed in the absence and presence of phosphate (Fig. 2). As shown in LSV of Fe-catechol system at pH 7, there are two apparent anodic peaks observed at around 0.49 V (A<sub>1</sub>) and 0.64 V (A<sub>2</sub>). The dominant species of Fe-catecholate complex at pH 7 is  $[Fe(cat)_2]^-$ , so the first anodic peak (A<sub>1</sub>) could be considered as its oxidative decomposition to  $[Fe(cat)]^+$  as shown in the following reaction:

$$243 \qquad [Fe(cat)_2]^- \rightarrow [Fe(cat)]^+ + Q + 2e^- \tag{5}$$

where Q denotes ortho-quinone (1,2-benzoquinone,  $C_6H_4O_2$ ), the oxidation product of catechol. Meanwhile, the second anodic peak (A<sub>2</sub>) appeared, which indicates that [Fe(cat)]<sup>+</sup> is further oxidized, resulting in the release of Fe<sup>3+</sup> as the applied potential increases (Eq. (6)). The LSV of Fe-catechol system at pH 5 where [Fe(cat)]<sup>+</sup> is dominant also supports that the anodic peak at 0.64 V (A<sub>2</sub>) could be related to the oxidative decomposition of [Fe(cat)]<sup>+</sup>.

249 
$$[Fe(cat)]^+ \rightarrow Fe^{3+} + Q + 2e^-$$
 (6)

250 In the presence of phosphate, two anodic peaks were also observed in the LSV of  $[Fe(cat)_2]^-$ . The first peak  $(A_1)$  appeared at almost the same potential as that for the decomposition of  $[Fe(cat)_2]^-$  to  $[Fe(cat)_1^+$  observed in 251 252 LSV of  $[Fe(cat)_2]^-$  only. The succeeding peak (A<sub>3</sub>), however, was shifted from 0.64 to 0.70 V when phosphate was 253 present, which indicates that this anodic peak does not probably arise from the oxidative decomposition of 254 [Fe(cat)]<sup>+</sup>. The LSV of catechol only solution at pH 7 showed that an anodic peak appeared at almost the same 255 position as the second anodic peak observed in LSV of [Fe(cat)<sub>2</sub>]<sup>-</sup> with phosphate, indicating that this anodic peak 256 (A<sub>3</sub>) most likely resulted from the oxidation of free catechol molecules. As discussed above (section 3.1), when 257  $[Fe(cat)]^+$  and phosphate react, FePO<sub>4</sub> and free catechol are produced (Eq. (4)), which supports A<sub>3</sub> peak 258 corresponds to the anodic reaction of catechol. From these results, the mechanism of the complex decomposition 259 process in the presence of phosphate could be elucidated as follows: (i)  $[Fe(cat)_2]^{-1}$  is oxidatively decomposed (Eq.

- 260 (5)) and (ii) its resultant product (i.e., [Fe(cat)]<sup>+</sup>) reacts with phosphate, followed by the formation of FePO<sub>4</sub> and
- 261 free catechol (Eq. (4)).



Fig. 2. Linear sweep voltammograms of catechol only at pH 7 ( $[H_2cat] = 1 \text{ mM}$ ), Fe-catechol only at pH 5 and 7 ( $[Fe^{3+}] = 1 \text{ mM}$ ,  $[H_2cat] = 1 \text{ mM}$  (pH 5) and 2 mM (pH 7)), and Fe-catechol-phosphate at pH 7 ( $[Fe^{3+}] = 1 \text{ mM}$ , [ $H_2cat] = 2 \text{ mM}$ ,  $[PO_4^{3-}] = 1 \text{ mM}$ ). Note that two different scales for current density are used and indicated by arrows.

3.3. Passivation of arsenopyrite by microencapsulation using Fe-catecholate complex with and without phosphate

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269 In the control experiment, the leachate pH was continuously decreased from 7.0 to 2.7 while the other two 270 cases were kept almost constant due to the buffering effects of Fe-catecholate complexes and phosphate (Fig. 3a). 271 Arsenopyrite was oxidized rapidly in the control; that is, dissolved As and Fe concentrations after 3 days reached 272 around 2.0 and 1.3 mM, respectively (Figs. 3b and 3c). Compared to this, when arsenopyrite was treated in the 273 solution containing Fe-catecholate complex, the release of As from arsenopyrite was apparently suppressed; that 274 is, dissolved As concentration after 3 days was around 0.7 mM-the released amount of As decreased by 65% 275 compared to that of control (Fig. 3b). It is also interesting to note that dissolved Fe concentration kept decreasing 276 with time (Fig. 3c), which indicates that  $[Fe(cat)_2]^-$  was sequentially decomposed (Eqs. (5) and (6)), then  $Fe^{3+}$ 277 released from the complex was precipitated (Eq. (7)).

279 In our previous study on microencapsulation of pyrite using Fe-catecholate complexes, it was confirmed that 280 [Fe(cat)]<sup>+</sup> and [Fe(cat)<sub>2</sub>]<sup>-</sup> formed the surface protective coating composed of Fe-oxyhydroxide on pyrite (Li et al., 281 2019), so arsenopyrite could also be passivated via the identical way, thereby suppressing the release of As from 282 arsenopyrite. In the presence of phosphate, however, the behaviors of As release as well as Fe precipitation 283 changed significantly: (i) dissolved As concentration was rapidly increased to 0.7 mM for 1 day similar to that of 284 control, but did not increase further, and (ii) dissolved Fe concentration increased from 3.8 to 4.1 mM after 1 day, 285 then decreased to 3.7 mM after 3 days (Figs. 3b and 3c). Based on the relationship between the released amounts 286 of As and Fe measured in the control experiment, the released amounts of Fe including both dissolved and 287 precipitated species were roughly estimated (see the dotted lines in Fig. 3c). As it can be seen, the precipitation of 288 dissolved Fe was negligible during 1-day leaching in the presence of phosphate but after 3 days, around 0.6 mM 289 of dissolved Fe was precipitated. This is substantially lower compared to the result in the absence of phosphate 290 (i.e., Fe-catecholate complex only) that around 1.8 mM of dissolved Fe was precipitated. These changes in As 291 release and Fe precipitation are most likely caused by the presence of phosphate that adsorbed to the surface of 292 arsenopyrite. As shown in Fig. 3d, dissolved P concentration decreased by 15% for 1 day even though dissolved 293 Fe was not nearly precipitated. This implies that the decrease in dissolved P concentration was mainly attributed 294 to its adsorption on the surface of arsenopyrite, not the precipitation with Fe<sup>3+</sup> forming FePO<sub>4</sub> (Eq. (4)). This 295 deduction is supported by phosphate sorption test which revealed that when arsenopyrite reacted with phosphate 296 only for 1 day, dissolved P was adsorbed on arsenopyrite surface, so its concentration decreased to a similar level 297 as for Fe-catecholate complex with phosphate (Fig. 3d). Elsetinow et al. (2001) reported that phosphate is adsorbed 298 on pyrite surface, then adsorbed phosphate may act as a site blocker for molecular oxygen adsorption and/or alter 299 the electronic structure of the Fe(III)-oxyhydroxide phases, which make electron transfer less energetically 300 favorable. Similarly, adsorbed phosphate could also limit the electrochemical reaction of arsenopyrite, and thus 301 the decomposition of Fe-catecholate complexes becomes sluggish compared to that in the absence of phosphate. 302 On the other hand, after 3 days, both dissolved Fe and P concentrations decreased (Figs. 3c and 3d). It is 303 noteworthy that dissolved P concentration obtained in the sorption test was almost not changed from 1 to 3 days, 304 indicating that the decreases in Fe and P concentrations are most likely caused by their precipitation. The decreased 305 Fe and P concentrations were both around 0.6 mM, implying that the precipitate with 1:1 stoichiometric ratio of 306  $Fe^{3+}:PO_4^{3-}$  (i.e., FePO<sub>4</sub>) was formed. Assuming that (i) the shape of arsenopyrite is sphere, (ii) all the precipitates

307 are present on arsenopyrite, and (iii)  $Fe^{3+}$  and  $PO_4^{3-}$  are precipitated as  $FePO_4$ , the thickness of coating was 308 theoretically calculated to be around 38 nm (see Supplementary Information).



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Fig. 3. Effects of Fe-catecholate complex and phosphate on arsenopyrite oxidation: changes in (a) pH, (b) dissolved As, (c) dissolved Fe (measured), and (d) dissolved P. Note that dotted lines in Fig. 3c denote total Fe concentrations including soluble and precipitated Fe species calculated based on the stoichiometry on the basis of dissolved As concentration measured in the control experiment ( $[Fe]_{tot} = 1.3/2.0 [As]_{dissolved}$ ).

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The residue treated with Fe-catecholate complex and phosphate for 3 days was analyzed by SEM-EDX, and it shows that on the surface of arsenopyrite, the signal of P was detected (Fig. S2). The weak signal of P indicates that the thickness of P-containing coating is probably thin, so the strong arsenopyrite signals (i.e., Fe, As, and S) are detected. To examine the coating in more detail, arsenopyrite treated with Fe-catecholate complex and phosphate was analyzed by XPS, which is suitable for analyzing very thin layer of coating (around ~6 nm). The XPS narrow-scan spectra of Fe  $2p_{3/2}$ , As  $3d_{5/2}$ , S  $2p_{3/2}$ , and P  $2p_{3/2}$  are illustrated in Fig. 4 and the corresponding

321 curve fitting parameters are summarized in Table 1. The Fe  $2p_{3/2}$  spectrum (Fig. 4a) suggests that the outermost 322 surface of treated arsenopyrite consists of (1) arsenopyrite (Fe<sup>(II)</sup>-(AsS) at 707.6 eV), (2) partly oxidized 323 arsenopyrite (Fe<sup>(III)</sup>-(AsS) at 709.2 eV), (3) ferric-oxyhydroxide (Fe<sup>(III)</sup>-O at 710.7 eV), and (4) ferric sulfate 324 (Fe<sup>(III)</sup>–SO<sub>4</sub> at 714.3 eV) (Corkhill and Vaughan, 2009; Grosvenor et al., 2004; Lara et al., 2016; Liu et al., 2020; 325 Nesbitt et al., 1995; Zhu et al., 2014). These assignments are supported by the As  $3d_{5/2}$  and S  $2p_{3/2}$  spectra (Figs. 326 4b and 4c); that is, the deconvoluted peaks of As<sup>(-I)</sup>–S (41.6 eV) and (AsS)<sup>2–</sup> (162.5 eV) observed in the As  $3d_{5/2}$ 327 and S 2p<sub>3/2</sub> spectra, respectively, are identified as originating from arsenopyrite/partly oxidized arsenopyrite while 328 a peak of  $SO_4^{2-}$  (167.9 eV) implies the presence of ferric sulfate (Han et al., 2011; Liu et al., 2020; Zhu et al., 2014). Moreover, the appearance of  $As^{(II)}-S$  (42.8 eV) and  $As^{(III)}-S$  (43.6 eV) coupled with  $S_2^{2-}$  (162.5 eV) and 329 330  $S_n^{2-}$  (n > 2; 163.5 eV) indicates the formation of realgar (As<sub>2</sub>S<sub>2</sub>) and orpiment (As<sub>2</sub>S<sub>3</sub>), and the remaining species 331 in the As 3d<sub>5/2</sub> spectrum (i.e., As<sup>(III)</sup>–O (44.7 eV)) arise from the soluble As species like AsO<sub>3</sub><sup>3–</sup> (Fan et al., 2018; 332 Liu et al., 2020). As illustrated in Fig. 4d-1, the deconvoluted P 2p<sub>3/2</sub> spectrum of arsenopyrite treated with "Fe-333 catecholate complex and phosphate" show three peaks of adsorbed  $PO_4^{3-}$  (132.5, 131.4, and 130.0 eV)—these 334 were also observed in the spectrum of phosphate-adsorbed arsenopyrite (Fig. 4d-2))-and a single peak at 133.4 335 eV, which is assigned to P<sup>(V)</sup>–O binding energy of ferric phosphate (Praneetha and Murugan, 2013; Wang et al., 336 2013; Zeng et al., 2017; Zhou et al., 2014). The XPS results revealed that the outermost surface of arsenopyrite 337 treated with Fe-catecholate complex and phosphate is composed of not only its oxidation products (e.g., ferric-338 oxyhydroxide, ferric sulfate, realgar, orpiment, and soluble As species) but also ferric phosphate. Based on the 339 results of LSV, leaching test, and surface analyses, the mechanism of coating formation by Fe-catecholate complex 340 and phosphate was confirmed: (i)  $[Fe(cat)_2]^-$  is oxidatively decomposed to  $[Fe(cat)_1]^+$  on the arsenopyrite surface, 341 (ii) [Fe(cat)]<sup>+</sup> reacts with phosphate, and (iii) FePO<sub>4</sub> coating is formed on the surface of arsenopyrite.



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Fig. 4. XPS spectra of arsenopyrite treated with Fe-catecholate complex and phosphate for 3 days: (a) Fe  $2p_{3/2}$ , (b) As  $3d_{5/2}$ , (c) S  $2p_{3/2}$ , and (d) P  $2p_{3/2}$  (d-1: arsenopyrite treated with Fe-catecholate complex and phosphate, d-2: arsenopyrite treated with phosphate only).

347 Table 1. XPS peak parameters and chemical states of Fe, As, S, and P obtained from arsenopyrite treated with Fe-

Spectral peak	Binding energy (eV)	FWHM	Chemical states
Fe 2p <sub>3/2</sub> <sup>a</sup>	707.6±0.1	1.2	Fe <sup>(II)</sup> –AsS
Fe $2p_{3/2}^{b}$	709.2±0.1	1.3	Fe <sup>(III)</sup> –AsS
Fe $2p_{3/2}^{b}$	710.7±0.1	1.7	Fe <sup>(III)</sup> –O
Fe $2p_{3/2}^{b}$	714.3±0.1	1.5	Fe <sup>(III)</sup> –SO <sub>4</sub>
As $3d_{5/2}^{c}$	41.6±0.1	1.0	As <sup>(-I)</sup> –S
As 3d <sub>5/2</sub> °	42.8±0.1	1.0	As <sup>(II)</sup> –S
As 3d <sub>5/2</sub> °	43.6±0.1	1.1	As <sup>(III)</sup> –S
As 3d <sub>5/2</sub> °	44.7±0.1	1.5	As <sup>(III)</sup> –O
$S 2p_{3/2}^{d}$	161.5±0.1	1.0	$S^{2-}$
$S 2p_{3/2}^{d}$	162.5±0.1	1.4	$S_2^{2-}/(AsS)^{2-}$
$S 2p_{3/2}^{d}$	163.5±0.1	1.1	$S_n^{2-}$ (n > 2)
$S 2p_{3/2}^{d}$	166.7±0.1	1.0	$SO_3^{2-}$
S 2p <sub>3/2</sub> <sup>d</sup>	167.9±0.1	1.5	SO4 <sup>2-</sup>
P 2p <sub>3/2</sub>	130.0±0.3	1.5	Adsorbed PO <sub>4</sub> <sup>3–</sup>
P 2p <sub>3/2</sub>	131.4±0.1	1.4	Adsorbed PO <sub>4</sub> <sup>3–</sup>
P 2p <sub>3/2</sub>	132.5±0.1	1.5	Adsorbed PO <sub>4</sub> <sup>3–</sup>
P 2p <sub>3/2</sub>	133.4±0.1	1.4	P <sup>(V)</sup> –O

348 catecholate complex and phosphate for 3 days.

349

<sup>a</sup> This peak has two multiplets located at lower and higher binding energies with 0.95 eV peak separation.

350 <sup>b</sup> This peak has three multiplets located at higher binding energies with 0.95 eV peak separation.

<sup>c</sup> This peak has a doublet located at a higher binding energy with 0.7 eV peak separation. The intensity ratio was 351 constrained to two thirds with the same FWHM. 352

353 <sup>d</sup> This peak has a doublet located at a higher binding energy with 1.18 eV peak separation. The intensity ratio was 354 constrained to one half with the same FWHM.

355

356 It is interesting to note that although the amount of precipitates formed by Fe-catecholate complex only was 357 larger than that formed by Fe-catecholate complex and phosphate (Fig. 3c), the performance on arsenopyrite 358 passivation was better when phosphate was present because dissolved As concentration stopped increasing after 359 FePO<sub>4</sub> coating was formed (Fig. 3b). In the case when arsenopyrite was treated by Fe-catecholate complex only, 360 dissolved As concentration was suppressed but continuously increased with time, which indicate that arsenopyrite 361 was not fully passivated. To further evaluate the passivation effects of Fe-catecholate complex in the absence and 362 presence of phosphate, treated arsenopyrite samples were leached again with fresh DI water (Fig. 5). As shown in 363 Figs. 5a and 5b, the significant amounts of Fe (0.30 mM) and As (0.36 mM) were leached out from the control 364 sample (i.e., arsenopyrite leached in DI water for 3 days); however, the releases of Fe and As decreased to 0.06 365 and 0.11 mM, respectively, when arsenopyrite was pretreated with Fe-catecholate complex. This indicates that 366 Fe-catecholate complex could inhibit the oxidation of arsenopyrite via the formation of Fe-oxyhydroxide coatings

367 limiting the contact of water and oxidants to mineral surface. When arsenopyrite was covered with FePO<sub>4</sub> coating, 368 the releases of Fe and As were further reduced to 0.04 and 0.09 mM, respectively. This result supports that the 369 performance of FePO<sub>4</sub> coating in suppressing the releases of Fe and As from arsenopyrite is better than that of the 370 coating formed by Fe-catecholate complex only. As shown in Fig. 5c, the solution pH after 1-day leaching was 371 decreased from 6.0 to 3.8, 4.3, and 4.2 for the cases of control, Fe-catecholate complex only, and Fe-catecholate 372 complex with phosphate, respectively, indicating that both coatings could limit arsenopyrite oxidation. However, 373 it is important to note that the acid-resistant properties of these two coatings are different. Figure 5d shows the 374 solubility of Fe<sup>3+</sup> in the absence and presence of phosphate as a function of pH, and it implies that in the absence 375 of phosphate, iron species becomes soluble at pH < 4 and pH > 10 while the precipitate formed in the presence of 376 phosphate is stable in the pH range of 3–11; that is, FePO<sub>4</sub> coating would be stable in the wider pH window 377 compared to that of Fe-oxyhydroxide coating.

378 Figure 6 shows the anodic polarization curves of untreated arsenopyrite electrode and the one treated with 379 Fe-catecholate complex and phosphate. Because arsenopyrite is dissolved in the anode, changes in the anodic 380 current densities at a certain potential could infer not only the effectiveness of coating but also the extent of 381 dissolution of these minerals (Tabelin et al., 2017d). The anodic current density profile of treated arsenopyrite was 382 substantially lower than that of untreated arsenopyrite. The amounts of electric charge generated/transferred 383 during 1 h polarization of untreated and treated arsenopyrite electrodes, which were calculated based on the areas 384 below the current density curves (Q  $[C] = I [A] \times t [s]$ ), were 0.5 and 0.3 mC, respectively, implying that even 385 under strongly oxidizing conditions, the presence of FePO<sub>4</sub> coating suppressed the anodic half-cell reaction of 386 arsenopyrite oxidation (Eq. (8)). This suppressive effect of FePO<sub>4</sub> coating on anodic dissolution of arsenopyrite 387 is most likely achieved by (i) limiting the contact of arsenopyrite and water and/or (ii) inhibiting the diffusion of 388 reaction products of arsenopyrite oxidation into solution.

$$389 \qquad \text{FeAsS}_{(s)} + 7\text{H}_2\text{O} \to \text{Fe}^{2+}_{(aq)} + \text{H}_3\text{AsO}_{3(aq)} + \text{SO}_4^{2-}_{(aq)} + 11\text{H}^+_{(aq)} + 11\text{e}^-$$
(8)



Fig. 5. Leachability tests of arsenopyrite treated in the control and by Fe-catecholate complex with and without phosphate: The changes in (a) dissolved Fe concentration, (b) dissolved As concentration and (c) pH, and (d) the solubility of  $Fe^{3+}$  in the absence and presence of phosphate.



394

Fig. 6. Chronoamperometric response of untreated arsenopyrite and the one treated with Fe-catecholate complex
and phosphate at an applied potential of +0.7 V vs. SHE.

397

# 398 4. Conclusions

399 Arsenopyrite oxidation plays important roles in not only releasing toxic As but also forming AMD, both of 400 which result in serious environmental problems. This study investigated the simultaneous use of Fe-catecholate 401 complexes and phosphate for suppressing arsenopyrite oxidation via the formation of FePO<sub>4</sub> coating on its surface. 402 Among the three Fe-catecholate complexes,  $[Fe(cat)_2]^-$  and  $[Fe(cat)_3]^{3-}$  were stable regardless of the presence of 403 phosphate while  $[Fe(cat)]^+$  became unstable when phosphate coexisted. This instability of  $[Fe(cat)]^+$  is highly 404 likely caused by the replacement of catechol molecule with phosphate forming FePO<sub>4</sub>. The formation of FePO<sub>4</sub> 405 after oxidative decomposition of [Fe(cat)<sub>2</sub>]<sup>-</sup> was evidenced by LSV. The results of SEM-EDX and XPS of 406 arsenopyrite treated with  $[Fe(cat)_2]^-$  and phosphate showed that arsenopyrite was covered with FePO<sub>4</sub> coating. 407 Moreover, the oxidation of FePO<sub>4</sub>-coated arsenopyrite was suppressed. Treatment of arsenopyrite with [Fe(cat)<sub>2</sub>]<sup>-</sup> 408 only also created Fe-oxyhydroxide coating and suppressed the dissolution of arsenopyrite; however, the acid-409 resistant property of FePO<sub>4</sub> was higher than that of Fe-oxyhydroxide under acidic conditions (pH < 4). This 410 indicates that when treated arsenopyrite is placed in an acidic environment (pH  $\approx$  3), FePO<sub>4</sub> coating can survive 411 and protect arsenopyrite from reaction with water and O<sub>2</sub> while Fe-oxyhydroxide would be dissolved. Thus, the use of  $[Fe(cat)_2]^-$  can be an alternative way of supplying  $Fe^{3+}$  to the arsenopyrite surface in place of the use of 412 413 H<sub>2</sub>O<sub>2</sub> for passivating arsenopyrite with FePO<sub>4</sub> coating.

414 The findings of this study suggest that the passivation of arsenopyrite using  $[Fe(cat)_{2}]^{-}$  and phosphate is 415 promising for limiting the problems caused by arsenopyrite oxidation; however, its direct application to TSF 416 would be impractical due to the acidic environment of TSF where Fe-catecholate complexes become unstable. 417 Although this passivation technique may work in TSF by increasing its pH to neutral-alkaline conditions, it is not 418 a sustainable approach due to the inconvenience in increasing the pH of TSF, containing acid-generating minerals 419 and metal ions, both of which buffer against the increase in pH. In the case of sulfide ore processing, flotation is 420 most commonly adopted as a final step to produce saleable concentrates and typically operated under neutral-421 alkaline conditions (pH > 7) to depress non-valuable sulfide minerals, such as pyrite and arsenopyrite (Aikawa et 422 al., 2020; López Valdivieso et al., 2006; Park et al., 2020b). This makes the passivation technique using [Fe(cat)2]<sup>-</sup>

423 and phosphate applicable to flotation tailings before its disposal into TSF. After treating flotation tailings by 424 microencapsulation using [Fe(cat)<sub>2</sub>]<sup>-</sup> and phosphate, sulfide minerals are coated with FePO<sub>4</sub> layer, and thus the acidification of TSF as well as the release of toxic metal(loid)s caused by the oxidation of sulfide minerals are 425 426 highly expected to be limited. The advantage of passivation approach is that the duration of treatment could be 427 dramatically shortened from centuries/millennia to decades or less compared to remediation options (e.g., 428 chemical neutralization), which makes the application of microencapsulation technique economically sound (Park 429 et al., 2019). However, some subjects in relation to "improvement on the amount of FePO<sub>4</sub> coating" and "long-430 term stability of treated arsenopyrite" need to be studied further for this technique to be successfully applied to 431 sulfide-rich mine wastes.

432

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