TREATMENT OF ARSENIC-CONTAMINATED LAND IN THAILAND USING DIATOMITE: PRELIMINARY FIELD SITE INVESTIGATIONS

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SUMMARY

Mining-related contamination of land and water by potentially toxic elements is a recognized problem in many parts of the world. Arsenic is one such element that is causing particular problems with regard to human and environmental health in some tin-mining areas in Thailand.

This project is designed to establish long-term field experiments to study the application of locally-available diatomite to As-contaminated land and wastes in a tropical context in areas of recognized arsenism and As-impacts on the environment.

This is a collaborative project between the Camborne School of Mines (CSM) (University of Exeter), the British Geological Survey (BGS) and the Department of Mineral Resources (DMR) of the Government of Thailand and is funded by the Overseas Development Administration’s (ODA) Technology Development and Research (TDR) programme and the DMR.

CSM has been investigating problems of land contamination and developing clean-up solutions for over a decade. In particular, the use of novel soil amendments to reduce the availability to the environment of potentially toxic elements (PTEs) in mining and processing wastes and contaminated land has been developed. Industrial minerals have formed the focus of this research which has included detailed laboratory experiments and the establishment of long-term field sites on metalliferous mine wastes in Cornwall, United Kingdom.

Diatomite has been shown to be one of the most promising potential industrial mineral amendments. It is a geological deposit formed from the siliceous remains of phytoplanktonic organisms (diatoms). Diatoms are common constituents of the marine and freshwater aquatic microflora. The mechanisms(s) of potentially toxic element sequestration are not fully understood. It is intended that this project will broach this area.

The first stage of this project is to identify As-contaminated sites in Thailand that are suitable for the establishment of long-term field plots involving the application of locally-available diatomite to As-contaminated land. This report describes work involved in identifying suitable sites for the establishment of field trials.

Samples of mining and processing wastes and waters in their vicinity were collected from three mining areas of known or suspected As-contamination in southern Thailand. The Ron Phibun District, Nakhon Si Thammarat Province has been the focus of much research into the causes of chronic arsenism recorded in the local population. The ODA has funded several related projects run by the BGS. These have focussed on identifying the source of the As-contamination causing the health problems in Ron Phibun District. The second area investigated was To Mo gold-Mine in Narathiwat Province on the border with Malaysia. It was known that the arsenopyrite is associated with the gold-bearing ore so a potential As-pollution problem around this mine was suspected. The Tham Thalu Subdistrict of Yala Province was the third area investigated. This area contains many lead and tin-mines which have been shown to be the main cause of potentially toxic element input into the Pattani River system. The cassiterite from these mines is closely associated with a wide variety of sulphide minerals. On exposure to the atmosphere these weather to produce acid rock drainage (ARD) containing elevated concentrations of PTEs (often including As). The pH, conductivity and oxidation - reduction potential (ORP) of the water samples were recorded as soon as possible after collection. These samples were then analysed in the laboratory by ICP-AES to determine the concentrations of Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn. The waste samples were first analysed for their As concentrations after aqua regia digestion to identify those samples containing less than 1000 µg As g⁻¹ which were then excluded from further analyses.
Those samples containing above this concentration were analysed for pH, conductivity and sequential analysis for the above elements. Selected samples were examined by X-ray diffractometry (XRD) and scanning electron microscopy (SEM) techniques. The two samples containing the highest As concentrations from the Ron Phibun and Na Sua-Tham Thalu sites were subjected to froth flotation and analysed further by XRD and SEM.

Results from XRD, SEM and sequential extraction analyses showed that the chemical characteristics of the sites differed considerably with respect to the chemistry of As (and other PTEs). The two mine sites at Ron Phibun contained elevated As concentrations, despite the removal of the high grade wastes from one site. Cd and Zn were also present at highly elevated concentrations (up to 179 and 2074 μg g⁻¹ respectively). Arsenic was present mainly as weathered arsenopyrite grains exhibiting scorodite rims and was of generally low availability. The To Mo Mine wastes consisted primarily of high purity silica sand. They contained less than 1000 μg As g⁻¹. These wastes showed a low potential for impinging on environmental and human health. The Na Sua and Tham Thalu mine wastes showed typical ARD characteristics of acidic pH values and high concentrations of Fe and PTEs. For example, the As concentration varied widely between 2946 and 14715 μg g⁻¹. The wastes were dominated by pyrrhotite, although one waste pile at Na Sua Mine was enriched in secondary cerussite and anglesite. The waste dumps showed evidence of surficial weathering with a large content of secondary minerals such as gypsum, jarosite and goethite. Both arsenopyrite and pyrite were found in these wastes. The water soluble As concentrations were generally higher in these wastes than for either the Ron Phibun or To Mo wastes. Mine wastes from this area have been implicated by other investigators as a source of contamination of local soils and surface waters although the effects on groundwaters were negligible.

Sites were chosen, subject to DMR approval, on the basis of two criteria, namely the total concentration of As in the substrates and the relative availability of the As in the waste. It would be beneficial to initiate two sets of field trials, one in the Ron Phibun area and one in the Tham Thalu Subdistrict as both these areas differed in their chemical and mineralogical properties with respect to As.

Future work concerned with the development of this project will revolve around three main areas:

- Establishment of long term field trials to investigate the use of diatomite in ameliorating As-contaminated land in a tropical scenario
- Establishment of column leach experiments in the UK and Thailand to investigate the effects of different waste types, diatomite types and waste - diatomite combination ratios
- Defining the precise mechanism(s) of As uptake by diatomite
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1. INTRODUCTION

1.1 Background to the project

Problems of mining-related land and water contamination have existed ever since man first mined and processed metal ores. The present state of such problems on a global scale has led to increased awareness of threats to environmental and human health which are occurring in certain parts of the world.

Camborne School of Mines (CSM), University of Exeter has been at the forefront of research into reducing the environmental impact of mining and beneficiation wastes for over a decade. The main thrust of this research has been in the novel field of applying industrial minerals to contaminated land in and around derelict metal mine sites in order to reduce the availability of inorganic contaminants. A variety of industrial minerals are potentially useful for this purpose (e.g. Mitchell, 1991; Gworek, 1992a,b) and diatomite has been identified as one of the most promising (Atkinson et al., 1990; Mitchell & Atkinson, 1991; Abrutat et al. 1994; Whitbread-Abrutat, 1995).

Diatomite (also known as diatomaceous earth and kieselguhr) is a naturally occurring form of biogenic silica produced by phytoplanktonic organisms. It occurs as economically viable geological deposits in many parts of the world and is used as an industrial mineral, primarily as a filter aid in beer and wine processing and for clarifying edible oils. To a lesser extent it is also used as fillers in paper, paint and plastics, as an absorbent and as an abrasive. Competition from other industrial minerals has caused a decline in the importance of diatomite in its traditional fields, but potential new markets are now developing, particularly in the biotechnology and hazardous waste treatment industries (Harries-Rees, 1994).

The mining and processing of metallic ores produces waste material that usually contains one or more potentially harmful elements at concentrations elevated above background. Arsenic is one such element commonly found in these situations. The tin mining and processing wastes around the village of Ron Phibun, Nakhon Si Thammarat Province, south Thailand are known to be enriched in As (e.g. Jariyawat & Piyawong, 1993; Fordyce et al., 1995; Williams et al., 1996). This, coupled with the documented As-related health problems of the Ron Phibun area and the existence of locally available diatomite deposits in north Thailand, provide an opportunity for the development of a long term investigation into the field-scale application of diatomite on contaminated land in a tropical context. It is hoped that the results of this project will have a generic applicability to similar situations elsewhere.

The main objectives of this project are to:

- Identify a site or sites possessing As contamination for the establishment of long term field trials
- Establish field trials to investigate the long term effects of diatomite addition to As-contaminated land under tropical conditions
Investigate and identify the mechanism(s) involved in the As-diatomite interaction

Undertake technology transfer with the DMR, Government of Thailand

1.2 Geochemistry of arsenic

Arsenopyrite (FeAsS) is a common accessory mineral in sulphidic ore bodies and is often associated with Ag, Au, W and base metal ores. Other less common As-containing minerals are also found in such situations, namely enargite (Cu₃AsS₄) and gersdorffite (NiAsS) and sometimes arsenides of Co and Fe. Pyrite (FeS₂) also contains appreciable quantities of As (up to 0.5% in some situations (Fordyce et al., 1995)). Sulphide minerals containing As are usually discarded during processing and smelting operations often leading to environmental problems owing to the high potential toxicity of arsenic.

Arsenopyrite (the most common As sulphide mineral) weathers under oxidizing conditions, the most common alteration product being the hydrous arsenate scorodite (FeAsO₄·2H₂O). Scorodite is generally found as a surface coating on other minerals or as very small discrete particles in the soil. The main influences on As availability are pH, Eh and the Fe content, as Fe and Al arsenates dominate in acid soils while the more soluble Ca₃(AsO₄)₂ prevails in calcareous soils.

In typical uncontaminated soils, the natural background As concentration is usually around 10 μg g⁻¹. This figure varies widely with the parent rock type and the presence of any underlying mineralization (Bhumbla & Keefer, 1994). Allen (1989) reported As concentrations in normal, uncontaminated soils as <0.5 - 30 μg g⁻¹.

Other mining sites that have caused, are causing, or have potential to cause, environmental problems in Thailand were also investigated by the authors. These included To Mo gold mine in Narathiwat Province and two mines in the Ban Tham Thalu subdistrict of Yala Province. Both of these areas are situated in south Thailand near the border with Malaysia.

This report describes fieldwork and the subsequent laboratory analytical work undertaken on waters and mining and mineral-processing waste samples collected during August 1996. The rationale was to identify sites suitable for the establishment of field trials to investigate the long term effects of applying diatomite (as a soil amendment) to As-contaminated substrates in a tropical (high rate of weathering) context. This is a collaborative project between CSM, the British Geological Survey (BGS) and the Department of Mineral Resources (DMR) of the Government of Thailand and is funded by the Overseas Development Administration’s (ODA) Technology Development and Research (TDR) programme and the DMR.

Site suitability was assessed using the following principle criteria:

- As content of the waste
- As availability of the waste
The first step in this process was a review of the available literature (most of the available source literature is in Thai). All of the solid field samples underwent a chemical analysis for total As to ascertain which samples contained most As. This screening process allowed resources to be concentrated on the samples from the sites of most concern. More detailed investigations were then made into As-related geochemical and mineralogical properties of the samples of particular interest. Water samples were collected to determine the impact of mining and processing wastes in the vicinity of nearby water bodies and to ascertain the As concentrations in waters standing on mining and processing wastes.

1.3 Overview of field sites visited

The sites visited in chronological order were: Ron Phibun District, Nakhon Si Thammarat Province; To Mo mine, Narathiwat Province; and Na Sua and Tam Talu mines, Yala Province.

1.3.1 Ron Phibun

Background

The district of Ron Phibun is situated approximately 800 km south of Bangkok in peninsular Thailand (figure 1.1). The relevant geography, geology and mining history of this area is described in Paijitprapapon and Ramnarong (1994), Fordyce et al. (1995) and Williams et al. (1996) and is summarized here.

In the late 1980s, the Ministry of Public Health of the Government of Thailand ran an epidemiological investigation into arsenic-related health problems associated with Ron Phibun District. Such problems included skin melanomas and carcinomas and at least one death. Elevated concentrations of As in the fingernails and hair of up to 80% of young people of school age were also recorded (Paijitprapapon & Ramnarong, 1994). Arsenic-contaminated well-water from a shallow aquifer was implicated as the primary cause of the high As load on the local populace, although possible alternative sources of As exposure were recognised such as dust inhalation and ingestion of contaminated food stuffs. Follow-up studies in 1992 and 1994 showed that the situation had not improved despite public education and the provision of rain water collection pots.

Two geochemical survey projects have been undertaken by the BGS and the DMR under the ODA’s TDR Programme (ODA/TDR). The first project (under BGS-ODA/TDR contract R5553) is described by Fordyce et al. (1995) and Williams et al. (1996). They carried out preliminary investigations to establish the main source of As contamination in groundwater and to determine the role of As-rich beneficiation wastes in processing plants in and around Ron Phibun town, and on mine sites situated in the Ron Na-Suang Chan mountains to the west of Ron Phibun (figure 1.2). The second investigation (BGS-ODA/TDR contract R6491) is currently underway. Its main aims are to determine the role of disseminated arsenopyrite in the
Figure 1.1: Geographical location of major towns in south Thailand and the mine sites visited.
Quaternary floodplain deposits as a source of As contamination in the groundwater and to formulate an appropriate risk mitigation strategy for implementation by the Thai authorities.

**Mining activities**

The local geology of the Ron Phibun area consists of lower Palaeozoic sedimentary strata intruded by Triassic granites which form the backbone of peninsular Thailand. Much of the eastern plain between the Ron Na-Suang Chan mountain range and the sea is overlain by Quaternary colluvial and alluvial deposits.

![Sketch map of the Ron Phibun area showing abandoned mine sites, including those visited. Note that not all the mine sites, roads and rivers are shown.](image)

Primary and placer cassiterite and wolframite deposits have been worked in this area for almost a century. Abundant pyrite and arsenopyrite are associated with these minerals. The main ore minerals occur in E-W veins typically extending for 10-40 m, averaging 10-20 m deep and 3-35 cm wide. Mining was usually by adits following the veins and by shallow shafts sunk from the surface to intersect the veins (Fordyce et al., 1995). Hard-rock mining occurred in the hills to the east of Ron Phibun village. This has now ceased owing to the collapse of the world tin price in the 1980s.
On the colluival plain NE of Ron Phibun, alluvial Sn deposits were exploited by dredging and open pit operations. Now all but one these operations have ceased. This has left a legacy of large ponds that are naturally revegetating.

There are two derelict mineral-processing plants in the area. One is located in the centre of Ron Phibun village and the other at the base of the Ron Na-Suang Chan mountains. The former contains piles of fine-grained processing waste lying open to the atmosphere (plate 1.1). This site is to be cleared of high grade wastes imminently. The latter site has been levelled and cleared.

![Plate 1.1: Interior of Ron Phibun processing plant](image)

Mineral-processing activities produced As rich waste piles at the mines on the steep mountain slopes. In the past year (1995-6), most of the most highly contaminated waste piles have been removed by villagers paid to transport the waste (in sacks) down a specially-driven track to the foot of the mountain. The bags of waste are presently stacked and covered with tarpaulins, with the intention of transporting to landfill (figure 1.2). To date, 1700 m$^3$ of the highest grade waste has been brought down the mountain, with a further 2000 m$^3$ still awaiting removal. This will restart in the next dry season (1997).

The mine sites have been graded, terraced and planted with trees. One undisturbed mine site was found. The site (known as Yip In Soi, plate 1.2) is situated on a very steep hillside directly adjacent to a tributary of the Hai Ron Na (figure 1.2). Some lithified processing waste was found and sampled for subsequent analysis, but the majority of the site appears to be composed of fist-sized rocks at angle of rest. The nature of the waste may make it difficult to apply diatomite during field trials.
Mining-related arsenic contamination in the Ron Phibun area

The main sources of mining-related As-contamination in the Ron Phibun area were identified (and tentatively prioritized) by the DMR (and reported in Williams et al., 1996) as being:

1. High grade arsenopyrite waste piles in bedrock mining localities
2. Sub-ore grade waste rock piles
3. Sulphide rich wastes from ore-dressing plants
4. Disseminated sulphide wastes from small-scale prospecting and flotation activities. This informal mining activity exacerbated the potential environmental hazard of any As-containing minerals present by using sulphuric acid in the flotation process. The resulting acidity increases As availability.
5. Alluvial tin workings

Jariyawat and Piyawong (1993) reported that the first two waste types occurred in five locations on the eastern flanks of the Ron Na-Suang Chan mountains above Ron Phibun (figure 1.2). The high grade waste piles contained 1-30% As and resulted from in situ flotation cells. The cumulative volume of this waste was estimated at approximately 2000 m$^3$. The associated waste rock piles primarily contain granite and gangue material often with 0.1-1% sulphide minerals.
Thirteen substrate samples were taken from the mines, processing plant and alluvium for the purposes of this investigation. See appendix 1 for more details.

1.3.2 To Mo Mine

Background

To Mo mine is a small lode-Au mining operation located in Narathiwat Province just inside the Thailand-Malaysia border (figure 1.1). The mine lies at the head of a narrow steep-sided valley. A brief introduction to the geography and mining history is provided by Fordyce and Williams (1994).

The mine was originally developed by a French company when the ore grade was about 2.5 g t\textsuperscript{-1}. The mine was reopened 8 years ago after 50 years of closure. During the war the area was bombed by the Japanese as the mining operations were run by an Allied power. An unexploded bomb was recently found adjacent to the mine. The cost of double-handling the tailings (see below) significantly increased production costs which required a higher ore-recovery to recoup costs. Present recovery rates are 7 g t\textsuperscript{-1}, in order to become economical this needs to be increased to 8-9 g t\textsuperscript{-1}. Consequently, the mine and plant are presently under maintenance only. Originally 80 people worked here with 50 working underground. There exists about 10 km of underground workings. There are 100,000 tonnes of proven reserves, however in order to be economically extracted, the grade requires working-up still further. To Mo is still the only gold mine in Thailand, although prospecting and exploration are currently underway in the north of the country around Chiang Mai.

The Au deposit is found in quartz veins. The most recently exploited vein varies in width from 15 cm to 2 m. The gold is associated with arsenopyrite, pyrite and stibnite. The deposit has a 5% Ag content and contains Ni (Fordyce & Williams, 1994).

Processing activities

The first step in ore-dressing is primary jaw crushing to 8 mm followed by screening. The +8 mm fraction is returned to the crusher. The -8 mm fraction is milled to -106 \(\mu\)m in a ball mill. Cyanide (-CN) is added at this stage. The pulp is then taken to a cyclone. The overflow is sent to settling tanks, the underflow returns to the mill. The tanks receive 50 % w/w solids. A retention time of 22 hours in the tanks produces a final grade of 7 g t\textsuperscript{-1} (most of the Au is liberated after 18 hours). A recovery of 96.4 % is typical. The process residue is gravity fed to a spiral. The overflow is used as a tailings thickener. Sodium hypochlorite is added to oxidize the cyanide. The cyanide is completely oxidized during the above residence time. Water is continually recycled during processing.

The tailings then enter the tailings impoundment. This is held by a hand-built, 12 m high reinforced concrete dam. The construction of this took approximately 4 months. Earlier this year, the tailings were planted with trees. During processing, the arsenopyrite causes few problems and passes directly into the tailings impoundment. Water quality is periodically monitored approximately 2 km downstream of the mine site (by road) by both the mine and
the DMR for CN and As. Results provided by the DMR show no significant downstream contamination by As, Cd, Cu, Mn, Pb or Zn.

The cyanidation removal process was installed after a torrential downpour caused flooding of the tailings dam 2 years ago resulting in CN related fish-kills downstream. Since this flooding episode, the tailings must be trucked approximately 5 km north-east of the mine to Ban Chum Thong for disposal in an HDPE-lined landfill (plate 1.3). Here the tailings is covered with 2-3 cm of soil which is rapidly eroding.

Plate 1.3: Ban Chum Thong tailings impoundment

Six solid samples and seven water samples were taken from the To Mo mine area for the purposes of this investigation. See appendix 1 for more details.

1.3.3 Tham Thalu Subdistrict

The Na Sua and Tham Thalu mines are located approximately 55 km southwest of Yala, in Yala Province, south Thailand (figure 1.1). There are many mines in this area draining into the Pattani River system which eventually reaches the sea at Pattani on the east coast of peninsular Thailand. Mining has occurred in Yala Province for 100 years. Most of the mining was centred on the mountainous area of the province. The area consists of narrow valleys surrounded by sheer limestone cliffs with many subsurface rivers. Fordyce and Williams (1994) provide a general summary of the geology of this area.

Impact of mining operations on the Pattani River system

The Pattani River system drains the central and eastern Thailand-Malaysia border area and enters the Gulf of Thailand at Pattani on the east coast of the peninsula (figure 1.1). One of the
headwater tributaries of this river drains the Tham Thalu Subdistrict. Many small abandoned Sn mines occur in this area. Much of the cassiterite was associated with sulphidic minerals including arsenopyrite. Several studies (in Thai) were provided by the DMR. They generally show an increase in metal concentrations in soils and river sediments downstream of the mined area, until the diluting effects of other tributaries ameliorate the situation further downstream.

Arrykul and Kooptarnon (1993) concluded that the main source of Pb pollution in the Pattani River system was the intensive Sn-mining operations in Amphoe Bannangsata (including the Tham Thalu Subdistrict). In March 1992, they sampled river waters and sediments from the tributary approximately 15 km downstream of Ban Tham Thalu before flowing into the main Pattani River. The sediments were shown to be enriched in Pb, As, Cd, Cu, Zn, Fe and Mn. The river water from this sampling station contained a low dissolved As concentration of 10.5 μg L⁻¹.

In July 1992, they collected sediment and water samples within 3 km downstream of Ban Tham Thalu and analysed them for As, Cd, Cu, Fe, Mn, Pb and Zn. Soils from the vicinity of Ban Tham Thalu were collected in October (1992) and suspended river solids from approximately 8 km downstream of Ban Tham Thalu were collected in November (1992). These samples were digested by aqua regia before analysis. Results are shown in Table 1.1.

Table 1.1: Chemical properties of the Ban Tham Thalu area (after Arrykul and Kooptarnon, 1993). River sediment and water samples were taken in July 1992, soil samples were taken in October 1993. The river sediment and water samples were taken from the same sampling station (approximately 3 km downstream of Ban Tham Thalu). Soils samples were collected from the vicinity of Ban Tham Thalu in October 1992. Suspended solids were collected from the river in November 1992, approximately 8 km downstream of Ban Tham Thalu.

<table>
<thead>
<tr>
<th>Element</th>
<th>Soil (μg g⁻¹)</th>
<th>Water (μg L⁻¹)</th>
<th>Sediment (μg g⁻¹)</th>
<th>Suspended solids (μg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>10.3</td>
<td>nd</td>
<td>2429</td>
<td>140</td>
</tr>
<tr>
<td>Cd</td>
<td>1.98</td>
<td>0.06</td>
<td>44.0</td>
<td>nd</td>
</tr>
<tr>
<td>Cu</td>
<td>34.5</td>
<td>0.06</td>
<td>674</td>
<td>88.1</td>
</tr>
<tr>
<td>Fe</td>
<td>991</td>
<td>1496</td>
<td>89980</td>
<td>17737</td>
</tr>
<tr>
<td>Mn</td>
<td>9.42</td>
<td>737</td>
<td>3402</td>
<td>1162</td>
</tr>
<tr>
<td>Pb</td>
<td>2.36</td>
<td>71.3</td>
<td>3788</td>
<td>426</td>
</tr>
<tr>
<td>Zn</td>
<td>33.6</td>
<td>190</td>
<td>2274</td>
<td>484</td>
</tr>
</tbody>
</table>

Soils in the vicinity of Ban Tham Thalu appear to be slightly elevated in Cd only, compared to normal uncontaminated soils (appendix 2), otherwise there is little noticeable mining-related soil contamination. The river water does possess elevated concentrations of Mn, Pb and Zn compared to uncontaminated freshwaters (appendix 2), but the concentrations are not considered to be a major problem.

The main route of contamination into the Pattani River system appears to be by river sediments and suspended solids. River sediment contained high concentrations of all the elements tested. Related to this, the suspended solids contained high concentrations of all elements apart from Cd. The lack of high concentrations of dissolved Cd and Cu reflects the
high pH of the river waters as they drain a region of limestone bedrock. This causes the precipitation of elements such as Cd, Cu and Fe. Other elements, e.g. Mn and Zn tend to be more soluble at such pHs. The solubility of As is controlled by several interacting factors, pH being just one.

To conclude, potentially toxic elements enter the Pattani River system by two routes according to the element in question. Manganese, Pb, Zn, and to some extent Fe, enter the system dissolved in the water column. All the elements, except Cd, appear to enter the system as solids suspended in the water column; but the river sediment is a much greater potential source of all these elements into the Pattani River. It should be borne in mind that the suspended solid and dissolved loads will vary considerably with the time of year.

1.3.4 Na Sua Mine

Suttakorn (1991) describes the mining geology of the Na Sua mine. What follows is a summarized limestone deposits (in the northwestern part). To the west lie skarn formations in which the cassiterite is found. Associated with the skarn are zoned sulphide mineral assemblages showing replacement by chalcopyrite, bornite, sphalerite, copper sulphate, galena, pyrite, arsenopyrite, silver, haematite, cassiterite and scheelite. The main sulphide mineral vein contains pyrrhotite, galena and sphalerite in a skarn formation. This shows a NW-SE orientation and also contains quartz, calcite, cassiterite and pyrrhotite. In 1972, a series of 24 boreholes covering 5000 m² were drilled in the area. From this survey, the estimated Pb, Zn, Sn and Ag reserves were calculated at 400,000 t. The deposit was shown to be 35-40 m deep, with granite and marble as a wider deposit.

The ore-body was exploited by open-pit mining (figure 1.3). Cassiterite was liberated from the sulphide vein by blasting. The ore-dressing was done on site by a process of crushing and gravity concentration. The enriched feed (containing high galena and pyrite concentrations) was further concentrated by froth flotation to produce a final concentrate of 70% cassiterite.

The site is currently abandoned and derelict. At the western end, the pit (showing the exposed ore-body) is now flooded. Southwest of the pit, on the slopes overlooking the site, processing equipment (crushers) overlook the main ore-dressing plant (figure 1.3). Adjacent to this is a small tailings impoundment from where the tailings were removed and placed by the river for dewatering. Running through the main drying area is a stream. This receives run-off directly from the drying piles. Immediately east of the drying piles the stream disappears underground into a limestone cavern exhibiting typical calcareous precipitation formations. Once dewatered, the tailings were transported to the eastern end of the site and dumped.

The major environmental impact of the site are the large dumps of lithified tailings dumped at the eastern end of the site (plate 1.4). These are barren and appear orange owing to extensive Fe oxide formation at the surface. Below the surface crust (about 3 cm) the waste appears black and highly sulphidic. There is no surface water course here as the river disappears underground before reaching this part of the site. AMD seepage is apparent from the base of the dumps.
Figure 1.3: Sketch map of Na Sua mine site showing sampling locations.
Plate 1.4: Plate of Na Sua mine site looking towards the flooded pit (hidden in background) showing the lead rich dump in the foreground (yellow).

Five solid mine waste and six water samples were taken from Na Sua for the purposes of this project (see appendix 1 for more details).

1.3.5 Tham Thalu Mine

Tham Thalu mine was the biggest mine in the area and is adjacent to the village of Ban Tham Thalu. It was first operated before WWII. The mine and processing plant have been abandoned for over a decade.

The general geology and ore geology of this mine is very similar to the Na Sua mine situation described above. The cassiterite deposit occurs in a scarn zone at the contact between the limestone (which outcrops as a hill) and the granite which outcrops lower down. Cassiterite was deposited from hydrothermal fluids. The cassiterite is associated with cerussite (lead carbonate), magnetite (and other Fe oxides) and arsenopyrite.

The open-cast mine is situated on the south side of the valley 100 m upstream of the village of Ban Tham Thalu (figure 1.4). The village contains the (now derelict) processing plant where ore was crushed (by stamps) and milled before undergoing washing and flotation. Monthly production of concentrate was in the range 18,000-24,000 kg, although this was of a low grade (25 %). The concentrate also contained 37 % of cerussite. During smelting, this ore mixture produced a Pb-Sn alloy.
Figure 1.4: Sketch map of Tham Thalu mine and processing area showing sampling locations

- **From Na Sua**
  - Waste dump
  - Sample location
  - Village

- Processing plant
  - TTS7

- Flotation waste impoundment
  - TTW7
  - TTS6
  - TTW8

- Ban Tham Thalu
  - TTS8
  - TTW9
The present state of the processing plant raises some cause for concern. Piles of weathered ore material and processing wastes lie openly exposed to human disturbance. The main valley river cuts through the processing plant and the village. There are substantial quantities of tailings and other wastes that have been deposited immediately adjacent to the river.

Plate 1.5: The Tham Thalu processing plant showing the opencast mine (background), derelict plant buildings (middle ground) and flotation waste impoundment (foreground).

Charoenchaisri (1996) monitored the input of potentially toxic elements to the environment surrounding the Sn and Pb mines in the Tham Thalu subdistrict. He found that the As and Pb concentrations in the well-waters of the area were very low and consequently unlikely to be causing any related health problems in the area. He analyzed the stream water before and after it passed the Tham Thalu processing plant. He showed that surface water As and Pb concentrations in the Tham Thalu subdistrict increases markedly to very high concentrations in the vicinity of the mine, processing plant and waste dumps. The highest As concentrations were found in August (1994) in the vicinity of the Ban Tham Thalu processing area. Elevated Pb concentrations were recorded immediately downstream of the mine, processing plant and
mine dumps. These high concentrations were reached despite the near neutral pH of the water as it drains limestone bedrock.
2. METHODS

2.1 Sampling techniques and sample preparation

2.1.1 Water samples

Surface waters were sampled at the To Mo mine sites and in the Ban Tham Thalu subdistrict. Both running stream waters and water standing on mine and processing wastes were sampled (see appendix 1 for further details). Waters were not sampled in the Ron Phibun district as the surface and subsurface waters of this area have been extensively surveyed by Dr. T. M. Williams of the BGS (see section 1.3.1).

Waters were collected by drawing into a 60 ml syringe that had previously been rinsed in the water to be sampled. This was then passed through a 45 μm cellulose nitrate membrane filter in a sealed filtration unit into a sterile 60 ml plastic bottle. The pH, conductivity and redox potential of the waters were recorded as soon as possible after collection, using a Whatman® pH μ-sensor, conductivity μ-sensor (corrected for temperature) and an ORP μ-sensor respectively. Sufficient ANALAR grade concentrated HCl was then added to produce a resulting 1% HCl solution in order to reduce microbial degradation and prevent ionic adsorption onto the container wall. Blanks of distilled water were treated and analysed in exactly the same way.

2.1.2 Mining and mineral-processing wastes

Approximately 500-750 g of bulk soil, mining and processing wastes were collected from selected sites for chemical analysis. At sites with a lithified crust, samples of the crust were taken and kept separate from the underlying tailings. Samples were stored in zip-lock polythene sample bags and transported inside polypropylene boxes. Two larger bulk samples were collected for column-leach experiment trials. These consisted of approximately 10 kg of flotation waste from the Ron Phibun ore-dressing plant and a similar quantity of waste rock-lithified processing waste from the Yip In Soi site. These samples were transported in four-nested aggregate sacks.

On arrival at CSM, the samples were immediately unpacked and dried at approximately 30 °C. The samples for analysis were dried for eight days and then sieved through a stainless sieve to extract the -2 mm fraction. This fraction was then riffled to produce approximately 20-30 g for grinding. This was ground in a tungsten carbide swing mill until a floury, non-gritty texture was achieved (d$_{50}$ ~10 μm)

2.2 Analytical techniques

The water samples were analysed by the Analytical Chemistry Section of the BGS for Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn by ICP-AES.
2.2.1 Preliminary screening to identify samples containing low As concentrations

A preliminary investigation was run on all the samples in order to identify those containing most As. The milled samples were digested by *aqua regia* and analyzed for As by atomic absorption spectrophotometry (AAS) using a Pye-Unicam SP9 Atomic Absorption Spectrophotometer coupled to a graphite furnace (see appendix 3 for the detailed methodology). This allowed the samples containing low As concentrations (i.e. <1000 μg g⁻¹) to be discarded and resources to be focussed towards fewer samples.

Once identified, the selected samples underwent further investigations, including X-ray fluorescence analysis (XRF), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), optical microscopy, pH and conductivity measurements and sequential analysis.

2.2.2 XRF Spectrometry

XRF scans were performed on samples RPS1, RPS3, RPS5, RPS6, RPS11, TMS3, TTS1, TTS1c, TTS7, TTS7c and TTS8 using a Philips PW1400 X-ray spectrometer. These samples were chosen from the range of those collected as they covered the total range of sample types collected from the field (appendix 1). This procedure identified the elements present in the samples and provided a semi-quantitative estimation of their concentrations. This allowed the intended analytical programme to be focussed towards a specific range of elements.

2.2.3 SEM

The element distribution of -2 mm grain size polished sample mounts was investigated subjectively under the SEM (using a Joel LSM-840 coupled to an Oxford Instruments (Link) Electron Dispersive Spectrophotometer). The primary purpose of this investigation was to identify the mineral phases of any As present in the sample. A secondary objective was to investigate the distribution of other potentially toxic elements in the sample. Reflected light microscopy was also utilised to this end in a limited capacity.

2.2.4 XRD

XRD analyses were conducted on ground samples to determine the main mineral phases (using a Siemens D-5000 X-ray Diffractometer). This technique has a minimum detection limit of around 5% so only the main mineral phases can be identified. Two samples containing the highest As concentrations (one from Yip In Soi mine and one from the Na Sua-Tham Thalu area) underwent froth flotation to separate the sulphides from the gangue and allow the identification of minerals that were otherwise masked by the more common minerals. See appendix 3 for the froth flotation methodology.

2.2.5 pH and conductivity

The methodology used for recording these properties is provided in appendix 3.

2.2.6 Sequential extraction analysis

Sequential analysis of soils involves subjecting a soil sample to progressively stronger chemical extractants and recovering the supernatant from each extraction step to quantify the
elements extracted. The rationale behind sequential extraction analysis of soils is based on Viets' (1962) concept of substances in soils existing in specific soil phases. These phases relate to the attraction of the substance for a particular soil component. He identified five main phases:

- Water soluble
- Exchangeable
- Sorbed and organically bound
- Bound and occluded in oxide and secondary clay minerals
- Residual (existing in the primary mineral lattices)

These phases can be further divided or amalgamated during the course of a soil investigation depending on the properties of the substrate and the nature of the investigation.

A literature review of many sequential extraction procedures was undertaken. Virtually all of these were concerned with the relative availabilities of cations and relatively little work appears to have been done in this field on anions (the predominant form of As in most soils and mine wastes). Waller (1995) undertook a sequential extraction for As on Cornish mine rock wastes and soils using extractants based on the work of Woolson et al. (1971, 1973). This method investigated the compartmentation of As between Al oxide-hydroxyides and Fe oxide-hydroxides and Ca carbonates. Fordyce et al. (1994) used a different method. They differentiated between the humic and fulvic organic fractions and Fe and Al oxide-hydroxides.

The purpose of the present investigation is to define how strongly As is held in the wastes. The fractions extracted in this investigation and the corresponding chemical extractants are shown in Table 2.1. The full experimental methodology is provided in appendix 3.

Table 2.1: Chemical extractants and the corresponding soil fractions extracted in this investigation.

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Fraction extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled water</td>
<td>Water soluble</td>
</tr>
<tr>
<td>Ammonium acetate</td>
<td>Exchangeable</td>
</tr>
<tr>
<td>Sodium pyrophosphate</td>
<td>Adsorbed and organically bound</td>
</tr>
<tr>
<td>Sodium hypochlorite</td>
<td>Sulphides</td>
</tr>
<tr>
<td>Hydroxylamine hydrochloride</td>
<td>Iron and manganese oxides</td>
</tr>
<tr>
<td>Aqua regia</td>
<td>Residual</td>
</tr>
</tbody>
</table>

The sulphide fraction has been separately extracted for the purposes of this investigation. It was decided not to separate the sorbed and organically bound fraction into its mineral and organic constituents separately as the organic content of all the waste samples was very low.

Sequential extractants are rarely, if ever, specific to a particular soil fraction as extractants usually overlap and attack a proportion of other phases. This effect can be minimized (but not eliminated) by careful selection of extractants and by optimizing the experimental parameters.
such as extractant time, temperature, substrate particle size and light conditions (with certain extractants).

Four blanks were run during the course of the sequential extraction analysis and two waste samples (TTS7 and TTS7c) were each replicated four times to allow calculation of statistical variation. Elements were quantified by AAS (except for K which required the use of FES).
3. RESULTS

Brief descriptions of all water and solid samples collected during the fieldwork are provided in appendix 1.

3.1 Surface water chemistry

Surface waters were collected from the To Mo and Tham Thalu areas only (as previously mentioned). Water element concentrations have been compared to typical values found in uncontaminated freshwaters in nature (appendix 2).

3.1.1 To Mo Mine

All water samples relating to the To Mo Mine site are relatively benign with respect to pH, conductivity and ORP (table 3.1). The waters draining from the mine entrance (TMW5) and approximately 2 km downstream of the mine (TMW6, 7) do not show any unusual features relating to the element concentrations measured. The samples taken from standing water on the two tailings dumps (TMW1-4) did, however, contain very high As concentrations. The K concentrations of all the To Mo water samples were high.

3.1.2 Na Sua Mine

The two samples of running water taken from Na Sua Mine around the tailings drying pile (TTW3, stream flowing through the drying pile; TTW4, immediately upstream of the drying pile) appear to be well-buffered against the acidifying effects of AMD. This buffering effect is presumably caused by high bicarbonate concentrations as the rivers flow over and through a limestone bedrock. Samples TTW3 and TTW4 show near neutral pH and near normal (for typical river waters) conductivity and ORP values (table 3.1), despite the immediate proximity of the drying piles, although TTW4 does exhibit a higher pH and a lower conductivity and ORP than TTW3. The stream flowing through the Na Sua site disappears underground (figure 1.3) re-emerging a few hundred metres further downstream and upstream of the Tham Thalu Mine. This stream was sampled approximately 1 km downstream of the Na Sua Mine site (TTW6). Again, the water appears well-buffered, although the pH and conductivity are noticeably higher than the running water samples. Aqueous concentrations of Ca and K are also higher. This is explained by the actions of a nearby marble quarry as exemplified by the highly turbid water.

The element concentrations of these water samples were normal compared to uncontaminated freshwaters (appendix 2) except for higher than expected K concentration for both and higher Fe, Mn and Zn concentrations for TTW3, reflecting the correspondingly higher conductivity. These elements presumably derive from the adjacent drying pile.
Table 3.1: Physico-chemical properties of water samples collected from the To Mo and Tham Thalu areas. Element concentrations were determined by ICP-AES and are expressed in mg l⁻¹. See appendix 1 for details of the sample type.

| Sample  | pH | Cond (μS cm⁻¹) | ORP (mV) | Al (mg l⁻¹) | As (μg l⁻¹) | Ca (mg l⁻¹) | Cd (μg l⁻¹) | Cu (μg l⁻¹) | Fe (μg l⁻¹) | K (mg l⁻¹) | Mg (mg l⁻¹) | Mn (μg l⁻¹) | Ni (μg l⁻¹) | Pb (μg l⁻¹) | Zn (μg l⁻¹) |
|---------|----|---------------|----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| TMW1    | 6.9| 150           | 114      | 0.87        | 2.18        | 20.8        | nd          | nd          | 1.3         | 2.96        | 0.74        | 0.063       | nd          | nd          | 0.043       |
| TMW2    | 7.4| 190           | 80       | 0.08        | 2.13        | 21.2        | nd          | nd          | 0.08        | 3.55        | 0.5         | 0.028       | nd          | nd          | 0.040       |
| TMW3    | 6.3| 480           | 78       | 0.08        | 2.32        | 44.1        | nd          | nd          | 0.1         | 6.99        | 1.95        | 0.087       | nd          | nd          | 0.024       |
| TMW4    | 8.4| 350           | 79       | 0.07        | 2.23        | 43.5        | nd          | nd          | 0.1         | 6.12        | 1.94        | 0.086       | nd          | nd          | 0.043       |
| TMW5    | 7.8| 250           | 92       | 0.02        | nd          | 39.0        | nd          | nd          | 0.07        | 1.95        | 4.77        | 0.039       | nd          | nd          | 0.043       |
| TMW6    | 7.3| 200           | 114      | nd          | 13.9        | nd          | 0.22        | 1.71        | 2.38        | 0.008       | nd          | nd          | 0.05       |
| TMW7    | 7.4| 130           | 113      | nd          | 13.3        | nd          | 0.06        | 1.22        | 2.32        | 0.005       | nd          | nd          | nd          | 0.05       |
| TTW1    | 2.6| 3200          | 461      | 93.8        | nd          | 467         | 0.729       | 4.686       | 180         | 2.72        | 83.5        | 29.9        | 0.25        | 0.673       | 62.1        |
| TTW2    | 2.6| 3100          | 451      | 115         | nd          | 549         | 0.625       | 3.601       | 102         | 3.07        | 105         | 37.9        | 0.27        | 1.06        | 50.6        |
| TTW3    | 6.5| 180           | 141      | 1.52        | nd          | 22.1        | 0.01        | 0.052       | 1.72        | 2.48        | 3.85        | 0.617       | nd          | nd          | 0.791       |
| TTW4    | 7.2| 110           | 116      | 0.04        | nd          | 13.9        | nd          | 0.31        | 2.07        | 2.47        | 0.087       | nd          | nd          | 0.028       |
| TTW5    | 2.9| 900           | 517      | 7.16        | nd          | 54.3        | 0.061       | 0.404       | 7.53        | 2.81        | 10.4        | 2.16        | nd          | 0.686       | 7.59        |
| TTW6    | 7.3| 270           | 157      | 0.35        | nd          | 50.5        | 0.007       | 0.29        | 2.95        | 3.36        | 0.504       | nd          | nd          | 0.149       |
| TTW7    | 2.4| 2300          | 353      | 11.1        | 1.35        | 107         | 0.151       | 2.132       | 579         | nd          | 10.4        | 9.85        | 0.217       | 8.26        |
| TTW8    | 7.0| 210           | 185      | 0.12        | nd          | 58.1        | nd          | 1.81        | 2.91        | 4.05        | 1.43        | nd          | nd          | 0.294       |
| TTW9    | 7.1| 210           | 155      | 0.30        | nd          | 42.0        | 0.01        | 1.16        | 2.37        | 3.41        | 1.97        | nd          | nd          | 0.442       |

Cond, conductivity (in μS cm⁻¹)
ORP, oxidation-reduction potential (in mV)
nd, not detected, i.e. below the limit of detection. The limits of detection (in mg l⁻¹) for the elements concerned are: Al, 0.02; As, 0.1; Ca, 0.05; Cd, 0.005; Cu, 0.005; Fe, 0.01; K, 0.5; Mg, 0.1; Mn, 0.001; Ni, 0.1; Pb, 0.1; Zn, 0.005
The chemistry of standing waters at the Na Sua Mine site differs markedly from that of the running waters described above. The water standing on, and seeping from, the Na Sua mine waste dumps (TTW1, 2, 5) all show low pH values, high conductivities and high ORP values, indicating a well-developed sulphide oxidation process. The water taken from the abandoned pit (TTW5) exhibited a pH of 2.9, a high conductivity (900 μS cm⁻¹) and a high ORP (517 mV) (table 3.1) suggesting that oxidation of the sulphides in the exposed ore body of the pit is occurring. This low pH was achieved despite the association of limestone with the ore-body (section 1.3.4). TTW5 correspondingly possesses high concentrations of Al, Cd, Cu, Fe, K, Mn, Pb and Zn.

Waters seeping from the base of the final tailings dump (TTW1 and 2) were very acidic (pH 2.6), possessing high conductivities (>3 mS cm⁻¹) and ORP values (>450 mV). They possessed very high concentrations of Al, Cd, Cu, Fe, Mn, Pb and Zn and high concentrations of Ca, K, Mg and Ni.

All the standing water samples taken from the Na Sua mine site exhibit properties indicative of ARD. All water samples taken from the Na Sua site possessed below limit of detection concentrations of As.

3.1.3 Tham Thalu Mine

Sample TTW7 was taken from standing water on the flotation waste-tailings impoundment at the Tham Thalu processing plant (figure 1.4, plate 1S). It exhibits properties similar to those standing waters sampled from the Na Sua Mine site (TTW1,2,5) in showing typical ARD characteristics. Sample TTW7 possessed the lowest pH (pH 2.4) of all the waters sampled during this investigation. It was also the only sample from the Na Sua-Tham Thalu area with an As concentration above the limit of detection (1.35 mg l⁻¹). It also recorded the highest Fe concentration.

Samples of stream water were taken immediately downstream of this impoundment (TTW8) and another waste dump further downstream (TTW9). Again the buffering capacity of the river water was apparent in the properties investigated, showing similar properties to TTW6 taken upstream of the Tham Thalu Mine and processing area, except that the TTW8 and TTW9 samples were elevated in Fe and Mn relative to TTW6.

3.2 Mining and processing wastes: chemistry

Comparison between element concentrations in the wastes and normal uncontaminated soils were not made because wastes and soils are inherently different substrate types.

3.2.1 Preliminary screening of samples

The results of the preliminary screening aqua regia digest are reproduced in table 3.2. The most apparent observation is the low As concentration of the To Mo waste samples (TMS1-5)
and river sediment (TMS6) relative to most of the other samples. The dredging waste/alluvium samples collected from the catchment north of Ron Phibun (RPS12 and 13) were also very low in As.

**Table 3.2:** Results of aqua regia screening digestions showing As concentrations found in field samples from the Ron Phibun area, To Mo mine and the Tham Thalu area.

<table>
<thead>
<tr>
<th>Sample</th>
<th>As (µg g⁻¹)</th>
<th>Sample</th>
<th>As (µg g⁻¹)</th>
<th>Sample</th>
<th>As (µg g⁻¹)</th>
<th>Sample</th>
<th>As (µg g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPS1</td>
<td>9465</td>
<td>RPS9</td>
<td>nd</td>
<td>TMS4</td>
<td>360±37.0*</td>
<td>TTS5</td>
<td>3266</td>
</tr>
<tr>
<td>RPS2</td>
<td>132</td>
<td>RPS10</td>
<td>1530</td>
<td>TMS5</td>
<td>832</td>
<td>TTS6</td>
<td>16600</td>
</tr>
<tr>
<td>RPS3</td>
<td>14950</td>
<td>RPS11</td>
<td>18448</td>
<td>TMS6</td>
<td>nd</td>
<td>TTS7</td>
<td>12592</td>
</tr>
<tr>
<td>RPS4</td>
<td>2094</td>
<td>RPS12</td>
<td>nd</td>
<td>TTS1</td>
<td>6396</td>
<td>TTS7c</td>
<td>13966</td>
</tr>
<tr>
<td>RPS5</td>
<td>42086</td>
<td>RPS13</td>
<td>nd</td>
<td>TTS1c</td>
<td>7777</td>
<td>TTS8</td>
<td>3880</td>
</tr>
<tr>
<td>RPS6</td>
<td>2879</td>
<td>TMS1</td>
<td>243</td>
<td>TTS2</td>
<td>8522</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RPS7</td>
<td>nd</td>
<td>TMS2</td>
<td>809</td>
<td>TTS3</td>
<td>3633</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>RPS8</td>
<td>4030</td>
<td>TMS3</td>
<td>496</td>
<td>TTS4</td>
<td>8750</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

RPS, Ron Phibun solid sample; TMS, To Mo solid sample; TTS, Tham Thalu solid sample
nd, not detected
*, sample standard deviation (n = 3)

The Ron Phibun samples varied considerably in their As concentrations. Samples from Maihom mine (RPS1-4) contained up to nearly 1.5% As (RPS3). Sample RPS2 consists of imported soil-like material into which trees had been planted. Samples from the abandoned Yip In Soi mine (RPS5-7, 10-11) also varied widely in their As concentration. The highest value recorded was over 4.2% for RPS5 and the lowest value was below the detection limit for RPS7. This illustrates the typical heterogeneity in the geochemical properties of mine wastes and has consequences for the establishment of field trials (see discussion). The flotation waste collected from the Ron Phibun processing plant (RPS8) contained almost 0.5% As. Assuming that this is mainly in the sulphide form, this sample should be useful for running column leach tests.

The samples from the Ban Tham Thalu subdistrict (including from both the Na Sua (TTS1-5) and Tham Thalu (TTS6-8) mines) contain at least 0.3 %As. The highest As concentrations were recorded from the Tham Thalu processing plant (TTS6 and 7) which contained over 1 %As. Samples TTS1-5 from Na Sua mine all contained over 0.5 %As.

The samples chosen from this initial screening exercise for further investigations were RPS1, 3, 4, 5, 6, 8, 10 and 11; TMS 2 and 5; and TTS1-8, including TTS1c and TTS7c as samples of weathered crust material. This range includes all the samples containing over 0.1% As. Two samples from the To Mo site were included (TMS2 and TMS5) because despite the relatively low As content of these wastes, the As concentration of the waters standing on them was very high (table 3.1; section 3.1.1). The weathered crustose materials overlying samples TTS1 and
TTS7 (TTS1c and TTS7c respectively) were analysed separately to the underlying wastes in an attempt to determine any differences in chemistry and mineralogy.

### 3.2.2 pH and conductivity

The most apparent observation that can be made from table 3.3 is that, despite the similarity in pH values between the Ron Phibun and the Tham Thalu samples, the conductivity of the Ron Phibun samples is comparatively an order of magnitude or so lower (see discussion for an explanation). There were no discernible differences in pH and conductivity between the samples from Maihom mine (RPS1-4) and Yip In Soi mine (RPSS-7, 10, 11). Acidity was moderately low varying between pH 2.97 and pH 3.79. The most acid sample (RPS3) corresponds with the highest conductivity of the Ron Phibun mine waste samples (RPS8 consists of flotation waste from the processing plant in Ron Phibun). In terms of pH and conductivity the Yip In Soi samples appear relatively benign. The high conductivity of RPS8 relates to the waste type, consisting of flotation waste that is undergoing weathering. The To Mo mine wastes showed pH measurements near neutral and normal conductivity measurements.

Table 3.3: pH and conductivity measurements of the selected mining and processing waste samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Cond</th>
<th>Sample</th>
<th>pH</th>
<th>Cond</th>
<th>Sample</th>
<th>pH</th>
<th>Cond</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPS1</td>
<td>3.12</td>
<td>215</td>
<td>RPS11</td>
<td>3.08</td>
<td>250</td>
<td>TTS4</td>
<td>2.54</td>
<td>2700</td>
</tr>
<tr>
<td>RPS3</td>
<td>2.97</td>
<td>400</td>
<td>TMS2</td>
<td>6.80</td>
<td>110</td>
<td>TTS5</td>
<td>7.23</td>
<td>1350</td>
</tr>
<tr>
<td>RPS4</td>
<td>3.23</td>
<td>129</td>
<td>TMS5</td>
<td>7.67</td>
<td>188</td>
<td>TTS6</td>
<td>4.46</td>
<td>2290</td>
</tr>
<tr>
<td>RPS5</td>
<td>3.11</td>
<td>230</td>
<td>TTS1</td>
<td>2.50</td>
<td>2000</td>
<td>TTS7</td>
<td>2.67</td>
<td>1080</td>
</tr>
<tr>
<td>RPS6</td>
<td>3.32</td>
<td>39</td>
<td>TTS1c</td>
<td>3.00</td>
<td>1440</td>
<td>TTS7c</td>
<td>2.69</td>
<td>3650</td>
</tr>
<tr>
<td>RPS8</td>
<td>3.60</td>
<td>39</td>
<td>TTS2</td>
<td>2.50</td>
<td>2390</td>
<td>TTS8</td>
<td>2.57</td>
<td>3000</td>
</tr>
<tr>
<td>RPS10</td>
<td>3.79</td>
<td>34</td>
<td>TTS3</td>
<td>3.41</td>
<td>245</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Cond; conductivity (in μS cm⁻¹)

All the samples from the Tham Thalu area exhibited very high conductivity values, but varied widely in their pH readings. The pH variations can be explained by referring to the sample type (appendix 1). The highest pH readings were recorded in the Na Sua mine drying pile (TTS5, pH 7.23) and in the Tham Thalu processing plant flotation waste (TTS6, pH 4.46). Despite these relatively high pH readings, the conductivity readings were still very high. The highest conductivity readings were recorded from weathered flotation waste in the Tham Thalu processing plant (TTS7c) and the processing waste dump downstream of the plant (TTS8).
3.2.3 XRF spectrometric analysis

Selected samples covering the range of sample types collected were analysed semi-quantitatively by XRF spectrometry (table 3.4). This procedure was used to identify which elements to focus on in the subsequent sequential analysis.

Table 3.4: Major, minor and trace elements identified from selected samples by XRF scanning.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major elements</th>
<th>Minor elements</th>
<th>Trace elements</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPS1</td>
<td>As, K, Si</td>
<td>Al, Ca, Fe, S</td>
<td>Cu, Ga, Mn, Pb, Rb, Sn, Ti, W, Y, Zn</td>
</tr>
<tr>
<td>RPS3</td>
<td>As, K, Si</td>
<td>Al, Ca, Fe, S</td>
<td>Cu, Ga, Mn, P, Pb, Rb, Sn, Ti, W, Y, Zn</td>
</tr>
<tr>
<td>RPS5</td>
<td>As, Fe, K, Si</td>
<td>Al, Ca, S, Zn</td>
<td>Cu, Ga, Mn, P, Pb, Rb, Sn, Ti, W, Y</td>
</tr>
<tr>
<td>RPS6</td>
<td>K, Si</td>
<td>Al, As, Fe, Rb</td>
<td>Ca, Cu, Ga, Mn, Pb, S, Sn, Ti, W, Y, Zn</td>
</tr>
<tr>
<td>RPS11</td>
<td>As, K, Si</td>
<td>Al, Ca, Fe</td>
<td>Cu, Ga, Mn, Pb, Rb, S, Sn, Ti, W, Y, Zn</td>
</tr>
<tr>
<td>TMS3</td>
<td>Si</td>
<td>Al, As, Ca, Fe, K, Ti</td>
<td>Cl, Co, Cr, Cu, Mn, Ni, Pb, Rb, S, Sr, W, Y, Zn</td>
</tr>
<tr>
<td>TTS1</td>
<td>Ca, Fe</td>
<td>As, K, Mn, Pb, S, Si, Sn, Zn</td>
<td>Al, Bi, Cu, Rb, W</td>
</tr>
<tr>
<td>TTS1c</td>
<td>Ca, Fe</td>
<td>As, K, Mn, Pb, S, Si, Sn, Zn</td>
<td>Bi, Cu, Rb</td>
</tr>
<tr>
<td>TTS7</td>
<td>Ca, Fe, S</td>
<td>As, K, Pb, Si, Zn</td>
<td>Bi, Cu, Mn, Sn</td>
</tr>
<tr>
<td>TTS7c</td>
<td>Ca, Fe, S</td>
<td>As, K, Pb, Si, Zn</td>
<td>Bi, Cu, Mn, Rb, Sn, W</td>
</tr>
<tr>
<td>TTS8</td>
<td>Fe, Si</td>
<td>Al, As, Ca K, Mn, Pb, S, Sn, Ti, Zn</td>
<td>Bi, Cu, P, Rb, W, Zr</td>
</tr>
</tbody>
</table>

Semi-quantitative estimates of amounts: major >1%, minor, 0.05-1%, trace (<0.05%) 

Based on this analysis, the following elements were chosen for further investigation: Al, As, Ca, Cd, Cu, Fe, K, Mg, Mn, Ni, Pb and Zn. Some elements that were shown to be present in relatively large amounts were not chosen for analysis in greater detail because of their general lack of potentially toxic behaviour or uncommon occurrence. These included Rb, S, Si, Sn and Ti. Note that As is present as a major element in all but one of the Ron Phibun samples investigated.

3.2.4 Sequential extraction analysis

Figures 3.1 to 3.11 illustrate the sequential extraction results. These figures show concentrations, however the ensuing text may express amounts as "proportions" based on a percentage of the total extracted, the total being 100%, where this has been calculated separately from these graphs.

**Aluminium**

The concentration of total Al is much higher in the Na Sua mine samples (TTS1-5) than in either the Ron Phibun or Tham Thalu samples (figure 3.1). The lowest total concentrations
recorded were for samples from the defunct flotation cells (RPS8 and TTS7). Discarding these two samples, the total Al concentration of the RPS samples varied between 0.39%-1.15%. The To Mo samples (TMS2 and TMS5) showed total Al concentrations of 0.24-0.39%. The Na Sua Mine samples contained the most Al, varying between 0.82 and 3.25%. The Tham Thalu Mine samples varied between 0.21% and 0.52%.

![Figure 3.1: Sequential analysis results for aluminium.](image)

Al was most available in the Na Sua and Tham Thalu samples, as indicated by the amount extracted by water. The Ron Phibun samples (with the exception of RPS8) contained noticeably more Al in the sodium pyrophosphate extraction (relating to absorption onto mineral surfaces, table 2.1) than the Na Sua and Tham Thalu samples (with the exception of TTS3). Despite containing the lowest total Al concentrations, samples RPS8 and TTS7 possessed, proportionately, the highest water soluble Al concentration. Proportionately, the differences between the sodium pyrophosphate extracted Al in the Ron Phibun and the Na Sua-Tham Thalu samples is much more marked.

Hydroxylamine hydrochloride primarily attacks any Fe and Mn oxides that are present (table 2.1). The To Mo samples contained the highest proportions of Al in this and the sodium hypochlorite fractions.

**Arsenic**

The lowest total As concentrations were recorded from the To Mo samples (TMS2 and 5, figure 3.2). The total As concentrations varied widely between the Ron Phibun and Na Sua-Tham Thalu sites from, 0.21% (RPS10) to 3.91% (RPS5) and 0.29% (TTS5) to 1.47% (TTS6).
The Ron Phibun samples contained relatively high concentrations of As in the sodium pyrophosphate (adsorbed) and hydroxylamine hydrochloride (Fe and Mn oxides) fractions. By contrast, the To Mo and Tham Thalu samples contain relatively much more As in the residual fraction. These trends become even more apparent when this scenario is considered on a proportionate basis. This probably relates to the degree of weathering which these samples have undergone (see discussion).

![Graph showing arsenic concentration](image)

**Figure 3.2:** Sequential analysis results for arsenic.

With the exception of the two To Mo samples and TTS7, TTS7c and TTS8, all the samples contain very low concentrations and proportions of water soluble and ammonium acetate extractable (exchangeable) As, reflecting the poor solubility of As ions in the presence of high Fe concentrations. The To Mo samples (TMS2 and TMS5) illustrate this well. The relatively high availability of As in these samples reflects the high dissolved As concentration in waters standing on these wastes (table 3.1). TTS7 (flotation waste from a defunct flotation cell) contained 599 µg g⁻¹ in the water soluble fraction alone, while the weathered crust overlying this deposit contained only 77.8 µg g⁻¹.
The Na Sua Mine samples showed the highest proportions of Zn in the *aqua regia* (residual) fraction. Noticeable in many of the Na Sua-Tham Thalu samples (TTS1, 1c, 5, 6, 7 and 7c) was the relatively large proportion in the sodium hypochlorite (sulphide) fraction. As with As, Ca, Cd, Cu, Fe, Mg and Mn, a very large proportion of water soluble Zn occurred in the TTS7 and TTS7c samples (about 40% and 25% respectively). The Ron Phibun samples generally showed high proportions of Zn in the hydroxylamine hydrochloride (Fe and Mn oxide) fractions compared to the Na Sua-Tham Thalu samples.

**Calcium, magnesium and potassium**

These three elements were investigated as they are essential plant nutrients required in large amounts. Ca and Mg salts also play a significant role in the neutralization of acidity produced during the formation of ARD. Ions of these elements may also compete with potentially toxic elements for interaction with diatomite particles, thus affecting the effectiveness of the intended treatment.

The Ca concentration is related to the mineralogy of the ore-bodies and the host rock. The ore-bodies of the Na Sua and Tham Thalu Mines exist as skarns in the country rock associated with limestone. The To Mo and Tham Thalu samples contained the highest Ca concentrations, with TTS5 (Na Sua drying pile) exhibiting by far the highest concentrations (figure 3.9).
water soluble fraction from the Tham Thalu flotation waste (TTS7, TTS7c) was very high in Cu, although the weathered crust possesses markedly less Cu in this fraction.

![Graph showing copper concentration](image)

**Figure 3.4:** Sequential analysis results for copper.

The Na Sua Mine final tailings dump samples (TTS1-4, figure 1.3) indicate the effects of more pronounced weathering showing proportionately more Cu to be present in the non-residual fractions compared to the drying pile (TTS5). In the Tham Thalu tailings impoundment (TTS6), the relatively high Cu concentration occurs in two forms only: sodium hypochlorite extractable (sulphides) and *aqua regia* extractable (residual). The Ron Phibun samples, although containing a much smaller quantity of Cu, indicate much greater effects of weathering, with enhanced proportions of Cu in the sodium pyrophosphate (adsorbed) and hydroxylamine hydrochloride (Fe and Mn oxides) extractable fractions.

**Iron**

Fe concentrations were highest in the Na Sua-Tham Thalu samples and lowest in the To Mo samples (figure 3.5). Sample RPS5 (suspected As hotspot at Yip In Soi Mine) possessed the highest Fe concentration of the Ron Phibun samples. The Tham Thalu flotation waste (TTS7, 7c) contained very high concentrations (about 7% and 1% respectively) of water soluble Fe.
Figure 3.5: Sequential extraction results for iron.

The Ron Phibun and To Mo samples reflected their more weathered natures and differing ore mineralogy in relation to their relatively large sodium pyrophosphate (adsorbed) and hydroxylamine hydrochloride (Fe and Mn oxides) fractions. Virtually all the Fe present in the Na Sua Mine samples (TTS1-5) was in the *aqua regia* (residual) fraction (compare with Ron Phibun samples). The Tham Thalu samples (TTS6-8) indicate a higher degree of weathering according to the relatively large proportion of Fe extracted by sodium pyrophosphate (reflecting Fe adsorbed on mineral surfaces). In the flotation waste (TTS7), about one quarter of the Fe occurs in water soluble form.

**Lead**

The Ron Phibun and To Mo samples contained very little Pb (figure 3.6). Samples TTS3 (separated Pb-rich dump, Na Sua mine) and TTS5 (Na Sua drying pile) contained the highest Pb concentrations reflecting the presence of high Pb concentrations in the Na Sua-Tham Thalu ore-bodies (sections 1.3.4 and 1.3.5; figure 1.3).
Figure 3.6: Sequential extraction results for lead.

Large proportions of Pb in the TTS3, 5 and 6 samples existed in the hydroxylamine hydrochloride (Fe and Mn oxides) fraction. TTS3 and TTS8 also contained almost 20% Pb in the ammonium acetate (exchangeable) fraction. The more weathered materials (TTS1c and TTS7c) contained more Pb in more available forms than the underlying, less weathered materials.

**Manganese**

Apart from the Ron Phibun flotation cell waste (RPS8), the Ron Phibun and To Mo samples contain very little Mn when compared to the Na Sua-Tham Thalu samples (figure 3.7). In the Na Sua-Tham Thalu samples, the concentration of water soluble Mn was greater than in the Ron Phibun and To Mo samples. Mn is generally more soluble than Fe and this is shown by a comparison of figures 3.5 and 3.7.

Most of the Mn in the Na Sua final tailings dump samples (TTS1, 1c, 2 and 4) was contained in the residual fraction, whereas the separated Pb rich dump (TTS3) possessed a relatively high concentration of Mn in the hydroxylamine hydrochloride (Fe and Mn oxides) fraction. The Na Sua drying pile (TTS5) showed high Mn concentrations in the ammonium acetate (exchangeable), sodium pyrophosphate (adsorbed), sodium hypochlorite (sulphide) and hydroxylamine hydrochloride (Fe and Mn oxides) fractions. In general, the Tham Thalu samples contained less Mn than the Na Sua samples, but it is relatively more available in the
latter, especially with respect to the water soluble concentration. This difference is even more marked when proportions of the total are compared.

**Figure 3.7:** Sequential extraction results for manganese.

In general, the Na Sua-Tham Thalu samples contain a much higher proportion of *aqua regia* extractable (residual) Mn when compared to the Ron Phibun samples, although samples TTS7 and 8 contain ~30% water soluble Mn. Apart from the processing wastes (RPS5, RPS8 and RPS11), the Ron Phibun samples exhibit relatively large proportions of Mn in the sodium pyrophosphate (adsorbed) and hydroxylamine hydrochloride (Fe and Mn oxides) fractions.

**Nickel**

The concentrations of Ni recorded in all the samples were very low and will not be considered further in this report.

**Zinc**

Zinc concentrations show a similar pattern to the other potentially toxic elements investigated in that the concentrations are generally much higher in the Na Sua-Tham Thalu samples than in the Ron Phibun and To Mo samples (figure 3.8). The suspected As hotspot of the Yip In Soi Mine site (RPS5) was unusual among the Ron Phibun samples in showing a high Zn concentration 90% of which was in the *aqua regia* (residual) fraction.
Cadmium

The Na Sua-Tham Thalu sites possess the highest mean Cd concentrations while To Mo possesses the lowest (figure 3.3). RPS5, RPS11 (both from Yip In Soi Mine), TTS5 (Na Sua Mine drying pile) and TTS6 (Tham Thalu processing plant tailings impoundment) are the only samples of real concern with respect to high Cd concentrations. Of great concern is the high availability (i.e. water and ammonium acetate extractability) of Cd in comparison to most of the other potentially toxic elements, with the exception of Zn. This is especially apparent when the fractions extracted are considered on a proportionate basis, for example, where the high proportion of water soluble Cd in most of the samples is obvious (especially in some of the Na Sua-Tham Thalu samples). The more weathered samples such as those from Ron Phibun and the weathered deposits from the Na Sua-Tham Thalu mines (TTS1c, TTS7c) show generally lower Cd concentrations when compared to the less weathered underlying tailings (TTS1, TTS7).

![Graph showing Cd concentrations](image)

Figure 3.3: Sequential analysis results for cadmium

Copper

The Cu concentrations recorded from the Na Sua-Tham Thalu samples are at least an order of magnitude higher than those from the Ron Phibun and To Mo samples, even the flotation waste from the Ron Phibun processing plant (RPS8) was relatively low in Cu (figure 3.4). The
The Ca in the To Mo samples is of unknown origin, but exists at a proportion of over 90% in the water soluble and ammonium acetate extractable (exchangeable) fractions. Proportions vary widely between differing fractions in different Na Sua-Tham Thalu samples with no obviously discernible trends. In general though, Ca availability is much higher in these samples than the other elements investigated thus far.

Magnesium also occurs in limestones and is found in mafic silicate minerals, particularly as a component of biotite mica and is therefore associated with granites. The To Mo samples contained up to 1500 μg g⁻¹ of Mg (figure 3.10). The Mg was presumably derived from biotite as limestone is not associated with the ore-body. The Ron Phibun samples contained very little Mg. The Na Sua-Tham Thalu sample contained most Mg with TTS5 possessing the highest concentration (19210 μg g⁻¹) and TTS8 possessing the lowest (<300 μg g⁻¹). Magnesium exists predominantly in the residual fraction in these samples, although the next biggest fraction proportionately is the water soluble fraction. The Tham Thalu flotation waste (TTS7) contained the highest water soluble concentration at >500 μg g⁻¹ (about 40% as a proportion); the Ron Phibun flotation waste (RPS8) contained over 35% (as a proportion) water soluble Mg.

![Graph showing concentration levels of various elements](image)

**Figure 3.9:** Sequential analysis results for calcium.
Figure 3.10: Sequential analysis results for magnesium.

Figure 3.11: Sequential analysis results for potassium.
There are fewer obvious differences between the sites with respect to the K concentration (figure 3.11) than were found with Ca and Mg, although the highest concentrations were still found in the Na Sua-Tham Thalu samples. TTS5 again possessed most K at 7332 µg g⁻¹. The Ron Phibun and To Mo samples contained relatively high concentrations and proportions of K in the water soluble, sodium pyrophosphate and sodium hypochlorite fractions compared to the Na Sua-Tham Thalu samples which contain over 95% of their K in the residual fraction. This compares to the To Mo and Ron Phibun samples which possess between 75% and 90% K in the residuum (excepting RPS8, the flotation cell waste).

3.2.5 SEM

SEM analysis for Pb was confounded by interferences with As and S, so despite the evidence from wet chemical analysis and XRD for the presence of Pb minerals, identification of these under the SEM was difficult.

Several samples were chosen for a qualitative SEM investigation in order to establish the distribution of elements of interest and As in particular. Plates 3.1 to 3.5 show the results of this investigation. RPS3 (Maihom Mine) and RPS5 (Yip In Soi, suspected As hotspot) were examined from the Ron Phibun area as they contained the highest As concentrations from their respective mine sites (at 1.5% and 4.2% respectively; table 3.2). Samples TTS1, Tc and TTS7c were examined from the Na Sua Mine and Tham Thalu Mine wastes respectively. This allowed a subjective investigation of the differences in element distribution between the weathered crustose material at the surface and the underlying, relatively unweathered material.

The difference in elements associated with As was most the most apparent observation between the Ron Phibun and the Na Sua-Tham Thalu samples. In the Ron Phibun samples, As appeared to be associated with Fe and S (arsenopyrite), but also with Fe alone suggesting the formation of scorodite, although the SEM set-up did not possess the capability to analyse for light elements. Plate 3.1 illustrates the situation well, showing a central arsenopyrite grain surrounded by a rim of scorodite. By comparison the Na Sua-Tham Thalu samples were noticeably more sulphidic with less evidence of weathering. As was associated mainly with Fe and S with little evidence of scorodite.

The presence of other elements and the appearance of grains also provided subjective evidence as to the physical and chemical state of the samples. RPS3 contained mainly quartz (Si), aluminosilicate minerals (high Al and Si) with W/Mn, cassiterite and Fe oxides also present. RPS5 exhibited similar minerals, but also contained small (approximately 3 µm in diameter) inclusions of Bi and Ag in some arsenopyrite grains, pyrite, micas and felspar.
Plate 3.2: Scanning electron micrograph of RPS5 flotation tails showing element distribution.

Plate 3.3: Scanning electron micrograph of RPS5 flotation concentrate showing element distribution.
Plate 3.1: Scanning electron micrograph of an arsenopyrite grain with scorodite rim found in sample RPS5.

The Na Sua-Tham Thalu samples contained a host of other base metals associated with S. For example, TTS1 contained some chalcopyrite and sphalerite as well as cassiterite, Fe oxides and evidence of Fe and As-Fe sulphates (Fe and As-Fe were in association with S, but the S peak was lower than the peak for sulphide minerals). Other elements recorded include Al, Si, K and Ca. This was typical of the samples investigated from this area. Some Fe and S-rich grains (pyrite) from TTS1 exhibited striation marks that may be the product of bacterial action. TTS7 contained S peaks with no other associated elements that may represent almost native S.

The surface crustose samples (TTS1c and 7c) contained evidence of weathering and agglomeration. Grains occurred in cemented clumps with masses of apparently amorphous mixtures of Fe oxides and sulphates. Galena grains with weathered rims were also found. Iron and S were major constituents. Other, minor elements were Sn (cassiterite), Ca (calcite) and silica.

Samples RPS5 and TTS6 were subjected to froth flotation in order to concentrate and separate the sulphide and gangue fractions to facilitate SEM and XRD analyses. The tails and float concentrates from each sample are illustrated in plate 3.2 to 3.5. SEM analyses were conducted for Al, As, Fe, S, Si, Sn, Pb and Zn on each of the four subsamples.
Plate 3.4: Scanning electron micrograph of TTS6 flotation tails showing element distribution.

Plate 3.5: Scanning electron micrograph of TTS6 flotation concentrate showing element distribution.
The RPS5 tails consists predominantly of Al and Si (aluminosilicates) with very small amounts of As, Fe and Sn evident at 30x magnification (plate 3.2). The RPS5 concentrate (RPS5 conc) is diminished in Al and Si, but enriched in other elements namely As, Fe and S with small quantities of Zn (plate 3.3). Arsenic, Fe and S appear related in distribution and Fe and S also occur together separately from As. Zinc also appears to be closely associated with S.

The Tham Thalu flotation waste impoundment sample tails (TTS6 tail, plate 3.4) contained noticeable amounts of Al, Si, Fe and S. Iron and S and Fe, As and S appear in the same grains. Aluminium and Si are generally not associated with any of these elements. There are several grains apparent in the main picture which contain none of the elements analyzed for.

TTS6 concentrate is completely dominated by Fe and S with appreciable quantities of As, Pb and Zn (all apparently associated with S, plate 3.5). Aluminum, Sn and Si are noticeably deficient.

3.2.6 XRD

The XRD scan technique used here will identify mineral phases that constitute a minimum of about 5% of the total.

Comparison of general mineralogy between areas

The three main areas from which samples were taken and subsequently analysed all differ markedly in their mineralogy. As expected, samples taken from the Ron Phibun area are generally dominated by the constituents and weathering products of minerals found in granite which forms the host rock of the ore-body (table 3.5). Both the Maihom and Yip In Soi mines were covered with waste rock with at least one As-rich hotspot identified on the Yip In Soi site. The general mineralogy of the two mines visited in this area is dominated by quartz, micas and felspars, with a small amount of kaolinite derived from the weathering of felspar.

The two To Mo samples investigated were almost pure quartz sand (table 3.5). This results from the quartz gangue in which the vein Au is found (section 1.3.2).

The Na Sua-Tham Thalu mine sites exhibit, by comparison, a very much more diverse mineralogy (table 3.5). This complexity results from four interacting sources: the skarn mineralization (involving close associations with limestone and granite), highly sulphidic mineralization, mineral processing techniques (concentrating certain mineral phases) and the effects of weathering. This provides a more complex scenario than either the Ron Phibun or To Mo situations for the development of a diverse mineralogy. The relatively low counts per second and the high level of background readings observed during XRD analysis in many of the Na Sua-Tham Thalu samples indicates a relatively large amount of amorphous material that results from the interaction of the afore-mentioned parameters and especially the effects of
weathering. This is reflected in the common occurrence of Fe oxide-hydroxides (goethite, lepidocrocite), sulphates (gypsum, jarosite, plumbojarosite) and sulphur among the trace minerals identified. Most of the Ron Phibun samples are derived from weathered waste rock although RPS5 and RPS6 were suspected as being high As processing wastes and RPS8 is a processing waste from the Ron Phibun processing plant. The To Mo samples are derived from the processing of a quartz vein hosting the Au. The Na Sua-Tham Thalu wastes are generally sulphidic in nature and are derived from processing wastes.

**Comparison of mineralogy within and between sites**

The Maihom and Yip In Soi mine wastes of the Ron Phibun area generally consist of the same minerals in slightly different proportions. At the time of sample collection (August 1996), the high-grade processing wastes had been removed from Maihom Mine leaving waste rock remaining, but Yip In Soi Mine had not then been cleared. This mine contained some areas of apparently lithified processing wastes. This assumption was supported by XRD analysis of a sample of one of these “hotspots” (RPS5). The -2 mm sample exhibits similar mineralogical characteristics to the other Ron Phibun mine waste samples in containing quartz, mica and felspars (table 3.5). After undergoing froth flotation to concentrate any sulphides present, arsenopyrite was identified as one of the major constituents (together with quartz). Sphalerite, pyrite and scorodite (and kaolinite) were identified in trace amounts. The relationship between arsenopyrite and scorodite is illustrated in plate 3.1. Scorodite is also found in these wastes as small discrete particles that contain about 50% of the As load. This is probably the material that provides the cement for lithification (T.M. Williams, BGS, personal communication). Other samples of Yip In Soi Mine waste (RPS6, 10 and 11) underwent XRD analysis and generally show mineralogical characteristics typical of the waste rock, although RPS1 1 contained noticeable quantities of cassiterite. Flotation waste from within the Ron Phibun processing plant (RPSS) contained a different mineralogy to the other Ron Phibun samples in being enriched in W-minerals, especially wolframite (as a major constituent) and scheelite (as a trace constituent) (table 3.5).

A between-sites comparison of the To Mo samples shows very little detectable difference, both samples consisting of almost pure quartz.

The most mineralogical variation between- and within- sites exists among the Na Sua-Tham Thalu samples. Most samples show quartz as the major mineral constituent (table 3.5). The remaining minor and trace constituents are varying mixtures of sulphides (predominantly pyrrhotite and pyrite), Fe oxide-hydroxides and sulphates (mainly jarosite and gypsum), cassiterite, calcite, fluorite, mica and sulphur. Arsenopyrite was detected in samples TTS3, 4 and 6. Within the Na Sua site alone, the drying pile and different parts of the final tailings dump vary widely in mineralogy. The final tailings dump samples (TTS1-4) possess quartz as the major mineralogical constituent. A comparison of the mineralogy of the weathered surface
crust and the underlying waste (TTS1 and TTS1c) indicates little difference in this subjective investigation, apart from the occurrence of sulphur in the more weathered crustal deposit. The separated waste pile apparently rich in Pb minerals (TTS3) turned out to possess relatively large amounts of cerussite and products from the weathering of galena (anglesite and plumbojarosite). The Na Sua drying pile (TTS5) was noticeably deficient in the aforementioned products of the weathering of sulphide minerals. The difference between this area and the final tailings dump may reflect the relative lack of disturbance of the waste in the drying pile; waste in the final tailings dump has been translocated from the drying pile and has therefore been subjected to an additional phase of weathering as unoxidized material was brought to the surface.

**Table 3.5: The main mineral constituents of the Thai waste samples as identified by XRD analysis**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Major</th>
<th>Minor</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>RPS1</td>
<td>Quartz</td>
<td>Mica</td>
<td>K-felspar, Na-felspar, kaolinite</td>
</tr>
<tr>
<td>RPS3</td>
<td>Quartz</td>
<td>Mica</td>
<td>K-felspar, Na-felspar, kaolinite</td>
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<td>RPS4</td>
<td>Quartz</td>
<td>K-felspar</td>
<td>Mica, Na-felspar, kaolinite</td>
</tr>
<tr>
<td>RPS5</td>
<td>Quartz</td>
<td>Mica</td>
<td>K-felspar, Na-felspar</td>
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<tr>
<td>RPS5 tails*</td>
<td>Quartz, arsenopyrite</td>
<td>Mica, Na-felspar, K-felspar</td>
<td>-</td>
</tr>
<tr>
<td>RPS5 cone*</td>
<td>Quartz, arsenopyrite</td>
<td>Mica</td>
<td>Sphalerite, pyrite, scorodite, kaolinite</td>
</tr>
<tr>
<td>RPS6</td>
<td>Quartz</td>
<td>Mica, Na-felspar, K-felspar</td>
<td>Kaolinite</td>
</tr>
<tr>
<td>RPS8</td>
<td>Wolframite</td>
<td>Quartz</td>
<td>Cassiterite, scheelite, ilmenite</td>
</tr>
<tr>
<td>RPS10</td>
<td>Quartz</td>
<td>K-felspar, Na-felspar, mica</td>
<td>Koalinite</td>
</tr>
<tr>
<td>RPS11</td>
<td>Quartz</td>
<td>-</td>
<td>K-felspar, Na-felspar, cassiterite, mica, kaolinite</td>
</tr>
<tr>
<td>TMS2</td>
<td>Quartz</td>
<td>-</td>
<td>Mica, K-felspar, Na-felspar</td>
</tr>
<tr>
<td>TMS5</td>
<td>Quartz</td>
<td>-</td>
<td>Mica, K-felspar, Na-felspar</td>
</tr>
<tr>
<td>TTS1</td>
<td>Quartz</td>
<td>-</td>
<td>Goethite, cassiterite, scheelite, pyrrhotite, mica, lepidocrocite, jarosite, sulphur, bixbyite (Mn$_2$O$_3$), ramsdellite (MnO$_2$)</td>
</tr>
<tr>
<td>TTS1c</td>
<td>Quartz</td>
<td>-</td>
<td>Gypsum, cassiterite, mica, lepidocrocite, jarosite, haematite, goethite, sulphur</td>
</tr>
<tr>
<td>TTS2</td>
<td>Quartz</td>
<td>-</td>
<td>Gypsum, goethite, cassiterite, mica, lepidocrocite, jarosite, pyrite, sulphur</td>
</tr>
<tr>
<td>TTS3</td>
<td>Quartz, plumbojarosite, cerussite (PbCO$_3$), anglesite (PbSO$_4$)</td>
<td>-</td>
<td>Pyrite, arsenopyrite, galena, goethite, mica, pyrrhotite, clinohlore</td>
</tr>
<tr>
<td>TTS4</td>
<td>Quartz</td>
<td>Plumbojarosite, arsenopyrite</td>
<td>Gypsum, plumbojarosite, arsenopyrite, rutile, goethite, phlogopite, pyrite, cassiterite, jarosite</td>
</tr>
<tr>
<td>TTS5</td>
<td>Quartz, calcite</td>
<td>Mica, pyrrhotite</td>
<td>Galena, sphalerite, cassiterite, kaolinite, fluorite</td>
</tr>
<tr>
<td>TTS6</td>
<td>Pyrrhotite, quartz</td>
<td>-</td>
<td>Galena, calcite, sphalerite, pyrite, arsenopyrite, gypsum, mica, fluorite</td>
</tr>
<tr>
<td>TTS6 tails*</td>
<td>Quartz, fluorite</td>
<td>Mica</td>
<td>K-felspar, goethite, gypsum, bassanite, pyrrhotite, pyrite, kaolinite</td>
</tr>
<tr>
<td>TTS6 cone*</td>
<td>Pyrrhotite</td>
<td>Stannite</td>
<td>Quartz, arsenopyrite, galena</td>
</tr>
<tr>
<td>TTS7</td>
<td>-</td>
<td>Sulphur, goethite, jarosite, gypsum</td>
<td>Quartz, galena, cassiterite, mica, lepidocrocite, sphalerite, pyrite, fluorite</td>
</tr>
<tr>
<td>TTS7c</td>
<td>-</td>
<td>Fluorite</td>
<td>Goethite, lepidocrocite, cassiterite, quartz, sulphur</td>
</tr>
<tr>
<td>TTS8</td>
<td>Quartz</td>
<td>-</td>
<td>Goethite, jarosite, K-felspar</td>
</tr>
</tbody>
</table>

*, mineralogy determined after froth flotation
The Tham Thalu waste impoundment sample (TTS6) was subjected to froth flotation. The resulting concentrate contained trace quantities of arsenopyrite. The waste from the froth flotation cell contained very large quantities of amorphous material with only trace quantities of a diverse range of minerals identifiable. The surface crust found on this waste was analysed separately and was found to contain fluorite in greater amounts. The dump downstream (TTS8) appears much less complex mineralogically than most of the other samples described above.
4. DISCUSSION

4.1 Summary of site characteristics

All the sites contained above background concentrations of As when total (aqua regia extractable) concentrations of As are considered. However, the nature of the As in the various substrates differed markedly between the sites. Sites also differed in terms of their substrate type, the presence of other potentially toxic elements and other soil properties.

4.1.1 Ron Phibun

The two mine sites investigated in Ron Phibun District had many features in common including the type of mineralization and mining methods. The recent histories of these sites differ considerably. Maihom mine has been cleared of high grade As-bearing wastes, whereas Yip In Soi mine still possesses such wastes although these are highly weathered and lithified and limited in extent. The rock wastes covering the majority of the two sites can be generally described as contaminated skeletal soils. The wastes consist of blocks of granite country rock and granite-related minerals (quartz, mica, felspars) and their weathering products, especially kaolinite. The wastes were moderately acid with low to normal conductivity. This reflects the low pH-buffering capacity of the waste and the high leaching regime of the local humid tropical climate and steep topography.

Despite the removal of high-grade waste from the former mine site, the residual As content of the waste remains moderately high in some areas. The sequential analyses and SEM and XRD investigations on the wastes from these two mines indicate that the As is present mainly as scorodite and arsenopyrite undergoing weathering. Other PTEs that are present at relatively high concentrations in some of the Ron Phibun mine waste samples are Cd and Zn (in Yip In Soi processing wastes).

The flotation waste from the Ron Phibun processing plant differs completely from the aforementioned wastes. This waste is enriched in oxide minerals, namely wolframite, quartz, cassiterite, scheelite and ilmenite. Several potentially toxic elements occur at relatively high concentrations, namely As (4270 µg g\(^{-1}\)), Cu (246 µg g\(^{-1}\), about 25% water soluble) and Mn (1464 µg g\(^{-1}\), about 23% water soluble). A large proportion of the As present occurs in the oxide-hydroxide fraction as with the Ron Phibun mine wastes. Other processing waste deposits from the plant were not sampled but it is suspected that these wastes are of a similar nature to this sample.

The two Ron Phibun mine wastes provide suitable sites for the establishment of long term field plots. They contain moderate concentrations of As with some arsenopyrite present which should slowly oxidize over time.
4.1.2 To Mo

The To Mo Mine wastes consist essentially of quartz sand of a reasonably high purity, with trace amounts of mica and felspars. The pH and conductivity of the wastes and their associated waters raised no cause for concern.

The As concentrations of the two To Mo mine waste samples investigated were 1125 μg g⁻¹ and 678 μg g⁻¹. Although these are the lowest As concentrations recorded in the samples chosen after screening, the proportion in the water soluble fraction was relatively high at about 0.3% respectively, when compared to the other samples investigated. This relatively high solubility probably reflects the low concentration of Fe and clay minerals in the waste. The samples also contained relatively high concentrations of Al, Ca, K and Mg. The concentrations of other PTEs were low.

The To Mo waste sites appear to be environmentally benign and would probably be unsuitable for the establishment of field trials involving diatomite given the more serious As contamination problems associated with other sites.

4.1.3 Na Sua-Tham Thalu

The sites investigated in the Tham Thalu subdistrict exhibited much more complex and diverse mineralogical and chemical properties than the Ron Phibun and To Mo sites. The standing waters sampled at the Na Sua-Tham Thalu sites showed properties indicative of ARD, i.e. they were highly acidic, possessed very high conductivities and ORP values and contained high concentrations of dissolved Fe and potentially toxic elements. The running waters were well-buffered against ARD run-off from the highly sulphidic wastes, although the elevated concentrations of Fe and Mn imply contamination derived from the mine wastes. There is evidence for the downstream transportation of these elements by suspension in the water column and transportation along the stream bed. Evidence from other investigations, e.g. Arrykul and Kooptarnon (1993) and Charoenchaisri (1996) supports this hypothesis (see tables 1.1 and 1.2).

The wastes themselves were shown to be highly acidic with high conductivities. The high pH of the Na Sua drying pile can be explained by the presence of calcite which would buffer the acidity generated by the oxidation of sulphide minerals. The lack of calcite in the main drying pile suggests that it has been weathered away. The translocation and disturbance of the waste from the drying pile to the final dump will have caused unweathered sulphidic material and calcite to be moved to the surface thus resetting the oxidation clock, causing increased weathering and dissolution of calcite compared to the drying pile.

The mineralogy of the Na Sua-Tham Thalu wastes is dominated by quartz and pyrrhotite. A variety of other sulphide minerals was observed by XRD and SEM, e.g. pyrite, arsenopyrite, galena and sphalerite. Residual cassiterite was also observed. The main gangue minerals were
quartz, mica, felspars, calcite and fluorite. One pile at Na Sua Mine had been separated as it was especially rich in Pb minerals, namely cerussite and anglesite. A third group of minerals was also present as the weathering products of the previously mentioned primary minerals. This group included sulphur, gypsum, jarosite, plumbogaraosite, bassanite, goethite, lepidocrocite, haematite and kaolinite. Goethite, gypsum and jarosite have been observed as weathering products in other sulphidic mine tailings, e.g. Ribet et al. (1995). They recorded trace metals, e.g. Ni, Cr, Cu to be closely associated with these minerals. This diversity in the mineralogy is reflected in the presence of many potentially toxic elements at high concentrations, e.g. Al, As, Cd, Cu, Pb, Mn and Zn. Calcium, K and Mg are present at relatively normal concentrations. The chemistry of the wastes is dominated, unsurprisingly, by Fe. The vast majority of each of these elements is present in the residual fraction indicating that a large reservoir of unoxidized material exists that is a potential source of PTEs in the future.

The highest concentrations of water soluble As were recorded from the Tham Thalu flotation waste (599 µg g⁻¹). This was reflected in the very high As concentration recorded in the water standing on this waste (1350 µg ml⁻¹). This waste also exhibited the highest concentrations of Cd (9.99 µg g⁻¹), Cu (404 µg g⁻¹), Fe (6.98 %) and Zn (2042 µg g⁻¹) and appreciable concentrations of the other elements investigated.

The Na Sua-Tham Thalu sites possess ample opportunities for the establishment of long term field trials and their Fe sulphide dominated mineralogy and chemistry would provide an interesting comparison with the well-weathered, silica-dominated wastes of the Ron Phibun sites.

4.2 Choice of sites for establishing long term field experiments

Each of the above sites possesses characteristics of As mineralogy and chemistry that differs from the other sites. Therefore, it would be beneficial to compare the dynamics of As chemistry - diatomite interactions under the different regimes existing at the different sites. Both the Ron Phibun and the Na Sua-Tham Thalu sites possess high concentrations of As. The former site contains As in arsenopyrite and scorodite in a highly weathered, skeletal soil environment; the latter sites possess As mainly in arsenopyrite, with relatively high concentrations of other PTEs mainly in the sulphidic form, although some samples contained relatively high concentrations of water soluble As and other potentially toxic elements.

The risks to public health and the environment in the Ron Phibun area from As-contaminated mine wastes on the flanks of the Ron Na-Suang Chan mountains are thought to be small (Williams et al., 1996). The To Mo mine wastes are also considered to pose negligible risk to the environment based on the results of DMR investigations and this study. The Na Sua-Tham Thalu wastes do pose a risk to the environment and potentially to humans. Potentially toxic
elements are thought to enter the main Pattani River system from these wastes. The wastes in the neighbourhood of Ban Tham Thalu village occur very close to occupied dwellings and must pose a high risk to human health. The establishment of field trials on the previously mentioned sites may have a supplementary benefit in reducing the risk to both the environment and human health by decreasing the solubility of As and other PTEs.

Sites suitable for the establishment of long term field trials are provisionally identified here as the Yip In Soi site and the Tham Thalu processing area, subject to DMR approval.

4.3 Further investigations

This investigation is the first step in a much larger study investigating the use of diatomite to treat As-contaminated land in Thailand. This report details work undertaken to identify suitable sites for the establishment of long term field trials.

Further work will investigate the following areas:

- Column leach tests will be set-up in the UK and Thailand to study the leaching characteristics of wastes from the chosen sites in combination with the chosen source of diatomite.
- Investigations into the detailed chemistry of the As-diatomite interaction will be undertaken with a view to explaining the mechanisms of the interactions.
- A detailed chemical survey of the chosen field sites to locate possible "hot-spots" will be undertaken before the sites are to be established.
- A long term environmental monitoring regime for the sites will require setting-up and administering.

It is anticipated that by the end of this project, many of the questions revolving around the mechanism of the diatomite-As interaction will be answered. Also, it is hoped that the establishment of long term field trials on contaminated land exhibiting different degrees and properties of contamination, will provide a useful research facility into a new and valuable method for reducing the impact of contaminated land on public health and the environment.
5. References


### APPENDIX 1: DETAILS OF SAMPLES COLLECTED FROM THAILAND (AUGUST 1996)

<table>
<thead>
<tr>
<th>Date collected</th>
<th>Sample code</th>
<th>Site</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>22/8/96</td>
<td>RPS1</td>
<td>Maihom Mine</td>
<td>From a lower terrace</td>
</tr>
<tr>
<td>-</td>
<td>RPS2</td>
<td>As above</td>
<td>More like soil: trees planted into this</td>
</tr>
<tr>
<td>-</td>
<td>RPS3</td>
<td>As above</td>
<td>From a middle terrace</td>
</tr>
<tr>
<td>-</td>
<td>RPS4</td>
<td>As above</td>
<td>From an upper terrace</td>
</tr>
<tr>
<td>-</td>
<td>RPS5</td>
<td>Yip In Soi Mine</td>
<td>Lithified processing waste</td>
</tr>
<tr>
<td>-</td>
<td>RPS6</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>RPS7</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>23/8/96</td>
<td>RPS8</td>
<td>Processing plant</td>
<td>Flotation waste from inside plant</td>
</tr>
<tr>
<td>-</td>
<td>RPS9</td>
<td>Ron Phibun street</td>
<td>Magnetic separation waste</td>
</tr>
<tr>
<td>-</td>
<td>RPS10</td>
<td>Yip in Soi Mine</td>
<td>General mine waste</td>
</tr>
<tr>
<td>-</td>
<td>RPS11</td>
<td>As above</td>
<td>Lithified processing waste</td>
</tr>
<tr>
<td>-</td>
<td>RPS12</td>
<td>Old dredging area</td>
<td>Well-vegetated, sandy in appearance</td>
</tr>
<tr>
<td>-</td>
<td>RPS13</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>25/8/96</td>
<td>TMS1</td>
<td>Ban Chum Thong tailings dump</td>
<td>Tailings trucked here from To Mo mine site</td>
</tr>
<tr>
<td>-</td>
<td>TMS2</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TMW1</td>
<td>As above</td>
<td>Standing water on above tailings</td>
</tr>
<tr>
<td>-</td>
<td>TMW2</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TMS3</td>
<td>To Mo mine site</td>
<td>From tailings pound on To Mo site</td>
</tr>
<tr>
<td>-</td>
<td>TMS4</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TMS5</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TMW3</td>
<td>As above</td>
<td>Standing water on above tailings</td>
</tr>
<tr>
<td>-</td>
<td>TMW4</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TMW5</td>
<td>As above</td>
<td>Water draining from mine entrance</td>
</tr>
<tr>
<td>-</td>
<td>TMS6</td>
<td>~2 km downstream of mine site</td>
<td>Stream sediment</td>
</tr>
<tr>
<td>-</td>
<td>TMW6</td>
<td>As above</td>
<td>Water taken from same place as TMS6</td>
</tr>
<tr>
<td>-</td>
<td>TMW7</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>26/8/96</td>
<td>TTS1</td>
<td>Na Sua mine tailings dump</td>
<td>Lithified crust. Fe staining, pervasive S² smell</td>
</tr>
<tr>
<td>-</td>
<td>TTS2</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TTS3</td>
<td>As above</td>
<td>Separated dump: supposedly rich in Pb carbonate</td>
</tr>
<tr>
<td>-</td>
<td>TTS4</td>
<td>As above</td>
<td>As for TTS1 and 2</td>
</tr>
<tr>
<td>-</td>
<td>TTW1</td>
<td>As above</td>
<td>AMD seepage from base of main tailings dump</td>
</tr>
<tr>
<td>-</td>
<td>TTW2</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TTW3</td>
<td>Na Sua mine drying pile</td>
<td>Streamwater running through drying pile sampled</td>
</tr>
<tr>
<td>-</td>
<td>TTW4</td>
<td>As above</td>
<td>As above</td>
</tr>
<tr>
<td>-</td>
<td>TTS5</td>
<td>As above</td>
<td>Lithified crust (Fe rich), soft black sediment beneath</td>
</tr>
<tr>
<td>-</td>
<td>TTW5</td>
<td>Flooded mine pit</td>
<td>Water in pit, bright green, in contact with exposed orebody</td>
</tr>
<tr>
<td>-</td>
<td>TTW6</td>
<td>Approx. 1 km down-stream of Na Sua mine</td>
<td>Turbidity of water very high owing to vicinity of marble quarry</td>
</tr>
<tr>
<td>-</td>
<td>TTS6</td>
<td>Tham Thalu processing plant</td>
<td>Waste from flotation waste/tailings impoundment</td>
</tr>
<tr>
<td>-</td>
<td>TTS7</td>
<td>As above</td>
<td>Flotation waste from adjacent to flotation cells and covered with semi-lithified crust</td>
</tr>
<tr>
<td>-</td>
<td>TTW7</td>
<td>As above</td>
<td>Water from flotation waste/tailings impoundment</td>
</tr>
<tr>
<td>-</td>
<td>TTW8</td>
<td>Stream immediately down-stream of impoundment</td>
<td>-</td>
</tr>
<tr>
<td>-</td>
<td>TTS8</td>
<td>Tailings dump approx 300 m from plant</td>
<td>Dump adjacent to stream near village. Covered with soil</td>
</tr>
<tr>
<td>-</td>
<td>TTW9</td>
<td>Immediately downstream of dump</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Ron Phibun</td>
<td>To Mo</td>
<td>Na Sua-Tham Thalu</td>
</tr>
<tr>
<td>---------------------</td>
<td>------------</td>
<td>-------</td>
<td>-------------------</td>
</tr>
<tr>
<td>Solids (mine and processing wastes)</td>
<td>13</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>Waters</td>
<td>-</td>
<td>7</td>
<td>9</td>
</tr>
<tr>
<td>Total</td>
<td>13</td>
<td>13</td>
<td>17</td>
</tr>
</tbody>
</table>
APPENDIX 2: TYPICAL ELEMENT CONCENTRATIONS IN UNCONTAMINATED FRESH WATERS (FROM ALLEN, 1989)

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg l⁻¹)</th>
<th>Element</th>
<th>Concentration (µg l⁻¹)</th>
<th>Element</th>
<th>Concentration (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.1-2</td>
<td>Cu</td>
<td>2-50</td>
<td>Mn</td>
<td>1-80</td>
</tr>
<tr>
<td>As</td>
<td>0.2-1</td>
<td>Fe</td>
<td>50-1000</td>
<td>Ni</td>
<td>5-100</td>
</tr>
<tr>
<td>Ca</td>
<td>0.1-100</td>
<td>K</td>
<td>0.1-1</td>
<td>Pb</td>
<td>1-20</td>
</tr>
<tr>
<td>Cd</td>
<td>1-10</td>
<td>Mg</td>
<td>0.5-20</td>
<td>Zn</td>
<td>5-50</td>
</tr>
</tbody>
</table>
APPENDIX 3: CHEMICAL ANALYSIS METHODOLOGY OF SOLID SAMPLES

*Aqua regia digestion*

This is a slightly modified method for the determination of As in mining and processing wastes.

Weigh out approximately 0.5g of sample into a 250 ml beaker. Add 10 ml concentrated nitric acid and cover with a watch glass. Heat on a hot plate until bubbling. Add 5 ml concentrated HCl and heat until the brown fumes are no longer emitted. Remove from heat and allow to cool. Dilute with a few ml of water. Filter through a no. 42 filter paper and dilute to 250 ml.

**pH and conductivity measurements**

Approximately 20 g of -2 mm sample material was mixed with 100 ml of demineralized water. This was left standing for approximately one hour, mixing every 10 minutes. After one hour, the pH of was recorded. The suspension was then filtered through a no. 42 filter paper. The first 10 ml of filtrate were discarded. The conductivity was then measured.

**Sequential extraction procedure (adapted from Waller, 1995)**

**Step 1: water soluble**

To 5 g of -2 mm sample in a centrifuge tube add 50 ml distilled water (pH 7) and stopper with a rubber bung. Shake for five hours. Remove rubber stopper and centrifuge at 4200 rpm for 30 minutes. Decant supernatant. Analyse extract by atomic absorption spectrophotometry (AAS).

**Step 2: exchangeable**

To residue from step 1 add 50 ml 1M ammonium acetate solution (buffered to pH 7 with acetic acid). Shake for one hour. Centrifuge and decant supernatant. Wash residue with 20 ml distilled water (shake for 10 min). Centrifuge as above. Add water to ammonium acetate extract and analyse by AAS.

**Step 3: organic and adsorbed**

To residue from step 2 add 50 ml sodium pyrophosphate (buffered to pH 7 with orthophosphoric acid) and shake for 15 hours. Centrifuge and wash as for ammonium acetate. Analyse extract by AAS.

**Step 4: sulphides**

To residue from step 3 add 50 ml 0.1 M sodium hypochlorite (adjusted to pH 9.5 with 6 M hydrochloric acid). Leave for 10 hours shaking every two hours for 10 minutes. Centrifuge and remove supernatant. Repeat from addition of sodium hypochlorite. Add supernatants together. Leach residue with 50 ml distilled water (acidifying suspension to pH 3 by dropwise addition of 1.5 M hydrochloric acid). Centrifuge and add supernatant to sodium hypochlorite extracts. Analyse extract by AAS.

**Step 5: iron and manganese oxides**

To residue from step 4 add 50 ml 1 M hydroxylamine hydrochloride (buffered to pH 5 with sodium citrate). Shake for one hour. Centrifuge and remove supernatant. Repeat from addition of hydroxylamine hydrochloride. Add the two supernatant liquids together then wash as with ammonium acetate. Analyse extract by AAS.
**Step 8: residual**

This final step is based on the *aqua regia* digest described above. However the procedure takes much longer owing to the larger sample size and particle size. Much more acid is required.

**Froth flotation methodology**

Mix approximately 300 g of fine-grained sample was in about 1 l water in a flotation cell.

Add a few drops of 5% CuSO₄ solution as a promoter (encourages bonding of partly oxidized sulphide minerals.

Mix for about three minutes).

Make up a 1% solution of amyl xanthate (the collector) and make staged additions of 4.5 ml of this to the sample mixture.

Condition the suspension mixture for three minutes.

Add the frothing agent (MIBC, methyl iso-butyl carbinol) as required.

Float for about five minutes selectively removing the sulphides.

Filter through a no. 3 filter paper in a Buchner funnel.

Dry in an oven at 80 °C keeping the float and tails concentrate separate for analysis.