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Factors controlling the release of metals and a metalloid from the tailings of a gold mine in Thailand

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Abstract: This study focused on assessing the release potential of various metals and a metalloid (arsenic; As) leached from gold mine tailings under three different degrees of acidity (pH 2, 4 and 6.5) using a synthetic precipitation leaching procedure (SPLP). Tailings were collected from four pits from 0 to 16 m depth, approximately. The samples were divided into the three types, based on their position in the tailings and on other physical characteristics, of the sulphide (*c.* 5 m depth), mixing (*c.* 1 m depth) and oxide (*c.* 10 m depth) zones. This study was primarily concerned with the concentrations of As and Mn, which were found to exceed the Thailand Industrial Effluent Standard (TIES) in the tailings from all zones. Principal component analysis revealed that the release of metals and As from the tailings under acidic conditions, as well as the metals and As mobility, was mainly controlled by the pH and redox conditions. Moreover, the first principal component had high positive loadings of Mn, Pb, Co and Ni ($R^2 > 0.80$), indicating that these four metals are either released into the environment from a common source or/and their geochemical behaviour in the aqueous phase is similar.

Keywords: Tailings; Leacheability; Metals; SPLP; Gold Mine

Supplementary material: Concentration of metals and As leached from the sulphide mixing and oxide zones at differing pHs are available at https://doi.org/10.6084/m9.figshare.c.3840154

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Nearly all mining processes cause adverse effects to the environment surrounding nearby communities (APWLD 2009). Even though mineral exploration and mining operations use high-technology equipment, it is difficult to ignore the unintended consequences that arise from toxic residues and other unwanted by-products. Typically, metal and metalloid contamination in the ecosphere is commonly caused by human activities that act as sources of emission, such as transportation, agriculture, industry, mining, landfill seepage, public utilities and household waste (Salomons 1995; Chotpantarat *et al.* 2014). This is particularly true for metal extraction mining, which can intensify the levels of contaminants in the environment in many forms, including gas, liquid and solid waste (Dudka & Adriano 1997). In general, tailings are produced by every metal mine site and their mineral processing, while waste rock is mostly generated in the process of gaining access to the ore and constitutes a small percentage of the total volume. The particle sizes of mine waste vary over a wide range between clay sized particles to boulder sized fragments. With respect to the mineralogy and geochemistry, the particle size, moisture content and type of mining equipment all vary with the physical and chemical characteristics of the mining wastes. Tailings are extracted from the original ores, and represent only a small fraction of the whole ore mass, and are then released into the tailings storage facility (TSF). Generally, tailings have the potential to release potentially toxic metal- and metalloid-laden leachates under an acidic condition that can be detrimental (toxic) to the surrounding environments (Lottermoser 2003; Benzaazoua *et al.* 2004; Sracek *et al.* 2004; Chotpantarat 2011; Chotpantarat *et al.* 2015).

The leaching of various toxic metals and metalloids or their salts (hereafter referred to just as metals and metalloids, respectively) from hazardous-waste dump sites, abandoned mine storage facilities and other contaminated sites has become a worldwide concern because of their harm to the environment and human health (Van Der Sloot 1996; Barna *et al.* 1997). Various metals in particular are pervasive and pose a long-term risk to the soil, surface water and groundwater quality. The severity of the environmental load from trace elements strongly depends on the metals' speciation, mobility and bioavailability in the soil (McBride *et al.* 1997; McBride 1999; Morin *et al.* 1999; Manceau *et al.* 2000; Wikiniyadhanee *et al.* 2015). These metals and metalloids can be assimilated and accumulate in plants and animals directly and via the food chain, whereupon they negatively affect health, including human health. The impact of these metals and metalloids on human health depends in part on their leachability and migration from the mine waste facility. To evaluate the migration potential of metals and metalloids, the study of their leachability has become an important geochemical tool to assess their current and future likely distribution (Hageman & Briggs 2000; Hage & Mudler 2004).

In Thailand, the Department of Primary Industries and Mine's Report (2012) revealed the danger posed by the Phuthapfa mines, where the defective tailings pond was shown to be leaking toxic metals and metalloids into the creek. The leakage of this leachate water from the TSF contained a high concentration of metals above the accepted national industrial standard of Thailand. Charuseiam (2012) reported that the waste rock in the three dump sites, and in particular in the transition and sulphide dump sites, generated acidic water into the surrounding environments, which then resulted in a high concentration of metal ions in the water, and potential adverse effects on the ecosystem.

Several methods to evaluate the potential of metals and metalloids to be leached have been reported. It has been suggested that the EDTA method and the two steps sequential extraction procedure can be used to investigate the metal availability for leaching from soils and wastes (Garrabrants & Kosson 2000). The toxicity characteristic leaching procedure (TCLP), synthetic precipitation leaching procedure (SPLP), deionized water leaching procedure and California waste extraction test are batch leaching procedures that can realistically quantify the mobility of metals and investigate the contamination level from contaminated glaciated sludge, tailings, agricultural soils and groundwater (Lackovic *et al.* 1997; Washington State 2003; Kim *et al.* 2005; McDonald & Webb 2006). On the other hand, the batch leaching TCLP approach was designed to simulate the concentrations of inorganic and organic constituents in leachates from co-disposal with municipal wastes in landfills (Francis & Masakarince 1986). Kosson *et al.* (2002) applied TCLP as an integrated framework to evaluate the potential of inorganic constituents leaching from wastes and secondary materials and assess the released pollutants in a real world situation. However, TCLP was specifically designed to evaluate leachates from landfills and is of limited application to access contaminants leached from industrial wastes, such as mine and mineral processing wastes (USEPA 1996, 1999). Rather, many studies have employed the SPLP to simulate leaching from precipitation or acidic solution and to evaluate the potential to leached metals and metalloids from mine tailings (Lackovic *et al.* 1997; Kim *et al.* 2005; Changul *et al.* 2010; Lortzie *et al.* 2015). These results can provide useful information to select an appropriate remediation technique. Nevertheless, there is only a limited literature on leaching at gold mines in Thailand. Thus, there is a need for a systematic study to investigate the quantitative levels of metals and metalloids contamination in the tailings of gold mines in Thailand.

Site description

The gold mine of this study, the ‘Phutab Fah Gold Deposit’, is located in the Northeastern part of Thailand (Fig. 1a). The mining began here in 2006. However, it contained a quite low grade gold ore compared with other commercial gold deposits in the world. The country rocks at the mine site are sedimentary sequences of sandstone, siltstone, shale and limestone, which belong to the Permian Pha Dua Formation. Subsequently, Triassic granodiorite intruded into these country rocks (Rodmanee 2000; Assawincharoenkij *et al.* 2017). The mineral deposit has been classified into the two groups of (1) gold ore; and (2) silver and copper ore. Based on its physical and chemical properties, the gold ore has been further categorized into the three groups of the oxide ore, sulphide ore and mixing or transition ore zones (Mungkhun 2008).

Significant levels of skarn, massive sulphide rock and gossan were deposited in the area. The lower tailings at the bottom of the TSF were dumped from the primary ore zone, including skarn and massive sulphide, and have an ocher colour (Fig. 2). The upper part of the tailings were dumped on top of the lower tailings and were from the sulphide zone, including gossan (Fig. 2) (Rodmanee 2000; ERIC 2012; Assawincharoenkij *et al.* 2017). The TSF is a wide pond located at 290 m above mean sea level and covers *c.* 13 hectares, being about 550 m long and 100 – 300 m wide (Mungkhun 2008), as shown in Figure 1b.

The acid mine drainage (AMD) generation potential of the waste rock from the Phutab Fah Gold Deposit area has been studied (Charuseiam 2012), while the tailings from this gold mine were investigated for their mineralogy and geochemistry (Assawincharoenkij *et al.* 2017), along with the mineralogy, paragenesis and genetic model (Rodmanee 2000; Zaw *et al.* 2006).

Materials and Methods

The sampling and analytical methods are divided into two parts:

Tailing samples

Tailing samples were picked up directly from the tailing pond of the gold mine at four pits, or sampling points (SP1, SP2, SP3 and SP4), from a depth of *c.* 0 to 16 m (Fig. 2). A piston core with drilling equipment was used to drill the tailing samples at each of the four pits. The tailing surface was *c.* 20 – 120 cm below the water level. Plastic films were applied to seal each sample tube instantly in the field, and then every 1 m of tailing samples were stored in double-sealed ziplock plastic bags for transfer to the laboratory. Subsequently, samples were dried in an oven at 105 ± 2°C for 24 h to remove the moisture and then manually crushed and disaggregated in a ceramic mortar and pestle before being sieved through a 0.09 mm (170 mesh) sieve. These particles consist of very fine sand and mainly silt and clay particles, which are the reactive areas that retain several metals in the tailings. The samples were then stored in plastic bags prior to use (Fey & Desborough 2004).

The SPLP

Examination of the potential leachability of the metals and metalloids from the tailings was performed following EPA 1312 with some adjustment of the methods employed. The leaching assay was prepared using a dilute mixed acid solution at the desired pH as follows. A 60:40 (w/w) sulphuric: nitric acid solution was used to adjust the pH of deionized water to pH 2, 4 or 6.5, as required, to yield the dilute mixed acid solution. Then, 2 g of tailing sample was added into 40 mL of the dilute mixed acid solution (pH 2, 4 or 6.5) and shaken automatically for 18 h at 30 rpm and ambient temperature (23 ± 2°C). Each leachate was then filtered through Whatman grade GF/C glass microfiber filters and the redox potential (Eh), pH and electrical conductivity (EC) were measured. Inductively coupled plasma spectrometry (ICP-MS) was used for the analysis of the concentration of metals and the metalloid arsenic (As), from which the potential leachability of metals and As under the three different pH conditions was evaluated.

Statistical analysis

The analytical data was evaluated by principal component analysis (PCA) and correlation analysis to determine the relationships between the SPLP test and extractable metals. Thus, the concentration of the evaluated metals (Co, Cu, Fe, Pb, Mn, Ni and Zn) and As in the tailing samples were taken as variables. The evaluated tailing sample characteristics (zones, replication, initial pH, final pH, EC and Eh) were included in the input matrix as variables. The PCA was performed on the correlation matrices of the data using the SPSS 17.0 software package. Pearson correlation coefficients for this study were also computed using the SPSS 17 statistical package.

Results and discussion

Physical properties of the tailing samples

The physical properties of the tailing samples, in terms of the depth of each sampling point, grain size and colour of samples, are reported in Table 1. The tailings were divided into the three zones, according to physical and chemical properties of the sulphide, tailings mixing

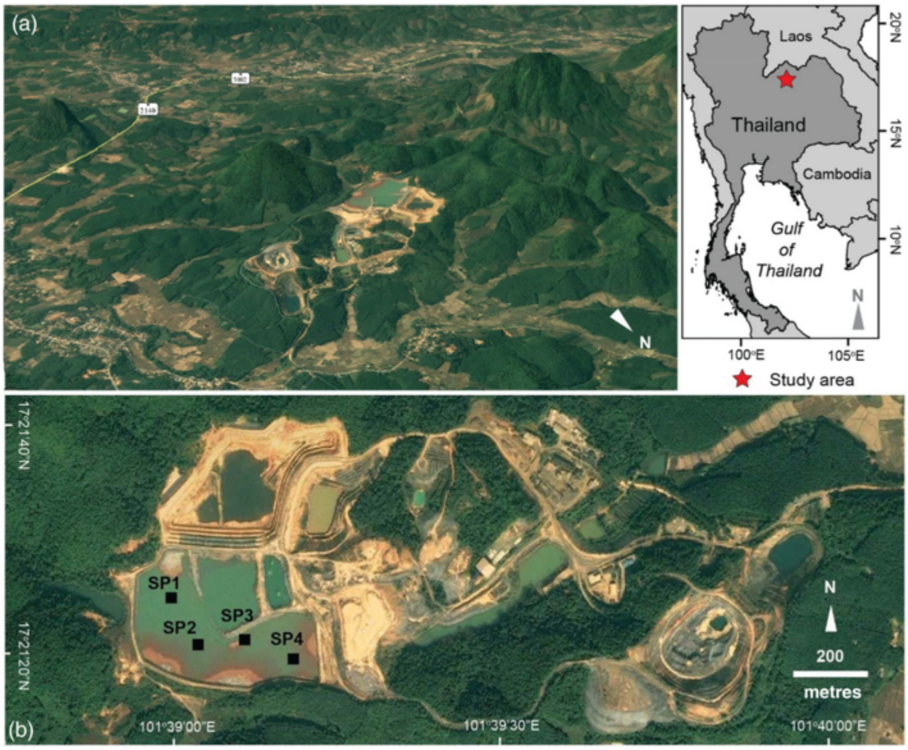

Fig. 1. (**a**) Three-dimensional view of the satellite image from Google Earth showing the topography of the study area and mining location. (**b**) Drill core locations (SP1–SP4) in the tailing pond (TSF) superimposed on the satellite image from Google Earth. (acquisition date 9 December 2013).

and oxide zones. The tailing samples were mainly composed of silt and clay, while CS4 and CS8 at SP4 consisted of very fine sand.

Leaching potential of metals and As using SPLP

Tailings from the sulphide ore zone

The results obtained from the SPLP to test the potential leachability of metals and As in the tailings from the sulphide zone are summarized (see Supplementary material). The concentration of metals and As in the SPLP leachate were higher in the leachate from an initial pH than at pH 4 or pH 6.5. In addition, Pb was detected in the pH 2 leachate but not at pH 4 or 6.5. Lead is a redox-insensitive metal with a solubility that depends more on the pH than on the redox potential, becoming more soluble at an acidic pH (Eugene 2007). Furthermore, the concentration of As leached at pH 2 (2.8 µg.L^{-1}) was about 1.65-fold higher than that at pH 4 (1.7 µg.L^{-1}) and pH 6.5 (1.7 µg.L^{-1}). When sulphide minerals are exposed to atmospheric oxygen, they generate acidic pore water, sulphate and metal ions, including Fe^{2+}. The tailings from the sulphide zone might have contained arsenopyrites, which would lead to the high concentration of As in the tailing sample. The oxidation of arsenopyrites, as shown in equation (1), releases a relatively high amount of As in the leachate (Blowes *et al.* 1998):

$$\mathrm{FeAsS(s)} + 1.5\mathrm{H_2O} + 2.75\mathrm{O_2(aq)} \rightarrow \mathrm{Fe^{2+}} + \mathrm{H_3AsO_3(aq)} + \mathrm{SO_4^{2-}}. \quad (1)$$

Other arsenic minerals, such as the sulphides realgar and orpiment, yield soluble arsenates as shown in equations (2) and (3):

$$4\mathrm{AsS} + 11\mathrm{O_2} + 10\mathrm{H_2O} \rightarrow 4\mathrm{H_2SO_4} + 4\mathrm{H_3AsO_4}, \quad (2)$$

$$\mathrm{As_2S_3} + 7\mathrm{O_2} + 6\mathrm{H_2O} \rightarrow 3\mathrm{H_2SO_4} + 2\mathrm{H_3AsO_4}. \quad (3)$$

Hamberg *et al.* (2016) revealed that at pH > 5, Fe^{2+} is immediately oxidized to Fe^{3+} and precipitates as Fe(OH)$_3$(s). According to the mineralogical analysis, based on scanning electron microscopy (Hamberg *et al.* 2016), such Fe(OH)$_3$ precipitates form rims surrounding the As-sulphide surface grains, which then act as a source of As in the leachates, as shown in Equation (4),

$$\mathrm{FeAsS(s)} + 4\mathrm{H_2O} + 3\mathrm{O_2(aq)} \rightarrow \mathrm{Fe(OH)_3}(s) + \mathrm{H_3AsO_3(aq)} + \mathrm{SO_4^{2-}} + 2\mathrm{H^+}. \quad (4)$$

The unsaturated condition in the upper part of the sulphide zone allows O$_2$ diffusion into tailings and subsequently oxidizes the sulphide minerals, but oxidation only occurs slightly below the water table since the rate of diffusion of O$_2$ is very low and sulphide oxidation decreases and eventually ceases with increasing depth (Nicholson *et al.* 1989). Furthermore, during the disposal process, the size distribution of the tailings may affect the transport of oxygen to the oxidation zone (Ritchie 1994). The re-mobilized metals could be released from Fe precipitates due to the low Eh condition. Similarly, Heikkinen & Räisänen (2009) revealed that Fe and a majority of Ni, Co and Zn were released into the pore water

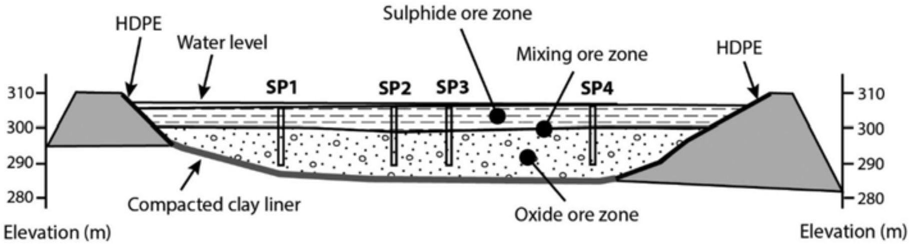

Fig. 2. Cross section showing the outline of the tailing pond (TSF) and the four drill core locations (SP1–SP4). Modified from Assawincharoenkij *et al.* (2017).

Table 1. *Physical properties of tailing samples*

Sampling point	Sample no.	Depth (m)	Average depth (m)	Grain size	Colour	Remark (Tailings from each zone)
SP1	CS2	1.0 – 1.5, 2.0 – 2.5	1.75	Silt	Dark grey	Sulphide zone
	CS3	4.0 – 4.5, 5.0 – 5.09	4.55	Clay	Dark grey	Sulphide zone
	CS4	6.0 – 6.13, 7.0 – 7.5	6.75	Clay	Reddish brown	Mixing zone
	CS5	8.0 – 8.5, 9.0–9.5	8.75	Silt	Reddish brown	Oxide zone
	CS7	10.0 – 10.5, 11.0 – 11.5	10.75	Clay	Reddish brown	Oxide zone
	CS8	13.0 – 13.5, 14.0 – 14.5	13.75	Clay	Reddish brown	Oxide zone
	CS6	16.0 – 16.5	16.25	Clay	Reddish brown	Oxide zone
SP2	CS1	0.0 – 0.5	0.25	Silt and clay	Dark grey	Sulphide zone
	CS2	1.0 – 1.5, 2.0 – 2.5	1.75	Silt	Dark grey	Sulphide zone
	CS8	5.0 – 5.5	5.25	Silt and clay	Dark grey	Sulphide zone
	CS3	6.0 – 6.5	6.25	Clay	Dark grey	Sulphide zone
	CS4	7.0 – 7.43	7.22	Clay with a little silt	Reddish brown	Mixing zone
	CS7	10.36 – 10.5	10.43	Silt	Dark grey	Sulphide zone
	CS5	11.0 – 11.5,12.0 – 12.5, 13.0 – 13.5, 14.0 – 14.5	12.75	Clay	Reddish brown	Oxide zone
	CS6	16.3 – 16.5	16.40	Silt	Dark reddish brown	Oxide zone
SP3	CS1	0.0 – 0.5	0.25	Silt	Dark grey	Sulphide zone
	CS2	1.0 – 1.5, 2.0 – 2.5, 3.0 – 3.5, 4.0 – 4.5	2.75	Silt	Dark grey	Sulphide zone
	CS3	5.03 – 5.14	5.09	Clay	Dark brown	Sulphide zone
	CS4	7.03 – 7.20	7.12	Silt and clay	Reddish brown	Mixing zone
	CS6	8.0 – 8.5, 9.0 – 9.5 10.0 – 10.5, 11.0 – 11.5	9.75	Silt and clay	Reddish brown	Oxide zone
	CS7	12.0 – 12.5	12.25	Silt	Reddish brown	Oxide zone
	CS5	14.0 – 14.5,15.0 – 15.5, 16.0 – 16.5	15.25	Silt and clay	Brown	Oxide zone
SP4	CS1	0.0 – 0.5	0.25	Silt	Dark grey	Sulphide zone
	CS2	1.0 – 1.5, 2.0 – 2.5 3.0 – 3.5	2.25	Silt and clay	Dark grey	Sulphide zone
	CS6	5.11 – 5.5	5.31	Clay	Dark grey	Sulphide zone
	CS3	6.0 – 6.5	6.25	Clay	Reddish brown	Mixing zone
	CS4	8.0 – 8.5, 9.0 – 9.5	8.75	Very fine sand	Reddish brown	Oxide zone
	CS7	11.0 – 11.5, 12.0 – 12.5	11.75	Silt and clay	Dark brown	Oxide zone
	CS8	14.03 – 14.28	14.16	Very fine sand	Very dark brown	Oxide zone
	CS5	15.0 – 15.5, 16.0 – 16.5	15.75	Silt and clay	Brown	Oxide zone

below the groundwater table. Regardless of the rate of oxidation, arsenopyrite (FeAsS) can generate relatively high contents of soluble forms of As in the tailings (Craw *et al.* 1999).

After extraction at an initial pH of 2, the final pH of the leachate from sample CS1 SP2 (pH = 5.75) was lower than that of all the other tailing samples from the sulphide zone, while the concentration of As (13.3 μg.L^{-1}) was higher than those of all the other tailing samples from the sulphide zone. The data indicate that the concentration of metals increases as the pH is decreased. Likewise, the final pH of the leachates from the sulphide zone tailings (pH = 6.51) was higher than those from the oxide (pH = 5.12) or mixing (pH = 3.57) zones. In addition, the concentration of metals in the tailings from the sulphide zone was lower than in the tailings from the two other zones. The dissolution of calcite accounts for the increased release of carbonate in solution and so the pH value of the solution increased (Bernhard 2010). Based on X-ray fluorescence analysis, Assawincharoenkij *et al.* (2017) reported that the CaO content in the sulphide zone (10 – 21 wt.%) was higher than that in the oxide zone (<10 wt.%), implying that significant levels of calcite ($CaCO_3$) were found in the sulphide zone. The results of this study are consistent with a study by Stefania *et al.* (2009) on the tailings from cyanidation processing, which showed that the leachate interacted with calcite, thus rendering a high pH value (pH 6.2 – 9.7) and a small amount of metals.

Figure 3 and Tables S1 – 3 shows the results obtained from the SPLP method for the sulphide ore zone. Leachates from an initial pH 2 had higher concentrations of As, Pb and Mn (10, 10 and 500 μg.L^{-1}, respectively) than the Thailand Groundwater Standard of the Pollution Control Department (TGS-PCD). Interestingly, the concentration of Pb in the CS1 SP4 sample (17.1 μg.L^{-1}) exceeded the TGS-PCD as well as in the other samples at pH 4 and 6.5. However, the concentration of Mn was high, ranging from 27.2 – 154.6 μg.L^{-1}, even at a final pH of 6. Moreover, the concentration of Mn leached from an initial pH 2 (1.0637 mg.L^{-1}) was 22.9- and 15.8-fold higher than that at pH 4 (46.5 μg.L^{-1}) and 6.5 (67.4 μg.L^{-1}), indicating that the metal solubility depended on the final pH. The retention and release of metals was pH-dependent, which is responsible for the soluble metal ions through sorption and co-precipitation processes (McGregor *et al.* 1998; Jönsson & Lövgren 2000; Kumpuainen *et al.* 2007). Pokrovsky & Schott (2002) explained that having a high concentration of H^+ ions in the solution (low pH) may compete with the metal ions for CO_3^{2-}- released from calcite and obstruct the metal-carbonate ($MeCO_3$) precipitation on the surface of the adsorbent. On the other hand, when the pH is higher there are more CO_3^{2-} ions available to react with metal ions to form $MeCO_3$ to precipitate, and so extend the adsorption capacity. In addition, Al-Degs *et al.* (2006) suggested the sorption process of metal ions on the surface of the sorbent occurred in three steps. The first was calcite dissolution releasing CO_3^{2-} into the solution. Then, the free metal ions (Me^{2+}) in solution interact with CO_3^{2-} to form $MeCO_3$ before

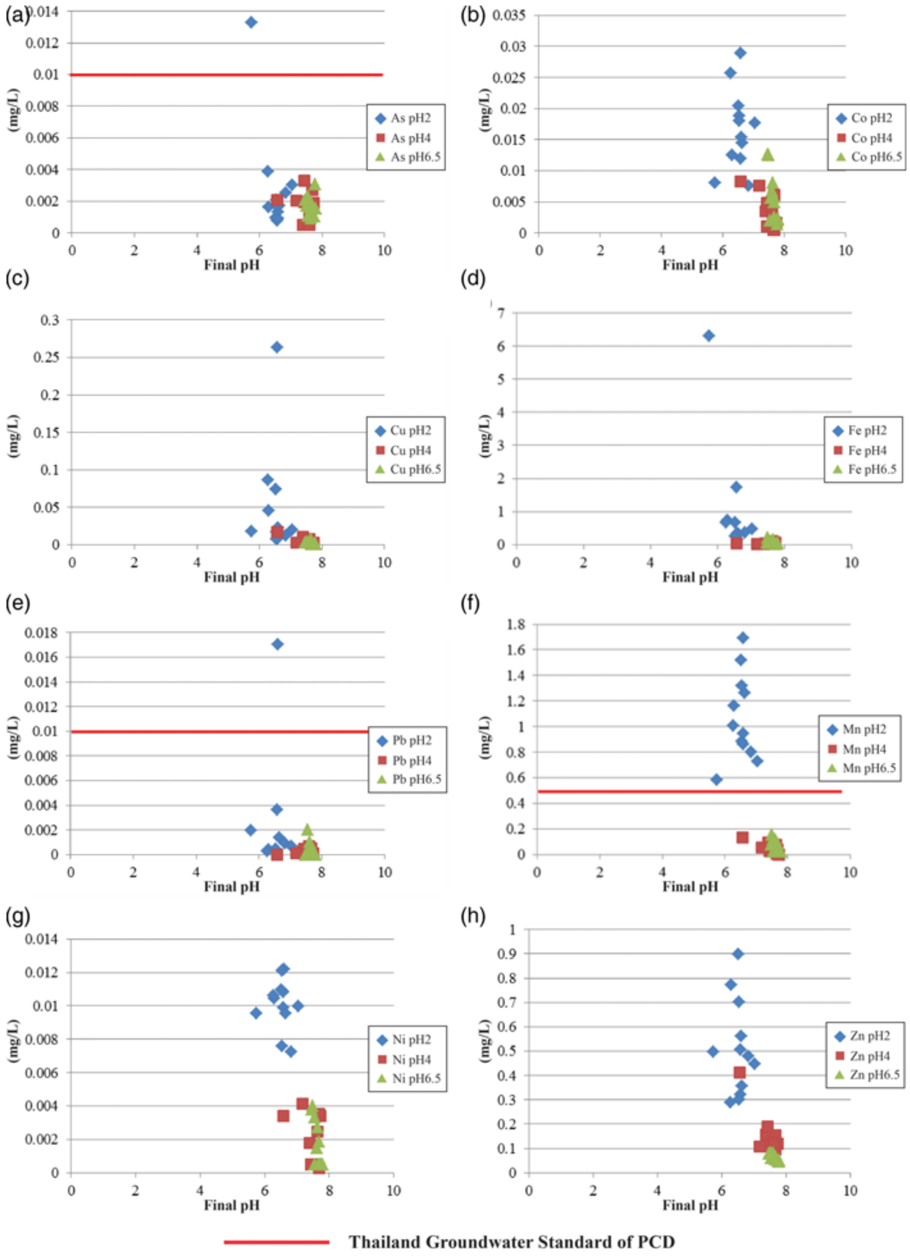

Fig. 3. Concentrations of (**A**) As, (**B**) Co, (**C**) Cu, (**D**) Fe, (**E**) Pb, (**F**) Mn, (**G**) Ni and (**H**) Zn in tailings from the sulphide zone, as derived using SPLP.

deposition on the surface of sorbent, as shown in equations (5–7):

$$-S - CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq), \tag{5}$$

$$Me^{2+}(aq) + CO_3^{2-}(aq) \rightleftharpoons MeCO_3(s), \tag{6}$$

$$-S - CaCO_3(s) + MeCO_3(s) \rightarrow [-S - CaCO_3 - MeCO_3](s). \tag{7}$$

According to the Le Châtelier principle, the formation of $MeCO_3$ from the above pathway decreases the amount of CO_3^{2-}, which then leads to further calcite dissolution and so more metal sorption.

Using the SPLP test, the amount of metals released in decreasing order from the tailing samples from the sulphide zone were:

$$\text{At pH 2: Mn} > \text{Zn} > \text{Pb} > \text{Co} > \text{Cu} > \text{Ni} > \text{Fe} \sim \text{As}.$$

$$\text{At pH 4: Zn} > \text{Mn} > \text{Co} > \text{Pb} > \text{Cu} > \text{Ni} > \text{As} \sim \text{Fe}.$$

$$\text{At pH 6.5: Zn} > \text{Mn} > \text{Co} > \text{Pb} > \text{Cu} > \text{Ni} > \text{As} \sim \text{Fe}.$$

As can be seen from Figure 3, the concentration of Co was quite high, which is in agreement with the study of Assawincharoenkij *et al.* (2017), based on electron probe micro-analysis (EPMA), of sulphide minerals that were composed of mainly Fe and noticeable amounts of Co (≤0.16 wt.%) and Cu (≤0.04 – 0.54 wt.%) in both the sulphide and oxide zones. This implied the presence of pyrite (FeS_2), pyrrhotite ($Fe_{(1-x)}S_2$) and chalcopyrite ($CuFeS_2$) in the gold mine tailings (Hassaan *et al.* 2015), which were identified by EPMA in the study of Assawincharoenkij *et al.* (2017). In addition, Ni and Co can be found as a trace metals within the structure of pyrrhotite (Gunsinger *et al.* 2006). The redox potential influences the solubility of metals, especially for Zn and Mn in this study, where their concentrations were greater than those of other metals. It is, therefore, advantageous to classify metals as redox sensitive or insensitive, according to their redox-dependent solubility. Here, Mn is classified as a redox sensitive metal as it can change its oxidation state within redox conditions that are common in the environment. Under oxidation reaction (reducing condition), a high concentration of Mn is released at a pH of <7.0, while the redox-insensitive metal status can explain the Zn concentration (Eugene 2007).

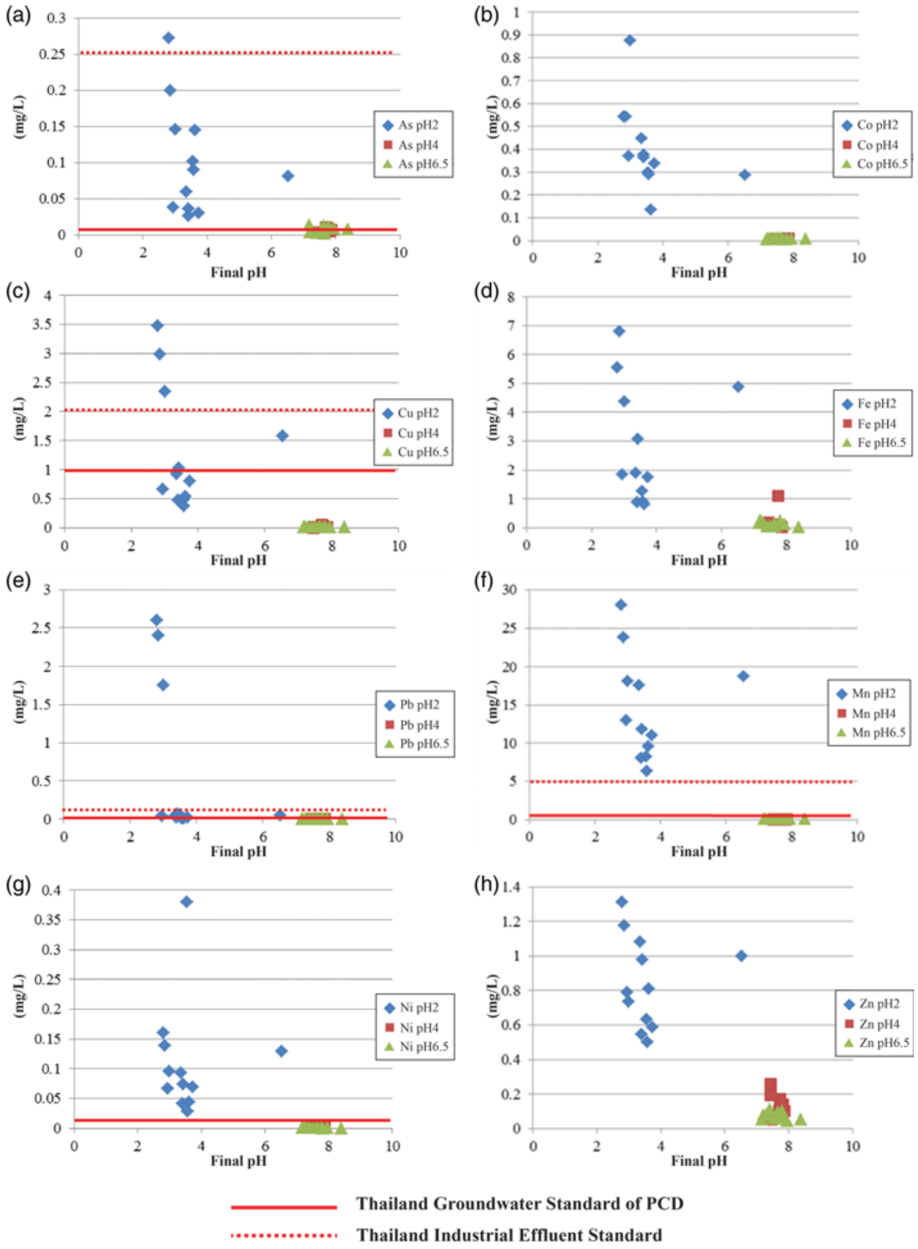

Fig. 4. Concentrations of (**A**) As, (**B**) Co, (**C**) Cu, (**D**) Fe, (**E**) Pb, (**F**) Mn, (**G**) Ni and (**H**) Zn in tailings from the mixing zone, as derived using SPLP.

Tailings from the mixing ore zone

The concentration of leached metals and As from the SPLP analysis at an initial pH 2 were higher than those at pH 4 and 6.5 (Table S4). This was especially true for the average concentration of As leached at pH 2 (102.2 µg.L^{-1}), which was 15.7- and 14.8-fold higher the average concentration at pH 4 (6.5 µg.L^{-1}) and 6.5 (6.9 µg.L^{-1}). Interestingly, as shown in Figure 4, when extracted at an initial SPLP pH of 2, the concentrations of Co, Cu, Fe, Pb, Mn, Zn and As from CS3 SP4 were higher than those from SP1 – 3, and the final pH of this sample (pH = 2.89) was lower than all the other samples in the tailings from the mixed zone. These results indicate that the metals and As might become more soluble at a lower pH and less soluble at a higher pH, as metals generally form oxy-hydroxide compounds at elevated pH values (Eugene 2007). In addition, Pb was detected in the leachate at pH 2, but not at pH 4 and 6.5. Some secondary sulphates and carbonates, such as anglesite ($PbSO_4$) and cerussite ($PbCO_3$), are poorly soluble. As mentioned in the ‘Tailings from the sulfide ore zone’ section, Pb is a redox-insensitive metal and its solubility depends on the pH rather than on the redox potential (Eugene 2007).

Table 2. *Thailand Groundwater Standard of Pollution Control Department (TGS-PCD) and Thailand Industrial Effluent Standard (TIES)*

Metal/Metalloid	TGS-PCD (mg/L)	TIES (mg/L)
Arsenic (As)	NA*	≤0.25
Cobalt (Co)	NA	NA
Copper (Cu)	≤0.10	≤2.00
Iron (Fe)	≤0.50	none
Lead (Pb)	none	≤0.20
Manganese (Mn)	≤0.30	≤5.00
Nickel (Ni)	NA	≤1.00
Zinc (Zn)	≤5.00	≤5.00

*NA, not available.

For the SPLP extraction at an initial pH 2, the final pH of the leachate from the mixing zone tailings (pH 3.57) was lower than those from the oxide (pH 5.12) and sulphide (pH 6.51) zones. In addition, the concentration of metals in the leachate from the mixing zone tailings was lower than those from the two other zones. Previously, Van der Sloot *et al.* (1997) and Jang *et al.* (2002) reported that metals tended to be leached to a greater extent under highly acidic conditions. From these above results, the concentration of metals leached from the mixing zone tailings strongly depended on the pH of the leaching solution.

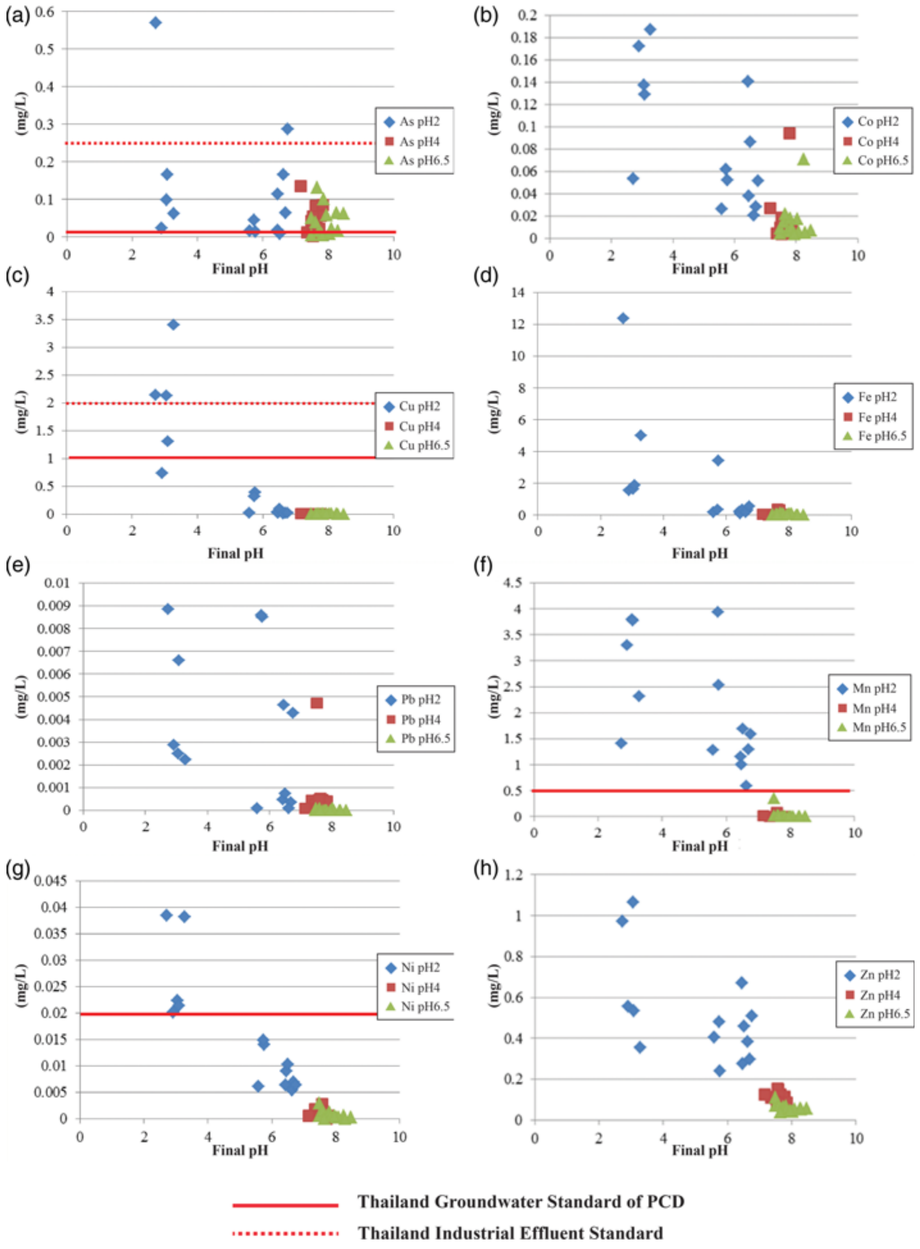

Fig. 5. Concentrations of (**A**) As, (**B**) Co, (**C**) Cu, (**D**) Fe, (**E**) Pb, (**F**) Mn, (**G**) Ni and (**H**) Zn in tailings from the oxide zone, as derived using SPLP.

The results also show that the leachate had higher concentrations of As, Cu, Pb, Mn and Ni than the TGD-PCD and the TIES, as shown in Table 2. Concentrations of transition metals, such as Cu, Zn and Ni, and metalloids, such as As, under AMD condition are generally affected by sorption and co-precipitation with hydrous iron oxides (Alpers *et al.* 1994; McGregor *et al.* 1998; Jönsson & Lövgren 2000; Kumpuainen *et al.* 2007). Cornell & Schwertmann (1996) reported that a large number of cations (Al, Cr, Ca, Ga, V, Mn, Co, Pb, Ni, Zn and Cd) can be substituted for iron in the goethite crystal lattice. Changul *et al.* (2010) found that the concentrations of Mn, Ni and Pb in the leachate increased under acidic conditions. Moreover, the concentration of Pb and Mn also appeared to be leached, implying mobility of these metals, even at circa neutral conditions.

Using the SPLP test, the amount of metals released in decreasing order from the tailing samples from the mixing zone were:

$$\text{At pH 2: Mn} > \text{Zn} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Co} > \text{As} > \text{Fe}.$$

$$\text{At pH 4: Zn} > \text{Pb} > \text{Cu} > \text{Mn} \sim \text{Co} \sim \text{As} > \text{Ni} \sim \text{Fe}.$$

$$\text{At pH 6.5: Zn} > \text{Mn} \sim \text{Co} > \text{Cu} \sim \text{As} > \text{Pb} > \text{Ni} \sim \text{Fe}.$$

Tailings from the oxide ore zone

Figure 5 and Tables S5 – 7 show the results obtained from the leachability of metals and As in the oxide ore zone. The concentrations of metals from the SPLP at an initial pH 2 were higher than those at pH 4 and 6.5. Lead was detected in leachate at pH 2, while it was not detected at pH 4 and 6.5. Furthermore, the concentration of As leached at pH 2 (117.8 µg.L^{-1}) was 2.78- and 2.83-fold higher than those at pH 4 (42.3 µg.L^{-1}) and pH 6.5 (41.6 µg.L^{-1}), respectively. The concentrations of Cu, Fe, Pb, Mn, Ni, Zn and As from SP4 were higher than those from SP1 – 3. It should be noted that for CS4 SP4, the concentrations of metals were high because it contained very fine sand. After extraction at an initial pH 2, the final pH of the leachate from the CS4 SP4 sample was lower than that for all the other samples from the oxide ore zone. Typically, soils with high amounts of organic matter or clay have a higher cation exchange capacity and buffering capacity than silty or sandy soils, and so have a lower metal leachability. Moreover, the adsorption and precipitation of metals in tailings are generally the major control factors of the metal concentration in the tailings, and they increase with increasing pH (McCauley *et al.* 2003; Heikkinen & Räiasänen 2008).

Table 3. *Pearson's correlation coefficient (R^2) between the physiochemical parameters and concentrations of metals and As*

Parameter	Zone	Rep.	Initial pH	Final pH	EC	Eh	As	Co	Cu	Fe	Pb	Mn	Ni	Zn
Zone	1.000													
Replication	0.000	1.000												
InitialpH	0.000	0.000	1.000											
FinalpH	−0.199	0.027	0.681	1.000										
EC	−0.101	0.005	**−0.816***	−0.608	1.000									
Eh	0.250	0.040	−0.358	−0.617	0.322	1.000								
As	0.392	0.049	−0.263	−0.456	0.182	0.360	1.000							
Co	0.150	−0.053	−0.401	−0.683	0.377	0.508	0.271	1.000						
Cu	0.226	−0.007	−0.380	**−0.749***	0.382	**0.542***	0.506	0.642	1.000					
Fe	0.138	0.016	−0.394	−0.624	0.382	0.417	**0.675***	0.399	**0.718***	1.000				
Pb	−0.008	0.014	−0.137	−0.312	0.149	0.203	0.239	0.667	0.499	0.318	1.000			
Mn	0.044	0.008	−0.420	−0.619	0.392	0.481	0.270	**0.892***	0.609	0.409	**0.739***	1.000		
Ni	0.019	−0.055	−0.348	−0.530	0.335	0.403	0.270	0.668	0.484	0.377	0.451	**0.711***	1.000	
Zn	−0.031	0.010	−0.692	−0.688	**0.559***	0.408	0.417	0.518	0.528	0.491	0.332	0.596	0.464	1.000

Single asterisk and bold type indicates a significant relationship between the two parameters ($P < 0.05$).

After extraction at an initial pH 6.5, the final pH of the leachate from the oxide zone tailings (pH 7.89) was higher than those from the sulphide (pH 7.64) and mixing (pH 6.62) zones, especially for the final pH of CS4 (pH = 8.47) and CS8 (pH = 8.30) in SP 4.

These results show that the leachate had higher concentrations of As, Cu, Mn and Ni than the TGS-PCD, and higher concentrations of As and Cu than the TIES. Furthermore, the concentrations of As and Cu were higher than the TGS-PCD and TIES at pH 2 from SP4, which were higher than at SP1 – 3. Moreover, this study found that the soluble concentrations of As and Cu in the leachate after extraction at an initial pH 2 from the oxide zone were relatively higher than those in the sulphide zone. This is in agreement with the study of Assawincharoenkij *et al.* (2017), who, based on ICP-MS, found that the As and Cu concentrations in the oxide zone ranged from 238 – 2870 and 750 – 2585 mg/kg, respectively, equivalent to 39 – 268 mg/kg of As and 222 – 425 mg/kg of Cu, respectively for the sulphide zone. They concluded that all sulphide minerals in the sulphide zone contained a low As concentration, but the As contents in the goethite composition was relatively high, and would be a possible source of As in the surrounding environment.

Using the SPLP test, the amount of metals released in decreasing order from the tailing samples from the oxide zone were:

$$\text{At pH 2: Mn} > \text{Zn} \sim \text{Co Cu} > \text{Pb} > \text{Ni} \sim \text{As} > \text{Fe}.$$

$$\text{At pH 4: Zn} > \text{Co} > \text{Pb} > \text{As} > \text{Mn} > \text{Cu} \sim \text{Ni} > \text{Fe}.$$

$$\text{At pH 6.5: Co} > \text{Zn} > \text{Mn} > \text{As} > \text{Cu} \sim \text{Ni} > \text{Pb} \sim \text{Fe}.$$

One unanticipated finding was that the concentration of Co was quite high when compared with other metals in this study. As can be seen in Figure 5, the concentration of Co was relatively high compared to that in the sulphide zone, which is in agreement with the study of Assawincharoenkij *et al.* (2017), based on the EPMA of sulphide minerals in the lower tailings (Hassaan *et al.* 2015). Moreover, Gunsinger *et al.* (2006) suggested that Ni and Co can be found as a trace metals in the structure of pyrthotite. In contrast to the extraction at pH 2, the As concentration in the leachate was higher than some other metals in the leachate at pH 4 (Mn, Cu and Ni) and pH 6.5 (Cu, Ni and Pb), which may be explained by the

Table 4. *Rotated component matrix dividing variables into four groups by PCA*

Rotated component matrix*				
	Component			
	1	2	3	4
Mn	**0.899**	0.299	0.123	0.017
Pb	**0.861**	−0.033	0.060	0.091
Co	**0.857**	0.272	0.209	−0.078
Ni	**0.717**	0.285	0.121	−0.085
Initial pH	−0.126	**−0.912**	−0.096	0.015
EC	0.136	**0.890**	0.002	0.001
Zn	0.380	**0.714**	0.203	0.046
Final pH	−0.423	**−0.665**	−0.459	0.058
As	0.125	0.191	**0.804**	0.103
Zone	−0.049	−0.211	**0.743**	−0.111
Fe	0.272	0.406	**0.639**	0.085
Cu	0.546	0.341	**0.571**	0.010
Eh	0.346	0.338	**0.495**	−0.002
Replication	−0.022	−0.004	0.021	**0.980**

The bold represent the group of parameters in each component. Extraction method: Principal Component Analysis. Rotation Method: Varimax with Kaiser Normalization. *Rotation converged in five iterations.

Table 5. *Variances explained by various factors*

Factor	Total variance explained								
	Initial Eigen value			Extraction sums of squared loadings			Rotation sums of squared loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	6.368	45.484	45.484	6.368	45.484	45.484	3.665	26.181	26.181
2	1.569	11.207	56.690	1.569	11.207	56.690	3.300	23.568	49.749
3	1.549	11.067	67.757	1.549	11.067	67.757	2.517	17.979	67.728
4	1.014	7.240	74.997	1.014	7.240	74.997	1.018	7.269	74.997
5	0.858	6.126	81.123						
6	0.621	4.435	85.558						
7	0.511	3.648	89.207						
8	0.427	3.050	92.257						
9	0.349	2.493	94.750						
10	0.207	1.479	96.230						
11	0.185	1.319	97.549						
12	0.154	1.101	98.650						
13	0.114	0.814	99.464						
14	0.075	0.536	100.000						

release of As from precipitates of Fe oxyhydroxides and oxides under reducing conditions. This condition can be induced by a raised groundwater table in the TSF (Heikkinen & Räisänen 2009).

Statistical analysis

The statistical summaries of the SPLP test data used for this study are shown in Tables 3 – 5. In Table 3, the concentration of metals and As found in the leachates of an initial pH of 2, 4 or 6.5 were first determined on the basis of linear correlation between the metal (and As) concentration and the physic-chemical pairs in terms of a significant correlation coefficient at the $P < 0.05$ level. Significant positive correlations were found between As-Fe ($R^2 = 0675$), Co-Mn ($R^2 = 0.892$), Cu-Fe ($R^2 = 0.718$), Pb-Mn ($R^2 = 0.739$) and Mn-Ni ($R^2 = 0.711$), indicating the likely existence of common source/ minerals of these metals in the leachate. In general, trace metals, such as Co, Mn, Pb and Ni, and the metalloid As, can be presented in the form of small mineral inclusions and chemical impurities in the host sulphides, such as pyrite, pyrrhotite and chalcopyrite (Vaughan & Craig 1978). The skarn-type gold deposit contains As that is generally associated with Cu, Pb, Zn, Cd, Ag, Au, Mo and Fe more than with W, Sn, Bi, Sb, Te, Ni and Co (Royle & Jonasson 1973). Using varimax normalized rotation, the principal component loadings are given in Table 4. The PCA allows the experimental data set to be viewed with three principal components, retaining the maximum possible variability within that set (Table 4). A component plot in rotated space is shown in Figure 6, which explains the three groups. Four principal components (eigenvalues >1) emerged that together accounted for more than 74% of the cumulative variance. The final factor model had four factors that accounted for 75.0% of the total variance in the SPLP test data (Table 5). The rotated component matrix indicated that Mn, Pb, Co and Ni appear in the first component; the initial pH, EC, Zn and final pH in the second; As, zone, Fe, Cu and Eh in the third component; and replication in the fourth component.

The PCA results (Table 5) show the first component (PC1) had the highest factor loading (3.67), followed by PC2, PC3 and PC4 with factor loadings of 3.30, 2.52 and 1.02 respectively. As can be seen in Table 4, the rotated component matrix obtained from the PCA extraction had variables included in each component.

The first component (PC1) accounted for the most important associations and was strongly correlated with the concentration of Mn, Pb, Co and Ni, as illustrated by the high factor loading in PC1.

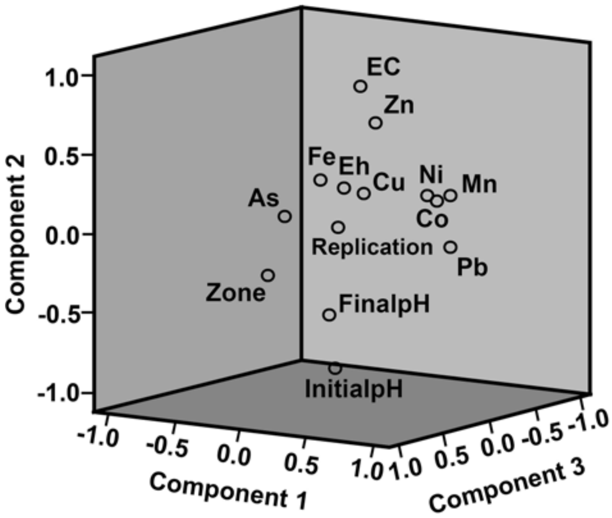

Fig. 6. A component plot in rotated space.

The input of PC1 was 26% of the total variance, with the largest eigenvalue 3.67 (Table 5), and had high positive loadings of Mn, Pb, Co and Ni in the range of 0.72 – 0.90. The correlation coefficient between Mn, Pb, Co and Ni was more than 0.80, which is significant at the $P < 0.01$ level. In general, it seems that the metals in PC1 are released into the environment under similar processes.

The second component (PC2) was mostly dependent upon the initial pH, EC, Zn and final pH, and contributed 24% of the total variance. It had the second largest eigenvalue 3.30 (Table 5) as well as high positive loadings of 0.67 – 0.91. In addition, the studies of Sutthirat & Changul (2013) and Esakku *et al.* (2008) confirmed that the effect of pH on leaching efficiency was the most significant factor that influences the intensity of metal release. Hofmann & Schuwirth (2008) found that the fate and behaviour of Zn in a TSF was relatively dependent upon the pH and redox potential values, since sphalerite is oxidized and releases soluble Zn from the immobile phases. Similarly, sulphide oxidation results in a decreased pH and then releases Ni and Zn in the pore water (Heikkinen & Räiasänen 2008).

The third component (PC3) was dominated by As, zone, Fe, Cu and Eh and accounted for 2.52 of the factor loading and 18% of the total variance. Since As is classified as a redox-sensitive metalloid and is more soluble under oxidizing conditions than under reducing conditions (Eugene 2007), this accounts for the observation that the concentration of As in the oxide zone was higher than in the sulphide zone. A strong relationship between As and Eh conditions has been reported in the literature, suggesting that both conditions regulate and control the release of metals and the formation of AMD depended on the dissolution and precipitation reactions of neutralizing and secondary minerals in the tailing (Alpers *et al.* 1994). The result indicated that the zone, As, Fe, Cu, and Eh were relatively high in the metal and As releasing process. The findings of this current study are consistent with those of Assawincharoenkij *et al.* (2017), who found the sulphide zone (upper tailing) contained large amounts of sulphide minerals that may be more readily oxidized and generate AMD. Although the oxide zone (lower tailing) appears to be a low potential source of AMD, this zone contains the highest concentrations of metals. Moreover, this study found the presence of pyrite (FeS_2) and chacopyrite ($CuFeS_2$) in the upper tailing as well. The common arsenate mineral, which is probably found in the oxidized zones of in-situ sulphide deposits and weathered zones of tailings, is scorodite ($FeAsO_4$ $2H_2O$), an alteration product of arsenopyrite (Alpers *et al.* 1994).

It is advantageous to classify metals as redox sensitive or insensitive according to their redox-dependent solubility. Iron and Cu are classified as redox sensitive metals that can change their oxidation state within the common redox conditions found in the environment (Eugene 2007). Under an oxidation reaction (reducing condition) at a $pH < 7.0$, higher amounts of As and these metals can be released. These findings enhance understanding of the solubility of metals dependent on redox potential.

The fourth component (PC4) was comprised of only replication, meaning that this factor is correlated (factor loading = 1.02) with a contribution of just 7% of the total variance.

The result of the PCA based on the most significant first four factors accounted for about 75% of the total variance and included eight of the observed 13 variables. Therefore, the first four factors can be used to describe the factors contributing to the metal/metalloid contamination in the area from tailings.

Conclusions

Thirty samples of gold mine tailings were collected from four pits in the tailing pond of a gold mine in Thailand from a depth of 0 – 16 m. The tailings contained high amounts of various metals, such as Co, Cu, Fe, Ni, Mn, Pb and Zn, plus the metalloid As. These findings suggested that high amounts of metals and As were found in the study area. In addition, the tailing samples in all zones were dark grey, reddish brown, brown and dark brown in colour and mainly consisted of silt or clay, except in the oxide ore zone, which consisted of very fine sand.

The potential leachability of metal contaminates in the gold mine tailings was determined using the SPLP test, and revealed that some mine tailings were severely contaminated by metals (Fe, Pb, Cu, Ni and Zn) plus the metalloid As, and had a high potential for the release of these metals. Metals in such leachates showed various final pH values, ranging from 2.72 to 8.47, depending on the mineralization of tailings and the initial pH of the leaching solution. Furthermore, the tailing in the mixing zone had relatively high EC and Eh values. The As, Ni, Mn and Pb concentrations in the sulphide and mixing ore zones exceeded the standard quality for groundwater for Thailand (TGS-PCD). In the oxide ore zone, the concentrations of leached As and Cu were higher than both the TGS-PCD and the TIES when leached at an initial pH 2. Additionally, the concentrations of As were higher than the TGS-PCD ($10\ \mu g.L^{-1}$) at all three initial leaching pH values (pH 2, 4 and 6.5). Hence, the findings of this study suggest that As has a relatively high risk of being released into the subsurface environment. The PCA analysis revealed that governing of the redox and pH conditions is important in handling the transport of metals and As in gold mine tailings affected by acidic conditions due to AMG.

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