

CHAPTER III

HEAVY METALS CONTAMINATION OF GROUNDWATER AND SURROUNDING SOILS BY TAILING LEACHATES FROM A GOLD MINE IN THAILAND

Abstract

Mining sites generally release substantial amounts of potentially toxic metals that are problematic to the environment and human health. This study evaluates the discharge of potentially toxic metals from the mill tailings of the Akara gold mine in Thailand. Metal analysis of the mill tailings were performed according to EPA method 3051. The concentrations of potentially toxic metals in the tailings were not over the Thailand Soil Standards for Habitat and Agriculture, except for Mn. A series of batch and column desorption experiments were conducted to investigate the sorption/desorption and mobility of various metals from the tailings under different pH conditions (pH 4, 7 and 10). Batch desorption experiments showed that the release of potentially toxic metals was pH dependent with Mn more easily released from the tailings than other metals. Using column experiments, the amount of metals released in decreasing order from the tailings were: Mn > Ni > Zn ~ Pb. The maximum concentrations in the leachate were Mn (40 mg L⁻¹), Ni (20 mg L⁻¹), Zn (30 mg L⁻¹), and Pb (18 mg L⁻¹) which were over the Thailand Industrial Effluent Standards. The metals concentration in the groundwater collected from shallow and deep wells at the mining site over a two-year period typically showed relatively high concentration of Mn supporting the well-controlled laboratory results of the batch and column desorption experiments.

Key words: tailings, gold mine, heavy metals, pH effect, desorption.

3.1 Introduction and Background

Mining activities generally release substantial amounts of wastes that later become problematic for the environment and human health. Release of potentially toxic metals at mining sites is generally caused by poorly designed and maintained storage facilities, poor environmental management of mining wastes and the consequences of acid mine drainage (Lottermoser 2003). Many previous studies have shown that potentially toxic metals released from mine wastes can lead to adverse health effects in animals and humans (Salomons 1995; Protano and Riccobono 1997; Macro et al. 2002; Passariello et al. 2002; Ramirez et al. 2002; Yukselen 2002; Abut et al. 2003; Lottermoser 2003; Neves and Matias 2008). These metals include lead, zinc, arsenic, nickel, copper which at trace quantities are essential for maintenance of metabolism in the organisms and humans but at high concentrations are toxic (ATSDR 2000a; ATSDR 2000b; ATSDR 2000c; ATSDR 2005). In addition, these potentially toxic metals are persistent and can accumulate in the environment for decades to millennia.

Vast masses of mill tailings are generated by the mining industry and the current amount of tailings is forecast to double over the next 20 to 30 years (Aswatharayana 2003). Leaching of toxic metals from tailings is expected to occur but when acid mine drainage conditions are present, the transportation and impact of potentially toxic metals at the site will increase considerably. However, at many sites, mine tailings may be a major source of pollutants. The severity of the negative environmental effects associated with mine tailings or tailings in an impoundment may not be evident initially but long after the mine's closure and tailings impoundment decommissioning (Blowes 1997). Therefore, it is very important to evaluate the amounts of potentially toxic metals that can be leached from the mine tailings along with the impact of the contamination on the environment in order to initiate adequate management practices to prevent and control pollution of the surrounding areas, surface water and groundwater systems in the vicinity of the mine.

Only two gold mines have been operating in Thailand; however, Akara Mine is the biggest one and consequently chosen for this study. The mine is located around

280 km north of Bangkok (Figure 3.1). It has been in operation for fourteen years. Waste rocks from the mining process are used in the construction of a tailings storage facility (TSF) or deposited in two mine waste emplacements as shown in Figure 3.1 along with the groundwater monitoring wells. Approximately 750,000 dry tons per year of tailings in the form of particulate suspensions are generated from ore processing (referred to as mill tailings) and deposited in the TSF. Results from an environmental impact assessment study conducted in 1999 revealed that shallow municipal wells in nearby villages intersected the shallow, unconfined, alluvial aquifers at depth between 1.5-7 m below ground surface and the groundwater table was approximately 6 m below ground surface.

Gold ore in the area is embedded in quartz and carbonate rocks in the sulphide boundaries, in fractures and as 20-micron belbs within the sulphides. In several potential ore zones, substantial amounts of pyrite (FeS_2) with subordinate sphalerite and chalcopyrite as well as sulphides are present which when exposed to oxygen and water may generate acidic water by oxidation reaction leading to acidic mine conditions and another source of pollution.

The main objective of this study was to determine the toxic metals leaching potential from mill tailings in the TSF of the gold mine. To achieve the objective, metal analysis of mill tailings were employed according to EPA method 3051 (EPA, 1994) and a series of batch and column desorption experiments were conducted to investigate the sorption/desorption and mobility of various metals from the tailings under different pH conditions. The experimental results were then compared with the groundwater quality data collected from monitoring wells in this area.

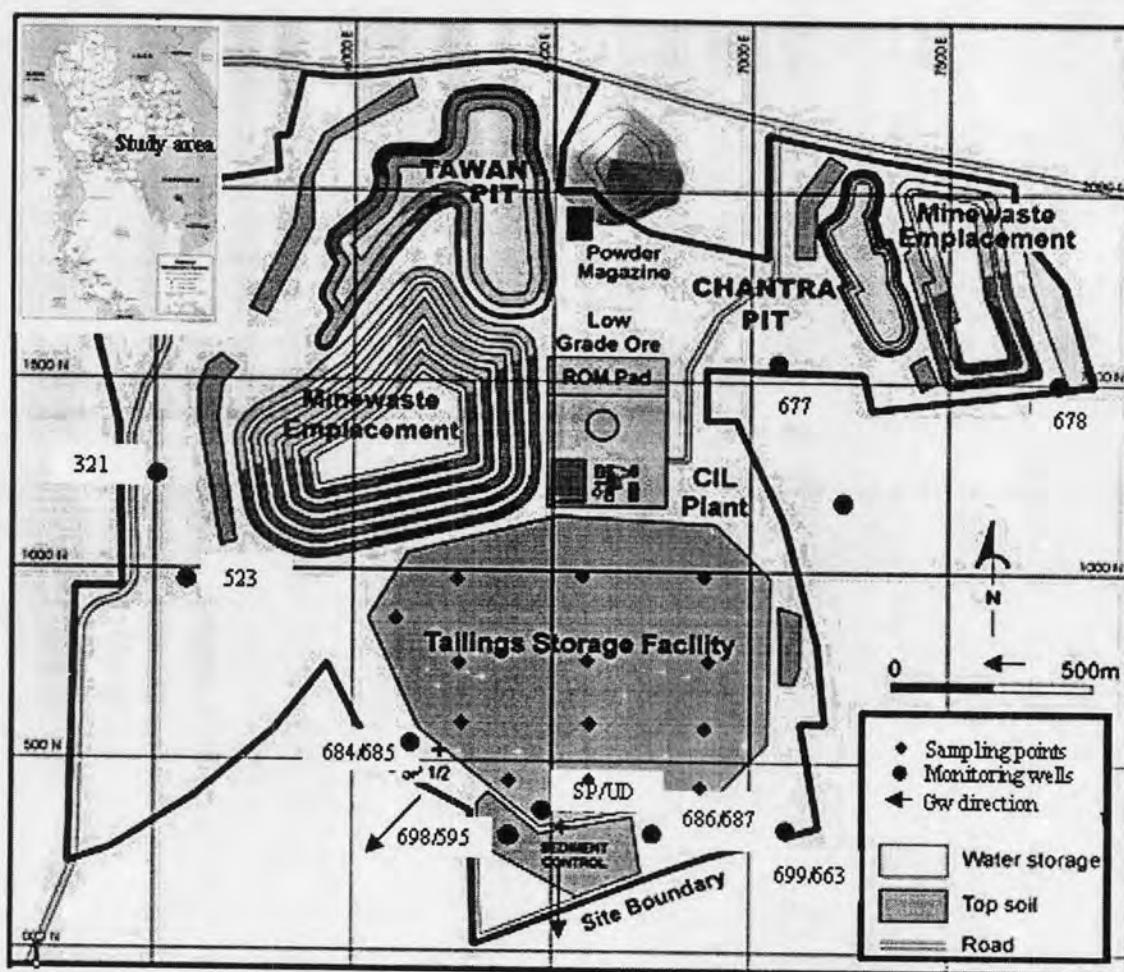


Figure 3.1 Akara mining site

3.2 Heavy Metals in Mill Tailings

The mill tailing samples were collected from 13 different locations distributed over the TSF area from 0-2 m below the ground surface (Figure 3.1). The samples were kept in clean plastic bags and transported back to the laboratory. Each sample was air-dried and sieved through a 0.075-mm mesh prior to being used in the experiments. Sieve analysis revealed that most tailing particles were very fine with average particle sizes between 0.075 mm and 0.002 mm.

The metal contents in the tailing samples were analyzed according to EPA Method 3051 (EPA 1994). A tailing sample of 0.5 g was transferred into a fluorocarbon microwave digestion vessel with 10 mL nitric acid and digested for 10 minutes. The sample was cooled and the supernatant diluted with 50 mL of deionized

water. The slurry was then filtered through Whatman filter paper (1.2 μm) and the aqueous phase analyzed using an inductively coupled plasma optical emission spectroscopy (ICP-OES). ³³

The metals analyzed by ICP-OES for mill tailings and top soils are presented in Table 3.1. The results show that the concentrations of the metals in the tailings were generally higher than those found in the top soil, except for the amount of iron. In the mining process, valuable metals are extracted from the ores and only the unwanted metals are left that are mostly toxic. Most of the metals found in the tailings did not exceed the Thailand Soil Standards for Habitat and Agriculture (PCD, 2004a). The Mn concentration in the tailings, however, exceeded the Soil Standards for Habitat and Agriculture (Mn standard is 1.8 mg g^{-1}).

Table 3.1 Chemical analysis of tailing solid samples at the Akara Mine

Metal	Concentrations of metals (mg g ⁻¹) ⁺			
	Top soil		Tailings	
	Range	Mean.±sd	Range	Mean.±sd
Aluminium	5.98-8.48	7.28±1.07	7.28-13.67	10.82±1.73
Arsenic	ND	ND	ND	ND
Barium	0.01-0.09	0.05±0.03	0.04-0.29	0.147±0.06
Bismuth	ND	ND	ND	ND
Boron	0.02-0.17	0.09±0.06	0.04-0.17	0.103±0.02
Cadmium	ND	ND	ND	ND
Calcium	0.59-3.47	1.69±1.10	24.21-51.76	41.80±7.73
Chromium	ND	ND	ND	ND
Cobalt	ND	ND	ND	ND
Copper	0.02-0.06	0.05±0.01	0.02-0.09	0.07±0.02
Iron	4.83-28.04	19.05±8.79	11.41-22.90	19.71±2.38
Lead	ND	ND	0-0.13	0.04±0.02
Magnesium	0.38-2.01	1.48±0.65	3.86-5.36	4.87±0.36
Manganese	0.03-0.18	0.12±0.06	1.67-2.84	2.49±0.26
Mercury*	0.028-0.381	0.127±0.147	0.12-1.73	0.40±0.46
Nickel	ND	ND	0.05-0.11	0.07±0.01
Potassium	0.67-2.15	1.45±0.58	2.37-2.79	2.53±0.11
Silver	ND	ND	ND	ND
Sodium	ND	ND	0.33-0.45	0.41±0.11
Strontium	0.01-0.03	0.02±0.01	0.02-0.05	0.04±0.01
Zinc	0.06-0.09	0.06±0.03	0.05-0.28	0.17±0.06

⁺ number of samples analyzed: top soil = 5, mill tailings = 22

* Unit: µg g⁻¹ of tailing

ND: not detected

3.3 Batch Desorption Experiments

Several buffer solutions were initially tested to select the most suitable solution for the experiments. The optimal buffers for pH 4, 7, and 10 were 0.14 M of NaAc (Sodium acetate 3-hydrate (CH_3COONa), $\text{pK} = 4.76$, M.Wt. = $136.08 \text{ g mol}^{-1}$), 0.124 M of PIPES (Piperazine-1,4-bis(2-ethanesulfonic acid) ($\text{C}_8\text{H}_{18}\text{N}_2\text{O}_6\text{S}_2$), $\text{pK}_2 = 6.80$, M.Wt. = $302.36 \text{ g mol}^{-1}$), and 0.0075 M of CAPs (3-(Cyclohexylamino)propan-1-sulfonic acid ($\text{C}_6\text{H}_{11}\text{NH}(\text{CH}_2)_3\text{SO}_3\text{H}$), $\text{pK}_1 = 10.40$, M.Wt. = $221.32 \text{ g mol}^{-1}$), respectively.

Desorption of Mn from the tailings under each condition is presented in Figure 3.2 while desorption of Pb, Zn, and Ni at pH 4 are presented in Figure 3.3. The results show that for pH 4, the tailings leached out higher amounts of heavy metals (Mn, Pb, and Zn) than for pH 7 and 10. For example, the total amount leached at steady state conditions, for pH 4, 7 and 10 were 1.20 , 0.38 , and 0.03 mg g^{-1} of Mn, respectively. The amount of Pb desorbed for pH 4 (0.10 mg g^{-1} of tailing) was more than for pH 7 and 10 (not detected). Moreover, at pH 4, the results show that the amounts of Mn leached were much higher than Pb and Zn. In other words, Mn was more easily leached than Pb and Zn. For the three pH conditions, pH 4, 7, and 10, the desorption of Mn reached steady state conditions after 48, 24, less than 24 hours, respectively. The leaching of Pb persisted longer up to 312 hours to reach the local steady state condition at pH 4. This could be due to the lower solubility of the lead species as compared to the other metal species (Sparks, 1995).

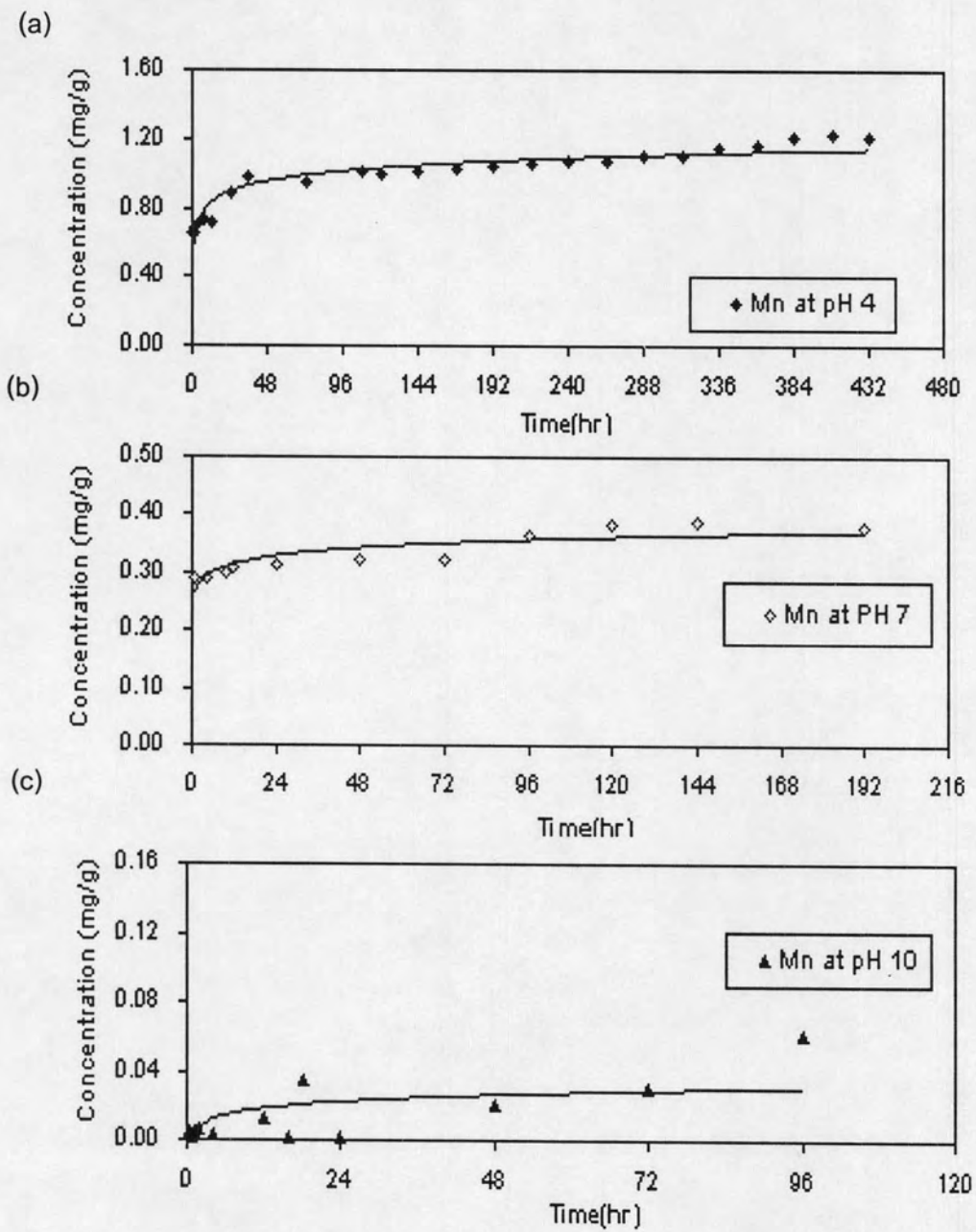


Figure 3.2 Amounts of Mn desorbed from tailings under different pH conditions
 (a) pH = 4 , (b) pH = 7 , (c) pH = 10

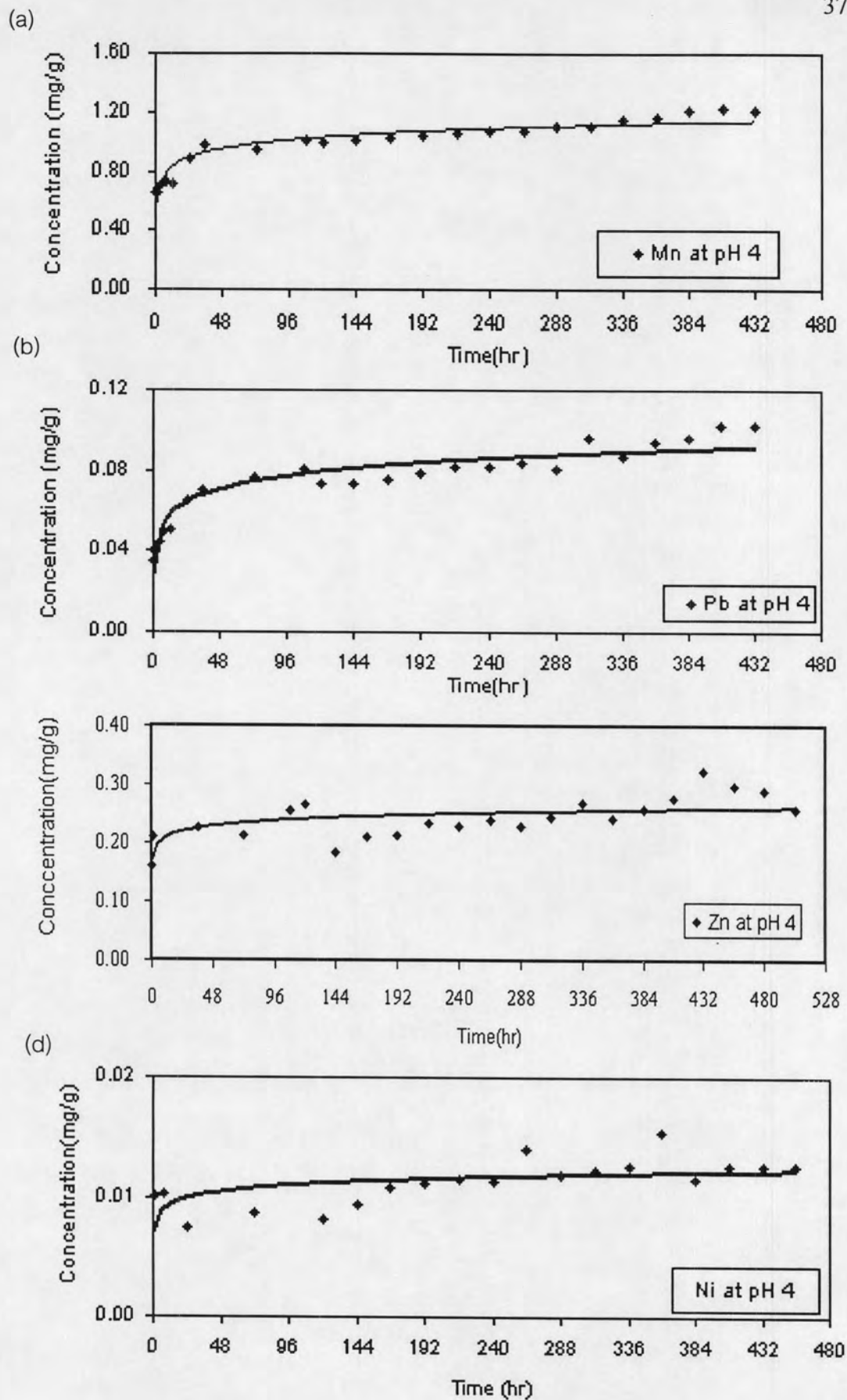


Figure 3.3 Amounts of Mn, Pb, Zn, and Ni desorbed from tailings under pH 4 conditions

From Figures 3.2 and 3.3, it is obvious that the leaching of heavy metals from tailings was pH dependent with heavy metals desorbing more under acidic conditions.

3.4 Column Desorption Experiments

The column desorption setup consisted of a reservoir, a peristaltic pump, a column, and sample collection (Figure 3.4). The column desorption experiments were conducted using an aqueous solution of 0.01 mol L^{-1} of NaNO_3 at pH 4 and 7. An acrylic column with a 2.5 cm inner diameter and 20 cm length was uniformly packed with 110 grams of air-dried tailings with a pore volume of 40 mL.

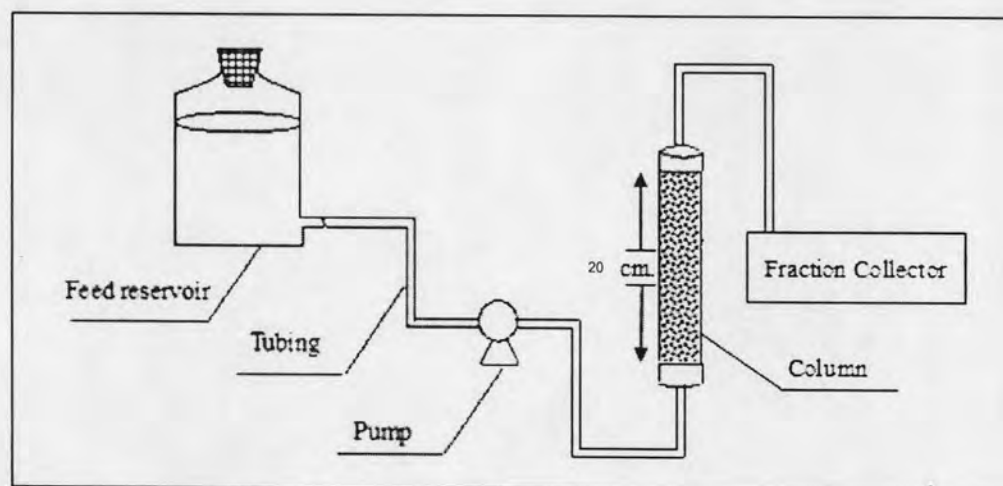
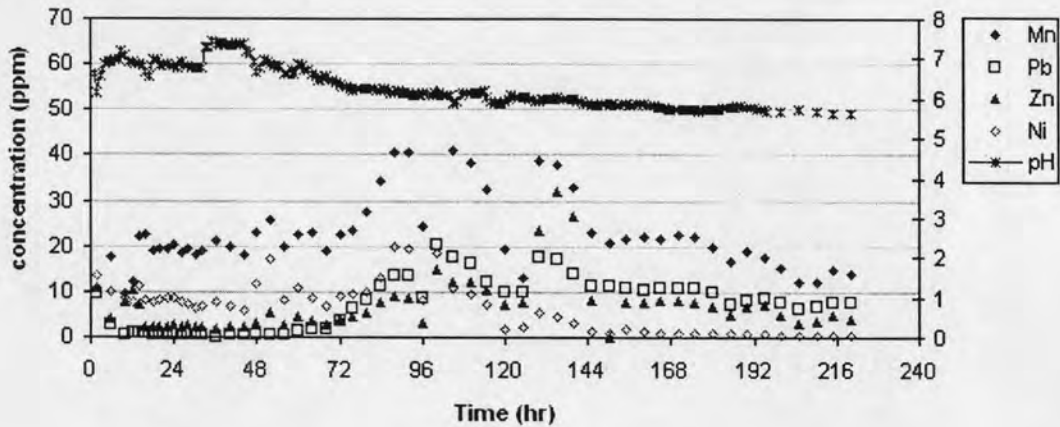


Figure 3.4 Desorption column experiment setup

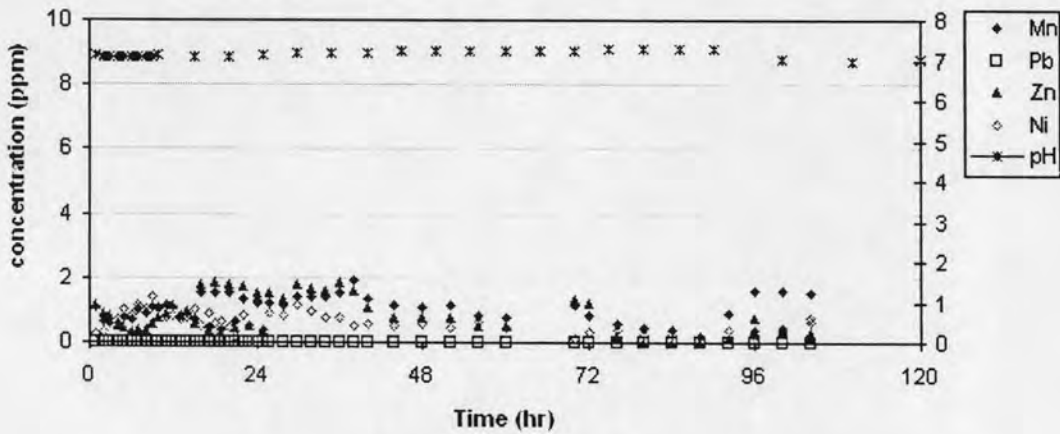
The column was kept under saturated flow conditions with flow entering at the bottom and exiting at the top. The flow in each column was 0.4 mL min^{-1} provided by a peristaltic pump. A fractional collector was used to collect the leachate from the column every hour. Ten mL of the sample was analyzed for metals using ICP-OES.

The column experiment results (Figure 3.5 a) showed that Mn^{2+} , Ni^{2+} , Zn^{2+} , and Pb^{2+} were leached at relatively high concentrations exceeding the Thailand Industrial Effluent Standards (Ministry of Industry 1996), especially under acidic

condition. These results were in accordance with the batch desorption experiment results, in which the desorption of heavy metals from tailings collected from the



(a) Acidic pH condition



(b) Neutral pH condition

Figure 3.5 Metal leaching from the column under various pH conditions

Akara mining area was pH dependent. The results as presented in Figure 3.5 showed that greater amounts of heavy metals desorbed from the tailings under acidic condition than under neutral condition. For example, the maximum concentration for Pb was 18 mg L^{-1} under acidic condition which was higher than neutral condition ($\sim 0.8 \text{ mg L}^{-1}$) and higher than the industrial effluent standard (0.2 mg L^{-1}). Even for Zn, Ni and Mn, desorption from tailings under acidic condition was higher than the industrial effluent standards (5 mg L^{-1} for Zn, 1 mg L^{-1} for Ni, and 5 mg L^{-1} for Mn). Figure 3.6 showed that the amount of released metals from the tailings was in the following order: $\text{Mn} > \text{Ni} > \text{Zn} \sim \text{Pb}$. For Zn, Ni, and Pb their cumulative mass curves (Figure 3.6) show that the curves reached a ‘plateau’ after 144 hours. The leaching behavior of Zn was quite similar to Pb. Mn and Ni became mobile at the beginning of the

experiment, when the pH of the pore water was about 7. Pb and Zn became mobile when the pH decreased to 5.7 or less.

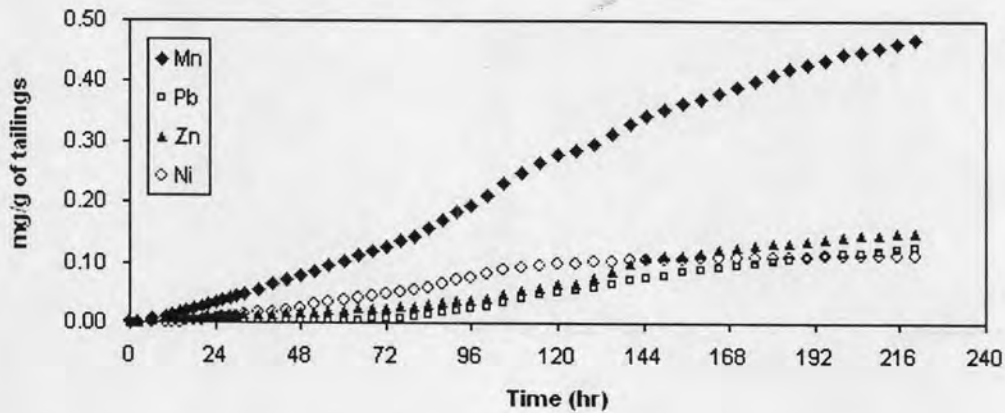


Figure 3.6 Cumulative amounts of Mn, Pb, Zn, and Ni versus time under the acidic condition

3.5 Discussion and Conclusions

In several potential ore zones, substantial amounts of pyrite (FeS_2) are present which when exposed to oxygen and water may generate acidic water by oxidation reaction (Brady and Hornberger, 1990; EPA, 1993) leading to acidic mine conditions which will result in the release of heavy metals. Once the release occurs, water containing heavy metals can migrate downward, and eventually contaminate the groundwater. The concentrations of Mn, Fe and SO_4^{2-} found at the underdrained (UD) and the seepage (SP) wells over a two-year period were higher than those found at the downstream ambient monitoring wells (see Figure 3.7 a-c). The monitoring wells are divided according to the groundwater depth: shallow and deep. Shallow groundwater wells (10 m depth) included wells no. 684, 698, 686, and 699; deep groundwater wells consisted of wells no. 685, 595, 687 and 663 as shown in Figure 3.1.

There is clear evident that the Mn, Fe, and SO_4^{2-} concentrations exceeded the industrial effluent standards (5 mg L^{-1} for Mn) and groundwater standards for drinking purposes (PCD, 2004b) (0.5 mg L^{-1} and 250 mg L^{-1} for Fe and SO_4^{2-} , respectively). These results support the occurrence of oxidation of sulfide (SO_4^{2-}) minerals in the TSF (Macro et al., 2002; Aswatharayana, 2003).

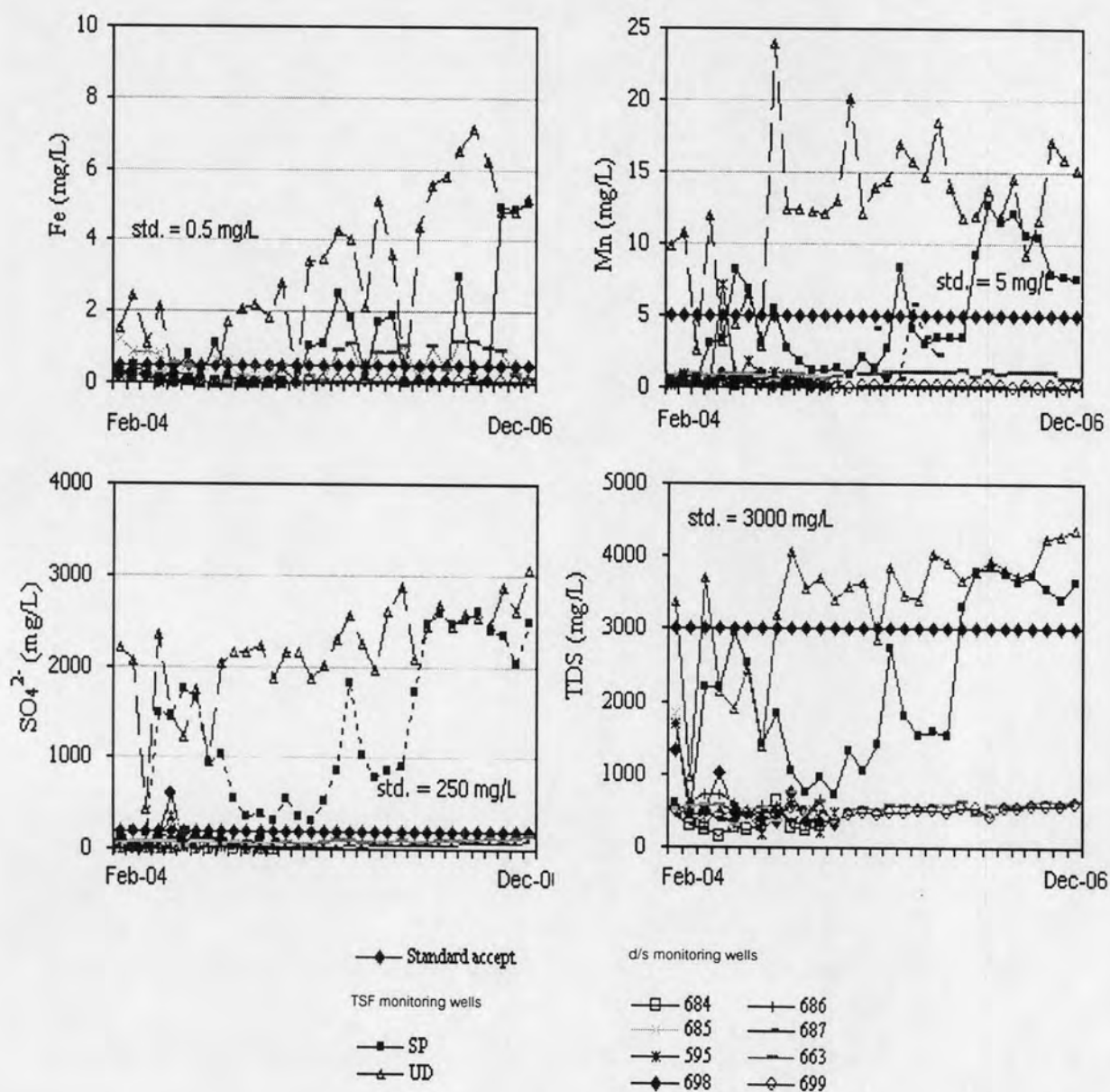


Figure 3.7 Monthly groundwater quality (Fe, Mn, SO₄²⁻, and TDS) of TSF and downstream (d/s) monitoring wells from February 2004 to December 2006

Furthermore, as shown in Figure 3.7 d, the concentrations of total dissolved solids⁴² (TDS) found at the UD and the SP wells were at the levels of 3,000-4,000 mg L⁻¹, which were higher than the TDS concentrations found at the ambient monitor wells. The increased TDS concentrations in the groundwater might have been generated from the oxidation of sulfide in the TSF (Macro et al., 2002).

Metal analysis according to EPA Method 3051 was employed to estimate the amounts of metals in the collected tailings from the TSF in the Akara mining area. The results showed that most of the metals found in the tailings did not exceed the Soil Standards for Habitat and Agriculture (PCD, 2004a); Mn was the exception. These results are in accordance with the high amounts of Fe and Mn in leachates from the tailings in UD and SP wells as shown in Figure 3.7 a and b.

The batch desorption experiments results shown in Figures 3.2 and 3.3 are crucial in the investigation of the leaching behavior of potentially toxic metals from TSF. The results in Figure 3.2 showed that for pH less than neutral (at about pH 5 – 6) a significant leaching of metals occurred, indicating that under acid mine drainage, mobility of metals increased.

From Figure 3.3, Mn is more easily leached than Pb and Zn. This agrees with results from UD and SP wells (Figure 3.7) that Mn was released more than other metals. Again, from Figure 3.3, it may be concluded that the desorption behavior from tailings depended on the metal species which might resulted from the difference in the solubility of each metal.

The results of the column experiments indicated that some of potentially toxic metals (i.e., Mn, Ni, Zn, and Pb) that leached from the tailing column exceeded the Industrial Effluent Standards (Ministry of Industry, 1996), especially those metals leached under acidic condition. As for the mobility of metals released from tailings, their mobility could be described in the following order: Mn > Ni > Zn ~ Pb. This observation might be described by the competition between metals and protons in the aqueous solution and characteristics of solubility of each metal at different pH conditions.

These findings support batch desorption experiments that the desorption behavior from tailings depended on pH and metal species. These results were also in agreement with the order reported by Dubrovsky (1986) on the Nordic Main tailings impoundment near Elliot Lake, Ontario, where metal mobility was $\text{Co} \sim \text{Ni} > \text{Zn} > \text{Pb} > \text{Cu}$. Moreover, Jurjovec et al. (2001) conducted a tailings column experiment and found that metal concentrations in the effluent water were controlled by pH. The metals in their experiment could be divided into three groups on the basis of their mobility. Zn, Ni, and Co became mobile at pH 5.7, and Cr, V, Pb, and Cd became mobile at pH 4.0. Cu concentrations remained unaffected by pH changes.

Interestingly, the amount of Fe was approximately eight times higher than Mn (shown in Table 3.1) in the tailings, but the amount of Fe leached was lower than Mn, at both the acidic and neutral conditions (the concentrations of Fe were not shown in the Figures 3.5 and 3.6). These results support the observed data at the UD well (Figure 3.7), where more Mn leached from tailings than Fe. Thus, understanding the leachability of each metal could provide reliable evaluation of the transport of metals in the groundwater and the extent of environmental contamination from mine tailings.

The results of this research highlight the need for necessary attention by responsible parties as metal leaching problems especially the high Pb concentration may arise after the mine's closure. In addition, in order to reduce the release of these potentially toxic metals into the environment, methods for reclaiming mining sites must be implemented. Even though some methods for the reclamation of a mining site, such as revegetation approach can reduce soil erosion and restrict leaching to groundwater (Burckhard et al., 1995), they can lead to other problems such as release of organic acids by plant roots and microbes in the rhizosphere which may combine with metals to form water soluble complexes or colloids (Burchhard et al. 1995; Ouyang et al. 1996) resulting in enhanced solubility and transport of these metals

This study illustrates the possibility of environmental contamination from the mining site, particularly after the mine's closure, as the metals in the tailings may be leached for decades or even centuries after a mine's closure (Gunsunger et al., 2006; Moncur et al., 2004; Pyatt and Grant, 2001). Groundwater monitoring wells should be carefully installed to monitor and evaluate the contaminated elements released from

mining activities, even after the mine site has been closed. Proper preventive efforts⁴⁴
should be considered and implemented to prevent future possible contamination.