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UNITED NATIONS INDUSTRIAL DEVELOPMENT ORGANISATION

PROJECT NO SI/THA/90/802/11-52/J13209

PADAENG INDUSTRY COMPANY LTD

THAILAND

MANAGEMENT OF ORE RESIDUES
AND SLUDGES FROM ZINC REFINING

FINAL REPORT

C J Appleyard
Environmental Resources
London W1H 3DB

Dr C Beinhoff
UNIDO

Dr Soporn Koottatep
Chiang Mai University
Thailand

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S. SUMMARY

S. SUMMARY

- S1 Padaeng Industry Company Ltd (PDI) produces 72,000 t/a zinc and 850 t/a cadmium at its refinery at Tak. Residues and sludges from refinery operations are stored on site in large PVC ponds. In addition, an intermediate product cadmium cake (from the period prior to the commissioning of the cadmium refinery) is stored on-site in two reinforced concrete/PVC ponds.**
- S2 An audit of current refinery operations was carried out in December 1992; the principal objectives being to establish long term environmental risks associated with present and past practices and procedures for process residue and process sludge management and to review environmental impact issues in general, including the impact of proposed major processing changes in mid-1994.**
- S3 The principal conclusions of the review include that:**
- . PDI operate the site essentially to a high level of environmental awareness and management.
 - . Escape of heavy metals such as zinc, cadmium, manganese and lead to the environment is presently very low. However, there is some evidence of contaminated leachate overflow from residue pond R1 and it is suspected that the natural exchange capacity of the soils prevents metals from reaching groundwater at this stage.
 - . Long term storage of "stabilised" silicate residues in single membrane ponds is satisfactory.
 - . Stabilised residue would appear to have substantial by-product value.
 - . Long term storage of "non-stabilised" silicate residues in single membrane ponds is not satisfactory without engineered provision for leachate collection, transfer and treatment.
 - . Long term storage of wastewater sludges in single membrane ponds is unsatisfactory because of the "liquid" characteristics of the low solids content sludges.
 - . The present method of containment of cadmium cake is unsatisfactory.
 - . Long term storage of Jarosite residue (from processing of calcine feed material after mid-1994) in single membrane ponds is unsatisfactory.

S4 The principal recommendations of the report are that:

- . The PDI monitoring protocol should be extended to include soils; also it should be subject to independent audit on a once per year basis.
- . The integrity of the under-drainage collection and recovery system should be fully maintained, particularly during the rainy season.
- . Facilities for leachate collection, transfer and treatment should be provided on all ponds containing non-stabilised silicate residues.
- . Storage ponds containing stabilised residue should be covered to minimise potential for infiltration of surface water.
- . A suitable by-product end-use should be developed for stabilised residues.
- . Wastewater sludges contained in ponds N2 and N3 should be removed for dewatering and possible stabilisation in admixture with silicate-based residue.
- . Cadmium cake should be processed to cadmium metal as soon as possible.
- . A simple building structure should be constructed around the existing storage ponds (because it will take at least 5 to 6 years to process the cadmium cake and because it is important to minimise airborne dusts and/or leachate generation when an operating face is exposed).
- . Jarosite residue should be contained in double membrane storage ponds.
- . Alternative hydrometallurgical or pyrometallurgical processes should be considered to convert Jarosite to hematite or other inert end product/by-product.

1. INTRODUCTION

1.1 Background

1.2 Terms of Reference

1.3 Revisions to Terms of Reference

1.4 Arrangement of report

1.5 Acknowledgements

1. INTRODUCTION

1.1 Background

Zinc ore is extracted by open cast mining from a deposit at Mae Sot near to Pha Daeng in Tak province in northwest Thailand and refined electrolytically at a plant near Muang Tak City some 85 km to the east to produce zinc ingot and die cast alloy (No 3) plus cadmium by-product (sticks and balls). The deposit at Mae Sot essentially comprises a high grade zinc oxide/silicate ore; principally hemimorphite (ie $Zn_4Si_2O_7(OH)_2H_2O$) and smithsonite (ie $ZnCO_3$) plus galena (lead containing) and pyrites (iron containing) components. The operation (Padaeng Industry Company Limited) accounts for the majority of Thailand's zinc production.

The mine at Mae Sot had been worked originally with direct export of the primary ore. However major extraction commenced in 1984 to coincide with the commissioning of the refinery at Tak. Overall capacity is now about 72,000 tonnes per annum of zinc and 850 tonnes per annum of cadmium. The cadmium refinery was commissioned in 1990. In 1984 the deposit was anticipated to have a life of 16 years, although this was based on a production level of zinc of 60,000 tonnes per annum.

Residues from the sulphuric acid leaching and purification processes are stored at the refinery site in large PVC-lined ponds. To date five such ponds have been constructed, providing a total storage capacity (ignoring the possibility of stacking to high level) in excess of 4.5 million cubic metres, of which approximately 65% has been taken up. A process of "lime stabilisation" was introduced in 1988 to achieve a greater degree of "stabilisation" and "fixation" of the heavy metals.

Similarly precipitated metal hydroxide sludges from wastewater treatment processes are also stored in large PVC-lined ponds. In this case four such ponds have been constructed, providing a total available capacity of about 1.0 million cubic metres of which about 60% has been taken up.

Finally, for the 5 year period prior to commissioning of the cadmium refinery plant, it was practice on-site to store the cadmium cake by-product in dedicated ponds. Such storage is still in place in spite of an intention to process the "cake" in combination with the ongoing production requirement.

In view of the hazardous nature of the three materials stored on site, including the aqueous components which could contain significant concentrations of zinc, cadmium and manganese, and in view of the relatively close proximity of the Ping River which eventually supplies Bangkok with most of its water supply, major concerns have been expressed by The Ministry of Industry as to the integrity of the methods used, including the policy of using single membrane liners and the storage of significant volumes of liquids.

Accordingly, the United Nations Industrial Development Organization (UNIDO) was invited to undertake a mission to review the technologies in place and to assess the risks involved both on a short and long-term basis.

1.2 Terms of Reference

The purpose of the project is to assist the Government of Thailand to determine the most appropriate technology(ies) to be employed by Padaeng Industry Company Limited (PDI) for:

- . treatment and final disposal of zinc ore residues;
- . wastewater treatment and final disposal of resulting toxic sludges;
- . storage of cadmium cake.

To carry out the mission UNIDO established a 3 man team comprising:

- . Dr C Beinhoff: Chief Unit Non-ferrous Metallurgy, UNIDO, Vienna.
- . Mr C J Appleyard: Consultant, Industrial Wastewater and Wastes Management, Environmental Resources Ltd, London.
- . Dr Suporn Koottatep: Dept of Environmental Engineering, Chiang Mai University, Thailand.

The specific expert duties (Terms of Reference) allocated to the "Expert on disposal of solid and liquid toxic wastes from zinc refining" (C J Appleyard) are documented in UNIDO Job Description reference SI/THA/90/802/11-51 and are listed below:

- . The UNIDO expert, assisted by a national expert, will undertake activities necessary...to produce a comprehensive report and recommendations covering the following:
 - . Evaluation of the present processing of the zinc ore and disposal of the resulting 750 ton per day of toxic residues into storage ponds as sludge.
 - . Evaluation of the present wastewater treatment system and disposal of the resulting several tons per day of toxic residue into the storage ponds in cake form.
 - . Evaluation of the present system of storing cadmium oxide indefinitely in cake form pending its sale or further refining.
 - . Evaluation of the two waste disposal methods proposed by PDI and MOI.
 - . Recommendations for improving present systems of generation and disposal of the two types of waste (sludge and cake). These may or may not include the PDI and MOI proposals.

Recommendations for improving the present system of storage of cadmium oxide cake on site.

1.3 Revisions to Terms of Reference

Following initial meetings held at the refinery site it became evident that the present ore body is scheduled to be exhausted in about 18 months time. This foreshortened life of the ore body is due in part to the expanded production achieved latterly but also to an over-estimation of reserves in 1984/85. As a consequence it is proposed to convert to a calcine-based input feed derived from an imported sulphide-based ore (probably from Australia). The plan presently is to build a roasting plant at the Maptaphut Industrial Estate, Rayong plus a 80,000 tonnes per annum zinc plant based on pyrometallurgical technology. The calcite produced on the roasting would be transported to Tak by road (600 km); also sulphuric acid which will be produced as a by-product from the roasting plant. Copper and cobalt would be returned to Rayong for recovery. The leaching and purification plant at Tak would be modified to the Jarosite process in which the ore is subsequently treated with hot sulphuric acid to dissolve zinc ferrite.

In view of the proposed changes it was agreed that the Terms of Reference be extended to reflect the cessation of silicate ore processing in mid-1994 and the probable introduction of the Jarosite process with its own unique environmental problems.

1.4 Arrangement of report

The report is presented in 10 sections plus a summary. Section 2 summarises the process chemistry associated with present operations including the Cadmium facility. The characteristics of the current "Silicate" ore body are tabulated; also a overall mass balance of inputs and outputs at the Tak site. Section 2 is completed with details of water usage and wastewater generation at the refinery together with a summary characterisation of the wastewater and waste sludges produced.

Section 3 reviews procedures for management and containment of process residues. Current and historic treatment and disposal methods are assessed (particular attention is paid to the method of residue stabilisation using lime). Also assessed are the design philosophies and operating procedures associated with Residue ponds 1 to 5 (assessment of structures, lining and cover materials, provision for leakage and leachate containment etc).

Sections 4 and 5 review relevant procedures and design issues for the management and containment of Cadmium cake and wastewater treatment sludges respectively. The extent of review is similar to that described above for containment of process residues.

Section 6 covers environmental monitoring, complete with a detailed review of data mainly for the two year period 1991-92. Section 6 also includes the results of analysis on samples of soils and waters collected during the survey and the results of leaching tests carried out on samples of residues and wastewater treatment sludges.

Section 7 provides a summary of relevant Thai legislation in relation to hazardous waste management and industrial wastewater discharges to surface waters. Section 7 also discusses relevant international standards and codes of practice for hazardous waste containment in general.

Section 8 describes the proposed process changes scheduled to take effect following exhaustion of the existing silicate ore body in 1994 and discusses environmental impacts concerning disposal of residues and sludges from processing of calcine.

Section 9 documents conclusions and recommendations; such conclusions and recommendations covering past, present and future operations.

1.5 Acknowledgements

Throughout the project the investigation team received full and enthusiastic cooperation from senior and operational management both at the refinery at Tak and the PDI head office in Bangkok. All documents requested were provided and plant/facilities inspections arranged as appropriate. In particular the help of the following personnel is acknowledged:

At the refinery, Tak

. Mr Suraphon	: Vice President - Operations
. Dr.-Ing. Kitisil Kalayanakoul	: Deputy Plant Manager
. Mr Sompong Krzivutinundh	: Assistant Plant Manager (Administration)
. Mr Suwit Uawanichkul Manager	: Research and Laboratory Department
. Mr Suwit Mekvibul	: Technical Service Department Manager
. Mr Suthep	: Environmental Manager
. Mr Boonsom	: Acid and Utility Department Chief Engineer
. Mr Kriangwoot Taecholarn	: Cadmium Plant Manager
. Mr Chatree Srinarawat	: Cadmium Plant Chief Engineer

At the PDI head office

. Dr. Satien Niltawach	: Vice President - Technical
. Dr. Surin Tanticharoenkiat	: Chief Metallurgist

2. PROCESS CHEMISTRY AND PLANT DESCRIPTION - SILICATE ORE

2.1 Ore characteristics

2.2 Process chemistry and outline plant description

Zinc process

Cadmium process

2.3 Water balance and wastewater management

Water balance

Wastewater characteristics

Wastewater treatment and disposal

Wastewater sludge mass balance

2.4 Materials balance and composition of residues

Process residues

Cadmium cake

2 PROCESS CHEMISTRY AND PLANT DESCRIPTION - SILICATE ORE

2.1 Ore characteristics

Silicate ore is extracted by open cast mining at Mai Sot and transported 85 km to the refinery at Tak. During the early years of extraction, the zinc content of the deposit averaged 24 to 25 percent. However, latterly the zinc content has fallen to within the range 18 to 22 percent. Other principal components include:

- . Silica (S_2O_2) 35-45%
- . Iron (Fe) 3-5%
- . Aluminium oxide (Al_2O_3) 10%
- . Calcium (Ca) 2%
- . Cadmium (Cd) 0.1-0.2%
- . Cobalt (Co) < 0.001%
- . Copper (Cu) 0.002%
- . Lead (Pb) 0.01%
- . Magnesium (Mg) 0.8-1.2%
- . Manganese (Mn) 0.2-0.3%

Up to 3 months storage of ore is provided at the refinery site to take account of the fact that mining activity has to be abandoned during the rainy season.

2.2 Process chemistry and outline plant description

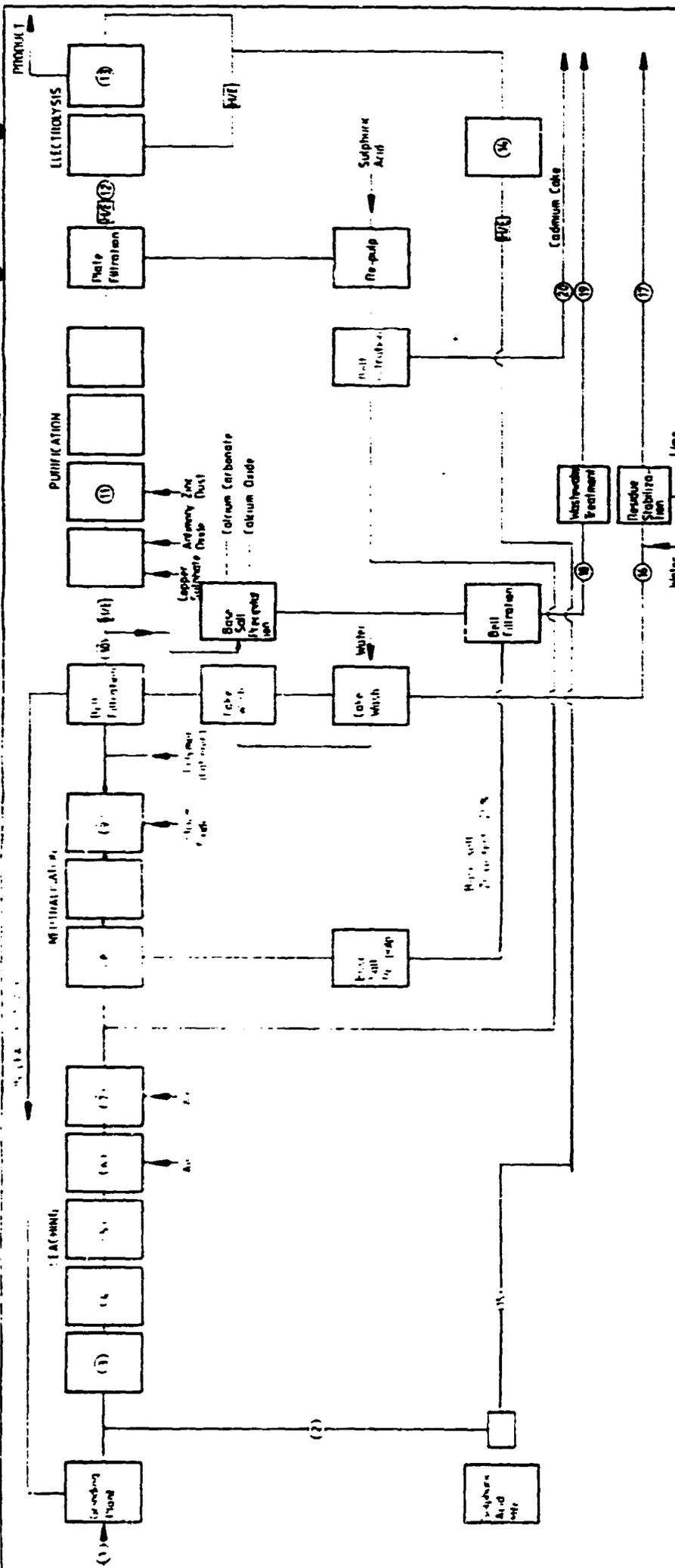
Zinc process

The principal steps involved in the zinc refining process include:

- . grinding;
- . leaching with sulphuric acid;
- . neutralisation;
- . purification; and
- . electrolysis.

The various processing stages are depicted in block diagram form in Figure 2.1, together with key process information.

Leaching to dissolve zinc, iron and other metals takes place in a series of five reactors. Sulphuric acid at 300 g/l strength is mixed with the ore after grinding and the temperature of the mixture raised to about 80 deg C in leach reactor No 1, progressively increasing to 90 deg C by leach reactor No 5. pH is controlled at 3.8 in reactor No 1, 2.5 in reactor No 2 and about 1.5 in reactor No 5. Air is injected to



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	
pH																					
Free acidity																					
Temperature																					
Aluminum oxide (Al ₂ O ₃)																					
Antimony oxide (Sb ₂ O ₃)																					
Artenic (As)																					
Cadmium (Cd)																					
Calcium (Ca)																					
Chromium (Cr)																					
Cobalt (Co)																					
Copper (Cu)																					
Lead (Pb)																					
Iron (Fe)																					
Mercury (Hg)																					
Magnesium (Mg)																					
Manganese (Mn)																					
Nickel (Ni)																					
Silica (Si)																					
Zinc (Zn)																					

ZINC PROCESSING AND REFINING - SILICATE ORE

FIGURE 2.1

reactors 4 and 5 to convert dissolved iron from ferrous to ferric form. The overall reaction time is 4 to 5 hours.

Dissolved iron is precipitated at the neutralisation step of the process. This is carried out in three reactors in series and involves the addition of basic salt to the first reactor (essentially $3 \text{ ZnO ZnSO}_4 \times \text{H}_2\text{O}$ - see below) which increases the pH of the liquor to pH 3 and addition of calcium oxide (CaO) to the third reactor to increase the pH to pH 4. Temperature is allowed to fall to about 80 deg C across the neutralisation step.

Precipitated iron, together with unreacted ore, is then removed by belt filtration to produce filter cake (residue) and filtrate (neutral solution). Unclear filtrate (ie first stage filtrate) is recycled to the grinding plant. The filter cake or residue is washed with water to recover neutral solution (product). Counterflow techniques are used to improve efficiency and reduce water input flows. Washed residue is discharged to the stabilisation plant (see below) prior to disposal to contained storage.

A proportion of the clear filtrate (together with a proportion of the wash liquors from the residue belt filters) is diverted to the basic salt circuit. This involves addition of calcium oxide and calcium carbonate to raise the pH to about pH 6 and results in the precipitation of basic salt, which is removed by belt filtration and returned to the neutralisation plant (reactor No 1) after re-pulping with neutral solution.

Filtrate from the basic salt belt filters is discharged to the wastewater treatment plant (see below) prior to disposal to lagoon storage.

Typically neutral solution contains:

·	Zinc (Zn)	135 g/l
·	Cadmium (Cd)	600-1000mg/l
·	Copper (Cu)	11-12 mg/l
·	Cobalt (Co)	1-2 mg/l
·	Nickel (Ni)	10-12 mg/l
·	Magnesium (Mg)	16 g/l
·	Calcium (Ca)	500-600 mg/l
·	Iron (Fe)	4-5 mg/l
·	Lead (Pb)	0.6 mg/l

In relation to iron removal the target is to maintain a dissolved iron content in neutral solution of less than 10 mg/l.

Neutral solution after heat exchange to increase temperature to 90 deg C is subjected to a single stage purification process (in four reactors in series) to remove the metals cadmium, nickel, cobalt and copper by cementation technique using zinc dust. In addition:

- copper sulphate (CuSO_4) is added to activate zinc dust so as to remove nickel easier; and
- antimony oxide (Sb_2O_3) is added to assist in the precipitation of cobalt.

All precipitates are removed by plate filtration, the purified liquor then being cooled to 35 deg C before transfer to the cell house for zinc recovery.

Typically purified solution contains:

Zinc (Zn)	135 g/l
Cadmium (Cd)	< 1 mg/l
Copper (Cu)	< 1 mg/l
Cobalt (Co)	< 1 mg/l
Nickel (Ni)	< 0.02 mg/l
Magnesium (Mg)	16 g/l
Iron (Fe)	< 10mg/l

Filter cake which contains the metals cadmium, copper, cobalt and nickel is re-pulped in sulphuric acid and then re-filtered on belt press units to produce cadmium cake, transferred to cadmium recovery (see below), and filtrate which is recycled to the processing circuit immediately upstream of the neutralisation plant.

The magnesium (Mg) content of purified solution is critical and must not exceed 20 g/l in order not to affect the efficiency of the electrolytic process.

This has resulted in a need to increase the rate of "bleed off" of filtrate (ie wastewater from the basic salt circuit) because the magnesium content of the ore body has progressively increased over recent years.

Manganese oxide (MnO) is added to the purified solution to give a concentration of 3 g/l in the electrolyte. This is to protect lead (Pb) in the anode.

Spent electrolyte is recirculated to the leaching plant after heat exchange to increase the temperature to 80 deg C plus and, after addition of fresh sulphuric acid, to increase the acid strength to 300 g/l.

Cadmium process

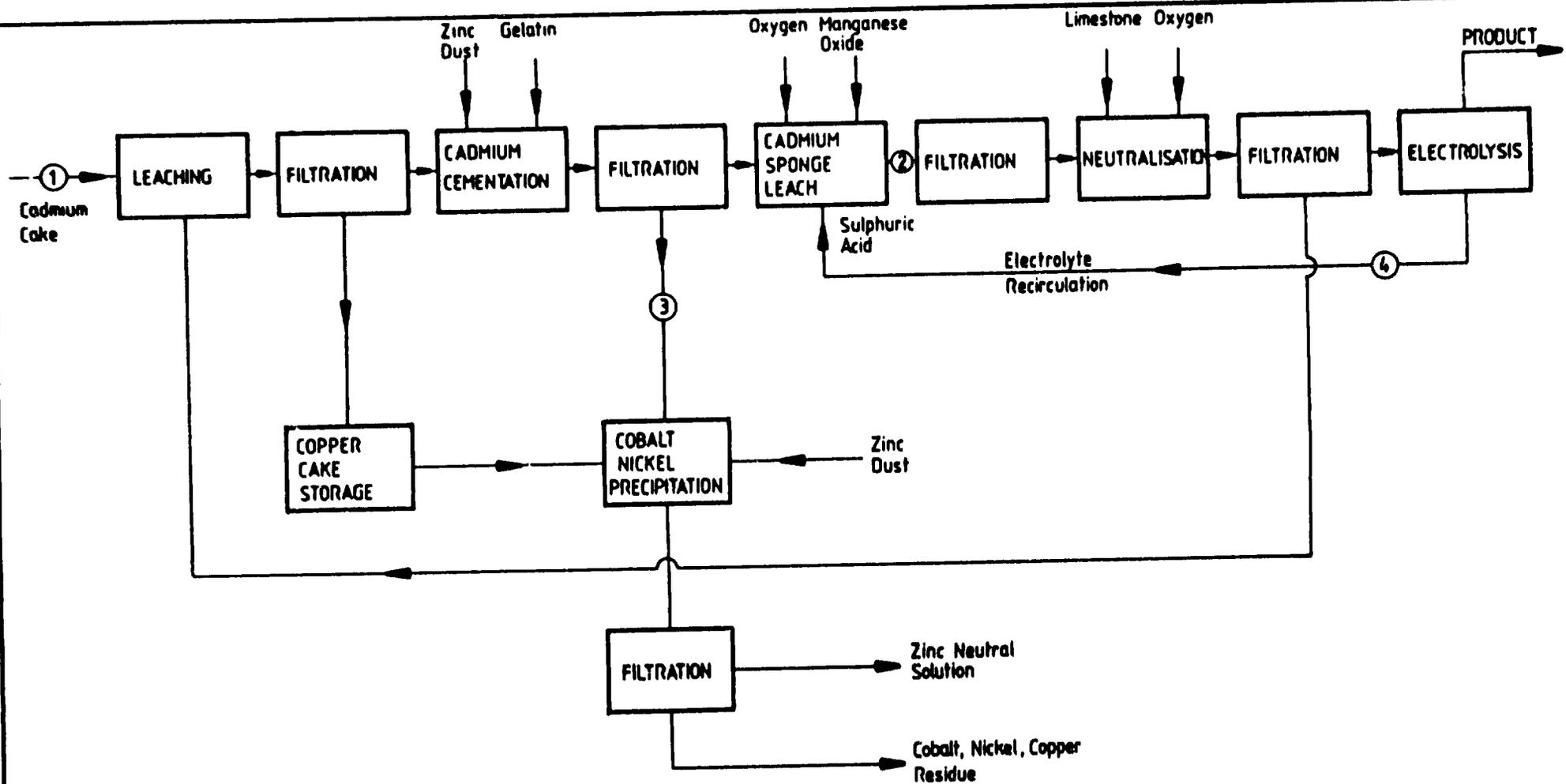
The principal steps involved in the cadmium refining process include:

- re-dissolution of cadmium, cobalt and nickel in sulphuric acid;
- cementation of cadmium to produce cadmium sponge leaving cobalt and nickel in solution;
- re-dissolution of cadmium by sulphuric acid leaching;
- neutralisation;
- electrolysis.

The various processing steps are depicted in block diagram form in Figure 2.2, together with key process information.

Leaching to dissolve cadmium, cobalt and nickel is carried out at 70 deg C and at an oxidation-reduction potential (ORP) of -200 mV. At this ORP copper is not re-dissolved and is separated as copper cake by filtration.

The cadmium, cobalt, nickel solution then passes to a cementation process where zinc dust is added together with gelatin, to precipitate cadmium but not cobalt and nickel.



	1 CADMIUM CAKE	2 CADMIUM SPONGE	3 ZINC SOLUTION	4 ELECTROLYTE
Cadmium	24.6%	70-80%	< 1%	50g/l
Copper	5.8%			
Cobalt				
Nickel	0.68%			
Zinc	18.9%	30-20%		30g/l
Free Acidity				2g/l

CADMIUM PROCESSING AND REFINING - SILICATE ORE

FIGURE 2.2

Cadmium precipitate is separated by filtration as cadmium sponge, whereas the filtrate from the cementation process is mixed with the copper cake formed previously and dosed with zinc dust to precipitate a cobalt, nickel, copper residue. After filtration, the residue is returned to the zinc plant for disposal with the main plant residue.

The zinc-rich filtrate from the cobalt-nickel-copper precipitation process is also returned to the zinc plant but in this case is recovered by mixing with neutral solution.

Cadmium sponge is leached with electrolyte sulphuric acid at 2 g/l strength; oxygen and manganese oxide being added to control the oxidation state and prevent evolution of hydrogen gas. Residual "sponge" is recycled to the initial leaching process. Cadmium solution is neutralised with limestone and filtered prior to passing forward to the cell plant for cadmium recovery.

2.3 Water balance and wastewater management

Water balance

Water is abstracted from the Ping River and used for a multiplicity of purposes including:

- . process and plant cooling
- . steam generation
- . ore and limestone grinding
- . reagent mixing
- . filter belt and cake washing
- . filter press cleaning
- . floor and plant washing
- . domestic purposes

An overall water balance for the site is detailed on Figure 2.3. The balance is based on an abstraction rate of 250 m³/h (6000 m³/d) of which:

- . 145 m³/h (3840 m³/d), or 58 percent, is used for process purposes, including steam generation;
- . 55 m³/h (1320 m³/d), or 22 percent, is used for non-process industrial purposes, mainly cooling but also lawn watering;
- . 40 m³/h (960 m³/d), or 16 percent, is used for domestic purposes;
- . 10 m³/h (240 m³/d), or 4 percent, is used for servicing the raw water treatment plant.

By far the largest process water use is for filter belt and cake washing in the leaching plant area. The balance shows a consumption of 69 m³/h (1656 m³/d) for this purpose. The bulk of this is discharged as wastewater via the basic salt precipitation circuit ie that use for residue washing and known as the weak or third filtration is treated together with a proportion of neutral solution (second filtrate) to produce a basic zinc salt precipitate. The filtrate from the subsequent dewatering step is discharged as wastewater.

As noted in Section 2.2, the concentration of magnesium passing forward to the electrolyte plant must be controlled below 20 g/l. As the concentration of magnesium in the ore body increases, as has been the trend for a number of years, the rate of circuit bleed-off to control magnesium concentration also needs to be increased. In practise this is achieved by adjusting the hydraulic balance on the basic salt circuit.

The water balance, therefore, and the quantity of wastewater produced is variable depending on magnesium content in the ore body.

The water balance included as Figure 2.3 shows a process wastewater discharge of 74.8 m³/h (1800 m³/d). However, it is understood that this can vary within the range 1500 to 2000 m³/d for the reasons noted above.

Of the 250 m³/h (6000 m³/d) abstracted from the Ping River, about:

83 m³/h (1992 m³/d) or 33 percent is accounted for as treated process effluent;

40 m³/h (960 m³/d) or 16 percent is accounted for as domestic use water;

39.8 m³/h (955 m³/d) or 16 percent is accounted for by evaporation;

57 m³/h (1368 m³/d) or 22 percent is accounted for as non-contaminated effluent which is discharged to the rainwater pond but subject to analysis and diversion to treatment as appropriate;

35 m³/h (840 m³/d) or 14 percent is accounted for as residue moisture content;

2 m³/h (48 m³/d) or 1 percent is accounted for as wastewater sludge moisture content.

Wastewater characteristics

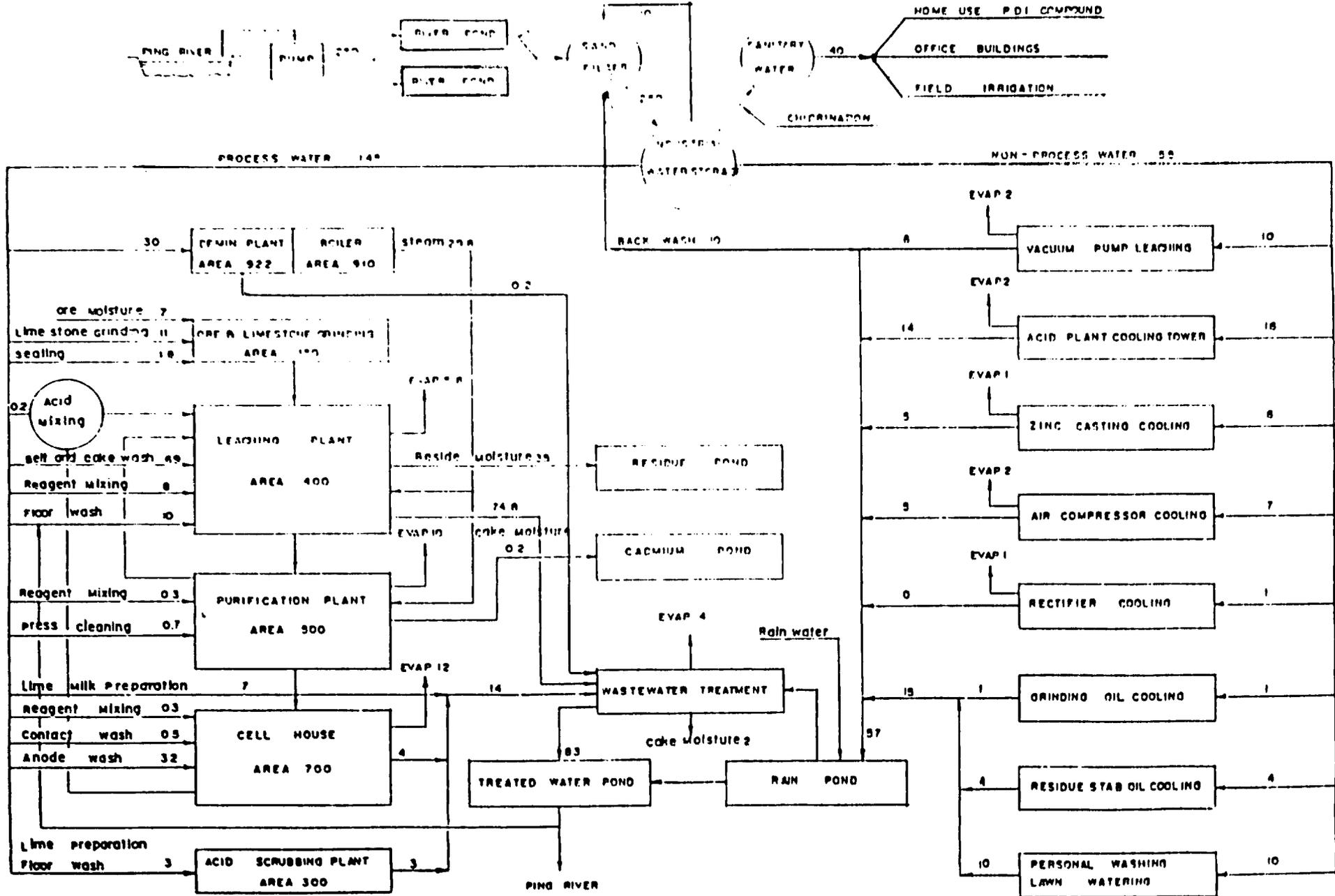
The bulk of process wastewater discharged to treatment originates from the basic salt circuit. Typical characteristics of the discharge from the basic salt circuit are summarised in Figure 2.1 and as follows:

pH	3.0
Cadmium	150 mg/l
Cobalt	< 1 mg/l
Copper	2-3mg/l
Iron	1 mg/l
Lead	< 1 mg/l
Zinc	1000 mg/l
Magnesium	5000 mg/l
Manganese	100 mg/l
Nickel	2mg/l

Other process wastewaters arise from demineralisation plant regeneration, cell house washing liquors and air scrubber plant liquors. However, these miscellaneous discharges are minor in composition terms when compared to the basic salt circuit bleed-off and are unlikely to impact significantly on the composition noted above.

Figure 2.3

PDI WATER BALANCE



PDI WATER BALANCE

UNIT M³/HR

Wastewater treatment and disposal

The wastewater treatment plant is designed to neutralise acidity and precipitate metals by reaction with milk of lime to high pH. Three neutralisation reactors mounted in series are provided, each with mixing, pH control and lime dosing facilities.

A polyelectrolyte is dosed to the neutralised mixture prior to transfer to a 300,000 m³ capacity neutralisation pond where settlement of precipitated metals and other suspended solids takes place.

Supernatant liquor from the neutralisation pond is discharged to a 550 m³ capacity settlement tank followed by two further pH control tanks designed for acid addition to trim pH to within the range pH 6-9 as required by the MOI prior to disposal to river via a 20,000 m³ capacity treated water pond.

The overall treatment system for process wastewaters is depicted in flow diagram form in Figure 2.4.

Wastewater sludge mass balance

Treatment of process wastewaters with milk of lime to high pH substantially precipitates the metals cadmium, copper, zinc and nickel as insoluble hydroxides. Magnesium and manganese also are precipitated. The sludge retained in the neutralisation pond therefore comprises mixed metal hydroxides in the proportions present in the combined process wastewater input to the plant up to a total solids concentration of about 10 percent depending on the extent of water loss achieved by evaporation.

Based on a typical net process wastewater discharge volume of 1992 m³/d and assuming typical concentrations as summarised above, the total quantity of sludge solids produced per day would amount to about 12 t/d on a dry weight basis.

This is equivalent to a volume loading of 120 m³/d assuming, as best case, the achievement of a partially dewatered cake containing 10 percent solids. As 5 percent solids content the volume loading on the system would be about 240 m³/d.

2.4 Materials balance and composition of residues

Process residues

The total quantity of process residues produced presently amounts to about 900 to 1000 t/d on a dry weight basis or about 1800 to 2000 t/d a wet weight basis. This compares to a disposal requirement for about 1000 t/d wet residues during the early years of the development when:

- production was based on 60,000 t/a zinc ingot compared to a present level of 73,000 t/a;
- the zinc content of the silicate ore body averaged 25 percent compared to a present day average of 17-18 percent.

The residues produced comprise:

an insoluble fraction, essentially unreacted ore body including $ZnOSiO_2$ and unreacted Fe_2O_3 , also ferric hydroxide as precipitated from the leach liquor during the neutralisation stage of the refining process;

a soluble fraction essentially sulphates of zinc, cadmium, cobalt, copper and nickel in the same concentration ratios as present in neutral solution but substantially diluted because of the various wash stages.

On a soluble basis only and assuming a water content of 50 percent, that is 1000 m³/d, the weight of metals discharged can be assumed as follows:

Zinc	5000 kg/d	(5000 mg/l)		
Cadmium	30 kg/d	(30 mg/l)	Cobalt	< 1 kg/d
Copper	0.5 kg/d	(0.5 mg/l)		
Nickel	0.5 kg/d	(0.5 mg/l)		

However all process residues are now stabilised with lime (Section 3 refers). If properly carried out this would have the effect of precipitating soluble metals as their insoluble hydroxides and thereby substantially reducing the total concentration of metals still held in solution.

Cadmium cake

Since November 1990 all cadmium cake produced as by-product to zinc production has been refined electrolytically on-site to cadmium. The plant has a design capacity of 2.4 t/d (850 t/a) although throughput presently is only 1.5 t/d (540 t/a), that is based on a cadmium content in silicate ore body of between 0.1 and 0.2 percent.

Prior to commissioning of the cadmium refinery in November 1990 all cadmium cake produced was stored as cake (Section 4 refers). On a wet weight basis such cake is reported to have the following composition:

Cadmium	24.6%	
Copper		5.8%
Nickel	0.68%	
Zinc	18.9%	

In addition the moisture content of the cake (estimated to be about 60 percent) would contain soluble zinc at the concentration of zinc in purified solution.

On this basis a typical cadmium cake production level of 1.5 t/d would have produced a wet cake loading of 3 t/d containing about 0.3 t/d of soluble zinc.

3 CONTAINMENT OF PROCESS RESIDUES

3.1 Method of approach

General

Period 1: 1986-87

Period 2: 1988 on

3.2 Assessment of "lime stabilisation" process

General considerations in stabilisation technology

Methods of process assessment

Assessment of PDI process

3.3 Arrangement of ponds and present status

3.4 Pond design basis and assessment of integrity

Basic design philosophy

Assessment of structures

Assessment of lining materials and method of application

Assessment of cover materials (Ponds R1 and R2 only)

Provision for leak detection and control of under-drainage

Provision for control of surface water run off

Provision for control of leachate

3 CONTAINMENT OF PROCESS RESIDUES

3.1 Method of approach

General

Since the refinery was commissioned in 1986, process residues have been stored on-site in a series of large impoundment lagoons. To date, six such lagoons have been constructed (R1 to R6) providing a total potential storage capacity of $4.6 \times 10^6 \text{ m}^3$, of which approximately $3 \times 10^6 \text{ m}^3$ (65 percent) has been taken up.

Period 1: 1986-87

During the first two years of plant operation, process residues were disposed of directly to impoundment reservoir following discharge from the belt filters as a friable cake. The cake had a moisture content of about 50 percent that is after cake washing as described in Chapter 2 but without stabilisation treatment. The first two ponds used (R1 and R2) essentially are filled with non-stabilised residue. The nature of the residue is as described in Chapter 2, Section 2.4, that is 50 percent solids (essentially unreacted ore and precipitated ferric hydroxide) and 50 percent moisture; the latter containing the range of soluble metals and other components generally found in "neutral" solution.

In addition, Period 1 covered the time of initial plant operation when the overall process efficiency was at a relatively low level, that is before the leaching, neutralisation and purification processes had been fully optimised.

In view of the relatively high zinc content of the residue within Pond R1 there is reported to be some potential in reprocessing.

Period 2: 1988 on

Since 1988 most process residues have been stabilised with lime prior to disposal. The process was developed by the R&D department of PDI with some additional input, particularly from Chulalongkorn University. The process involves addition of up to 4 percent lime on a dry weight basis and results in soluble metals within the moisture content of the cake being precipitated as hydroxides. This is followed by reaction of the excess lime with the silica content of the residue to produce a calcium silicate hydrate.

Chemical stabilisation is claimed to be satisfactory when the lime content added exceeds 1.6 percent on a dry weight basis. However, the higher the lime content (up to 4 percent) the greater is the degree of stabilisation. Curing time is reported to be about 2 days.

For various reasons, including mechanical breakdown of the lime mixing/blending plant, some non-stabilised sludge is produced from time to time. Non-stabilised sludge is deposited in semi-fluid form in a temporary lagoon (currently R4) and reprocessed at a later date.

3.2 Assessment of "lime stabilisation" process

General considerations in stabilisation technology

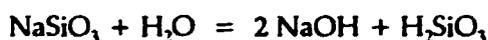
Stabilisation is the process whereby a hazardous waste is converted into another form by chemical means making it unavailable to the environment on a long term basis. Solidification is the conversion of a liquid, sludge or semi solid into a solid form. However, solidification does not guarantee stabilisation and the terms 'solidification' and 'stabilisation' are often used synonymously although they mean different phenomena.

Many stabilisation processes are not able to deal effectively with relatively small quantities of "organic" contaminants in primarily inorganic waste types and this is an important consideration in assessing the potential viability of stabilisation.

What brings about stabilisation is the solution and precipitation chemistry of the water (for metals) and the partition coefficient and bonding phenomenon between the waste and the binder.

A meaningful approach to stabilisation involves an understanding of such fundamental chemical concepts as pH, solubility, solubility product constant, partition coefficient and types and nature of chemical bonding. An examination of solubility product constants provides the form which a given waste must be converted.

One potential complication with stabilisation technology involves the use of alkali metal silicates as binder additives. However, the chemistry of alkali metal silicates indicates that their addition can sometimes do more harm in a stabilisation process. The alkali metal silicates are essentially salts formed by a weak acid (eg Silicic acid H_2SiO_3) and a strong base (eg sodium hydroxide NaOH) represented by:



When such salts come into contact with water they immediately dissociate into the base and the acid, resulting in a strongly alkaline medium.

Amphoteric metals such as zinc, aluminium, selenium, arsenic and lead potentially leach out as their respective anions.

Under these circumstances use of alkali metal silicates should be avoided.

Methods of process assessment

To overcome many of the doubts and problems associated with the stabilisation technology a testing protocol has been established, particularly in the USA and Canada.

Technical criteria normally used to evaluate the effectiveness of stabilisation processes include contaminant mobility based upon:

- extraction, leaching and permeability tests; and
- structural integrity of solidified material based upon measurement of physical properties.

Environment Canada and the US EPA have developed and validated 16 laboratory test methods for evaluating the physical and chemical properties of stabilised wastes.

These 16 tests comprise:

- . 7 No physical tests
 - bulk density
 - specific gravity
 - moisture content
 - hydraulic conductivity
 - unconfined compressive strength
 - freeze/thaw weathering resistance
 - wet/dry weathering resistance

- . 5 No chemical or leaching tests
 - equilibrium extraction
 - toxicity characteristics leaching procedure
 - acid neutralisation capacity
 - sequential neutralisation capacity
 - dynamic leach test

- . 4 No micro morphological evaluation methods
 - x-ray diffraction
 - scanning electron microscopy
 - energy dispersive x-ray analysis
 - optical microscopy

A minimum of four replicates is recommended for the chemical or leaching tests and, depending on the desired application of the results, more replicates may be required to attain greater precision.

The test methods were chosen for full characterisation of the chemical and physical factors that affect the leachability of a waste from:

- . the degree of chemical immobilisation of the contaminants, that is contaminant speciation and solubility under various conditions and acid neutralisation capacity;

- . the degree of physical immobilisation of the contaminants, that is contaminant mobility in the solidified matrix;

- . the potential for contact of groundwater with the waste, that is matrix hydraulic conductivity, strength and weathering resistance.

It is likely that the US EPA/Environment Canada protocol for assessment of stabilised water could become an international norm.

Assessment of PDI process

The PDI stabilisation process appears to suffer from none of the disadvantages noted at the beginning of this sub-section above. The addition of lime to the re-pulped residue (at dose levels of about 4 percent on a dry weight basis) appears to produce a well stabilised end product with minimum potential for leaching. The absence of any organic components is a major advantage in this case.

The efficacy of the PDI stabilisation process was assessed in three ways. Firstly, a report dated 1989 from the Metallurgy and Materials Science Research Institute of Chulalongkorn University has been reviewed (Appendix A refers). This report concluded that the results of a toxicity test based on procedure documented by the MOI showed that the 4 percent lime stabilised ore residue from PDI leached out only very small amounts of heavy metals when compared to the standard issued by MOI and that the residue could be classified as non-hazardous on that basis. In addition, the results of a Shake Test demonstrated similarly that leaching from a 4 percent lime stabilised residue was significantly lower than the MOI standard.

Secondly, the results of ongoing tests carried by PDI were assessed and similar conclusions to the above report were arrived at (Chapter 6 refers).

Thirdly, independent leaching tests were carried out as part of this investigation and these again demonstrated the efficacy of the PDI stabilisation process (Chapter 6 refers).

The overall conclusion is that the PDI stabilisation process, if correctly carried out, produced a residue with very low leachability potential and satisfactory physical characteristics. Such residues essentially can be considered non-hazardous and long term storage poses minimum risk to the environment, although the potential for water penetration and migration must be minimised to reduce potential long term leachability factors (Chapter 6 refers).

On the other hand the tests carried out at Chulalongkorn University demonstrated that the potential to leach metals from non-stabilised residues is high (due to the significant soluble metal content of the residue mass).

Non-stabilised residues therefore must be considered hazardous and the design of long term storage ponds must be carefully considered, particularly in relation to control of leachate.

Risks associated with embankment failure would relate to the problems of leachate control only since the structural integrity of the ore residue would not likely be affected.

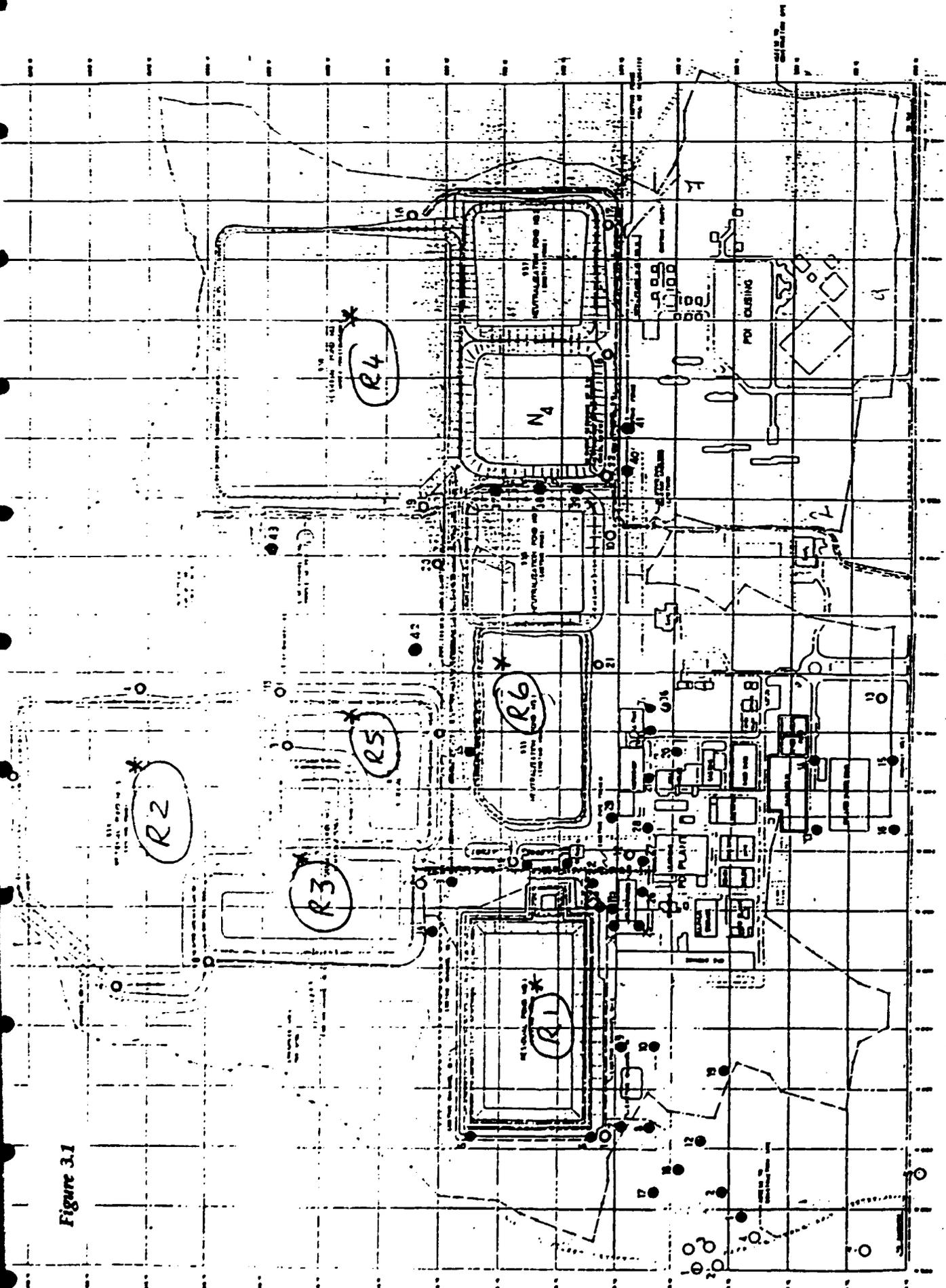
3.3 Arrangement of ponds and present status

The overall layout of ponds for storage of process residues is shown on Figure 3.1. Residue ponds are referenced R1 to R6, whereas ponds for storage of wastewater sludges are references N1, N2, etc.

Table 3.1 - Composition (typical) of Residue in Ponds R1 and R2

	Pond R1 Residue %	Pond R2 Residue %
Zinc (ZnO)	3.01	1.37
Silica (as SiO₂)	37.1	55.8
Aluminium (as Al₂O₃)	7.15	9.83
Calcium (as CaO)	13.78	8.9
Potassium (as K₂O)	1.54	1.51
Titanium (as TiO₂)	0.28	0.03
Magnesium (as MgO)	1.06	-
Sulphur (S)	16.47	7.23
Manganese (as MnO₂)	0.7	0.78
Iron (as Fe₂O₃)	6.63	7.02
Lead (as PbO)	0.33	1.37
Zirconium (as ZrO₂)	-	0.31
Copper oxide (as CuO)	0.01	-

Figure 3.1



In summary the current status of residue ponds R1 to R5 is as follows:

- R1: Full non-stabilised residue (capacity 500,000 m³).
- R2 Full non-stabilised residue (capacity 500,000 m³).
- R3 95 percent full of stabilised and non-stabilised residue (capacity 1.7 million m³). Some dewatering required particularly in one corner.
- R4 20 percent full - stabilised sludge only (capacity 1.3 million m³).
- R5 20 percent full - non-stabilised sludge only, that is used on temporary receptor only prior to reprocessing (capacity 230,000 m³).
- R6 Originally N1 but recently emptied and now used for collection (by pump transfer) of water phase from ponds R3, R4 and R5 (capacity 380,000 m³).

3.4 Pond design basis and assessment of integrity

Basic design philosophy

The design of residue ponds is based on the principle of providing embankment structures to hold the residues according to the specified volume. The design basis is on slope stability analysis so that the embankment can withstand the total pressure of the quantity of residues stored in the pond. The contained residues will apply constant force onto the embankment. This force will be resisted by the passive pressure of the soil below, friction and cohesion as well as surface elements such as vegetation and walls. If the forces tending to cause movement exceed those resisting it, a slide occurs. Slope stability analysis is used to predict such slides before they occur, that is to estimate the safety factor.

Assessment of structures

Design details for residue pond embankment are shown as Figure 3.2. This shows a typical cross-section of the embankment. The side slope of the embankment facing the residue is 1:2, while the side slope of the external side is 1:2.5. There is a key trench about 3 m wide and 1.5 m deep at about 2 m from the centre line of the embankment. The width of the embankment is 3 m and the depth of the embankment varies according to location and elevation of natural soil. The dimensions of each pond are as shown in Table 3.2.

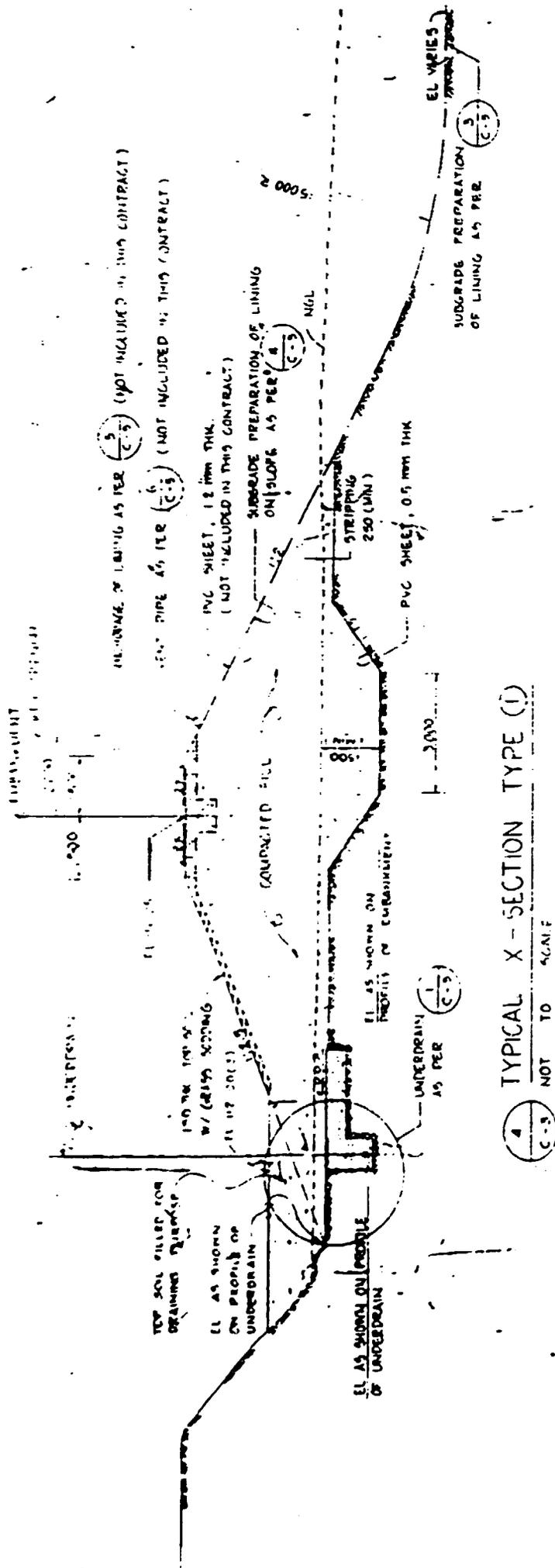
Materials used in the construction of the embankments are selected by the resident engineer. Embankments are constructed in successive layers for the full width of the cross section with each layer not exceeding 20 centimetres in depth. Each layer of material is compacted uniformly until the maximum dry density is obtained. The specification indicates a dry density of 95 percent as determined by AASHTO T-99.

The compaction of selected material to this specification is a common design basis for all small earth-filled dams in Thailand. Slope protection for embankments also follows the same practice. In general, small earth filled dams in Thailand are constructed to heights of between 10 and 30 m and such dams can withstand a certain degree of earthquake shock. Potential for failure will depend:

Table 3.2 - Physical sizing of residue ponds

Pond No	Width (m)	Length (m)	Depth (m)	Volume m ³	Level of embankment (m)	Level of bottom of pond (m)
R1	189.25	332	9.5	507160	116.394	106.894
R2	129	161	9.75	550727	119.2	109.45
	220	269.6				
	126.5	149.4				
R3	168.5	205.25	6.5	1031179	123.5	114 - 120
	131.25	205.25				
	273.25	428.25				
R4	404	471	6.25	1345000	120.75	111
R5	124.5	132	9	276000	123.5	113 - 115
	102.5	261.5				

Figure 3.2



firstly on the strength of soil in the dam itself and in the foundation beneath the dam, that is to ensure sufficient resistance to shearing stress; and

secondly, the potential for seepage of water through the foundation which would create a condition likely to deteriorate the stability of the dam.

In relation to the construction of storage ponds at PDI, the embankments appear well constructed with optimum compaction. The structure beneath the embankment is mainly rock. Also, the method of construction used increased shear strength between normal soil and the embankment. It is considered, therefore, that the stability of the embankments will withstand the pressure of ore residues. Also since the ponds are lined with PVC sheet, which will prohibit water seepage through the ground and embankment structures, the risk of failure of embankments due to water seepage is very low.

However, in common with general practice of embankment design in Thailand, no account has been taken of earthquake risks. This is because Thailand is not in an active earthquake zone, although minor tremors could be experienced from time to time. Figure 3.3 shows a seismological overview of the region. It is apparent that earthquake activities generally are concentrated in southern China, Burma and the Andaman Sea. The seismic probability map supports the view that most of northern Thailand lies in a zone of potential minor damage. However, even if structures are damaged by earthquake activity the stability of the stabilised ore residues is such that the deposit would remain intact. As a result there is little potential risk to water supplies from storage of stabilised residues. Non-stabilised residues also would likely remain stable from a structural point of view. However, risks from leachate discharge would be significant.

Assessment of lining materials and method of application

The lining material used on the residue ponds is PVC sheet (1.2 mm). The PVC sheet used conforms to TIS (Thai Industrial Standard) 575-2528. The sheets are bonded together by hot air welding with vacuum test overlap with of 150 mm. Prior to PVC lining the subgrade is prepared to provide appropriate conditions for the lining. Such subgrade preparation is well graded and compacted. PVC sheet is then laid at the bottom of the pond prior to residue being deposited. New lining initially is kept in place using sand bags placed at intervals on top of the PVC sheeting.

The consultants conclude that the method of lining of ponds with PVC sheet essentially is adequate for protection against possible entry of leachate into groundwater. However some leakage is still possible. For example, the weight of trucks and tractors may damage the PVC sheet and this would be difficult to detect on an ongoing basis.

It should be noted that R1, the first residue pond, was lined with asphalt sheet (5 mm). There is doubt over the integrity of asphalt sheet on a long term basis. In addition the residues in R1 were not stabilised and leakage could, in the longer term, be a problem.

Assessment of cover materials (Ponds R1 and R2 only)

At present, only two residue ponds are covered. Pond R1 was first covered with 50 to 100 cm of top soil and then later covered with 1.2 mm PVC sheet. After that about 1 m of top soil was used to cover the whole pond. Around the periphery of the

embankment a gutter was constructed to collect rainwater followed by controlled discharge to a ditch running around the outside of the residue pond. A similar procedure was used for pond R2 except that in this case top soil has yet to be provided over the PVC sheet. The consultants understand that the reason for not covering with top soil is that in the future the ore residues may be reprocessed for zinc recovery. Theoretically the installation of a PVC 1.2 mm cover sheet should prevent rainwater ingress to the pond. However tractors loading top soil onto the sheet could cause damage. Also considering the large area involved, achieving a 100 percent seal would be difficult to achieve.

Provision for leak detection and control of under drainage

All ponds are provided with under drains which collect at strategic points in order to observe/detect any leakage arising from a pond. This construction detail is also shown in Figure 3.2. PVC pipe (150 mm) is laid under and along the embankment. The PVC pipework conforms with TIS 17-2523 class 8.5. The pipes are perforated with slots sized 100 x 6 mm, laid in the underdrain system consisting of coarse aggregate and fibre filter material which allows water to flow freely into the perforated pipe. All water collected in this way is pumped to the main collection pond R6 and returned to process. The design principle is satisfactory.

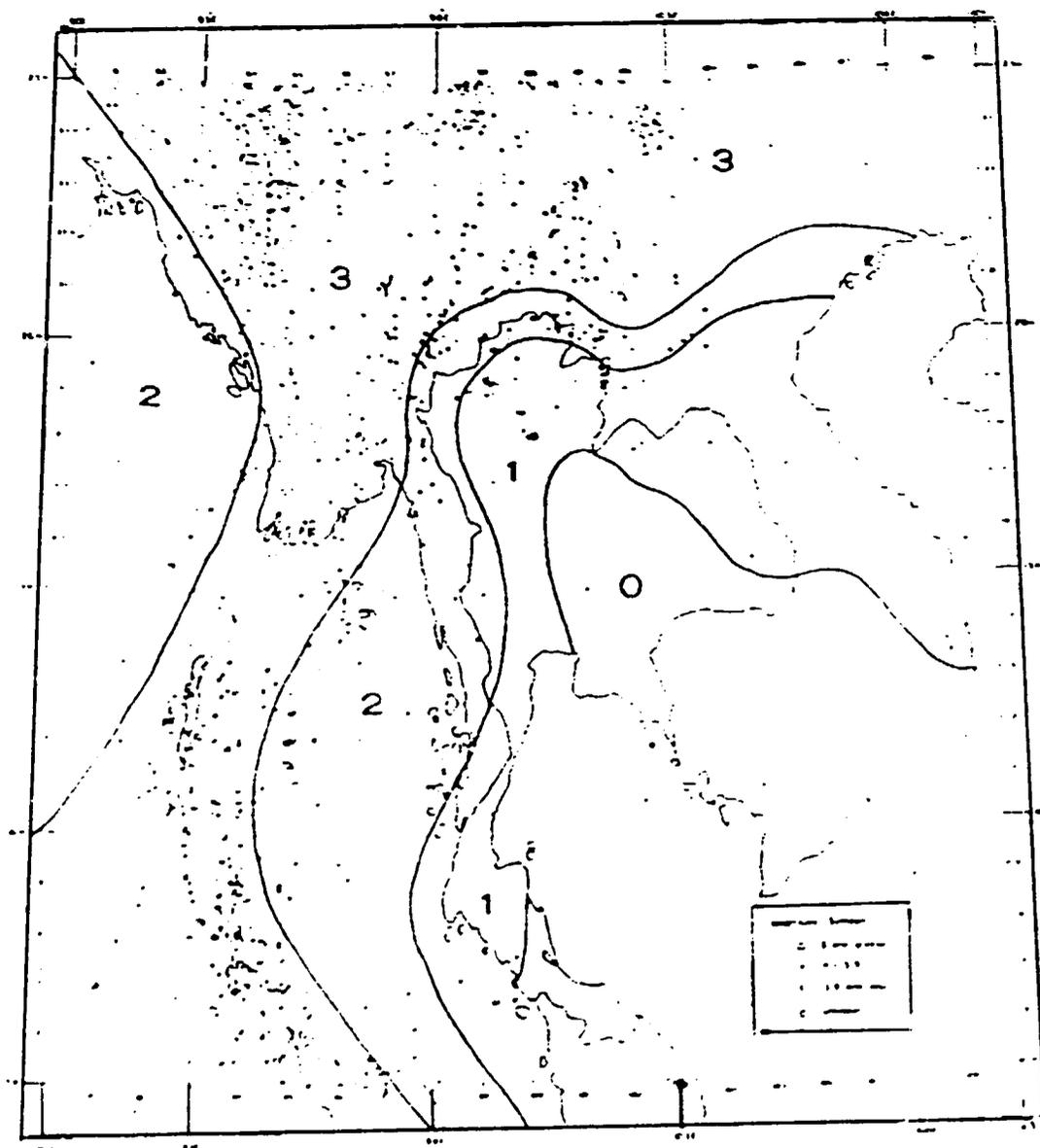
Provision for control of surface water runoff

Surface water runoff from residue ponds R1 and R2 first collects in the gutter on top of the embankment as noted above and then overflows via specific overflow channels into the open ditch running around the outside of the pond and then, via a surface water channel, to the River Ping. The discharge channel is controlled by a sluice gate. It was stated by PDI that the water in the ditch is checked at the start of the rainy season. If the water quality is satisfactory the sluice gate will be opened. If the quality exceeds effluent standards, the water will be pumped back to pond R6 together with any under-drainage water.

Provision for control of leachate

Since the water content of the ore residue is high (about 50 percent), airborne dusts are not anticipated within the pond area. However, spillage of ore material along roadways could become a problem when evaporative drying is complete. Such potential risks are controlled by periodically spraying water from road tankers. There is no provision for collection of leachate from ponds already filled with residue and covered. As noted above, water ingress to such ponds cannot be prevented and remedial action probably will be required in this regard.

Figure 3.3



Seismicity Map of Thailand and adjacent areas
(After Natalaya and others, 1985) & Earthquake
Probability Legends (Modified from EGAT, 1984)

Zone 0 = No damage Zone 2 = Moderate damage
Zone 1 = Minor damage Zone 3 = Major damage

4 CONTAINMENT OF CADMIUM CAKE

4.1 Background and method of approach

Background
Proposals for processing cadmium cake

4.2 Storage pond design basis and assessment of integrity

Basic design philosophy
Assessment of structures
Method of construction and materials
Assessment of cover materials
Provision for leak detection and control of under-drainage
Provision for control of surface water run-off
Provision for control of leachate

4 CONTAINMENT OF CADMIUM CAKE

4.1 Background and method of approach

Background

Cadmium is a significant by-product of zinc processing and refining. The base material, cadmium cake, is produced as a precipitate during purification of zinc neutral solution. Cadmium cake, which has a moisture content of between 50 and 60 percent and which also contains the metals copper, cobalt, nickel and zinc, has a composition (on a wet weight basis) typically as follows:

·	Cadmium (Cd)	24.4%
·	Copper (Cu)	5.8%
·	Nickel (Ni)	0.68%
·	Zinc (Zn)	18.9%

Since November 1990 all cadmium cake produced has been refined electrolytically to cadmium metal.

However, all cadmium cake produced before November 1990 is stored on-site in two reinforced concrete basins.

Proposals for processing cadmium cake

PDI's intention is to process all stored cake into cadmium metal and this could be achieved using the spare capacity on the refining plant already installed, that is by increasing the throughput of cadmium metal from 1.5 to 2.3 t/d.

However, because the world market price for cadmium metal presently is lower than the actual cost of production, there has been no incentive to process the cadmium cake produced before the new plant was installed.

Presently, it is estimated that 8000 t of cadmium cake are stored on-site, containing about 2000 t of cadmium metal. Based on present production levels therefore, it would take 2500 days or 7 years to clear the backlog.

However, after conversion to calcine feed material in mid-1994 (Section 8 refers), the normal throughput on the cadmium plant will reduce to 1 t/d, compared to an available capacity of 2.3 t/d. This would have the benefit of reducing the time required to clear the backlog from 7 to 5 years (assuming a start date of mid-1993).

4.2 Storage pond design basis and assessment of integrity

Basic design philosophy

The design philosophy adopted for the cadmium ponds is similar in concept to that used for the residue ponds (Section 3 refers). However, a double membrane has been used, comprising a layer of reinforced concrete and PVC sheeting.

With the reinforced concrete lining the basic strength of the structure is increased in relation to slope stability, although the design of the external slopes is similar to that used on the residue ponds.

Assessment of structures

Some detail on the design of the cadmium ponds is shown in Figure 4.1. The figure shows the plan of the ponds with cross-section. The side slope of the internal embankment is 1:1.75, whilst the side slope of the external embankment is 1:2. There is a "key" trench 3 m wide underneath the embankment. The width of the embankment is 4 m and the depth is 4 m. There are two ponds each 2 m wide and 45.3 m long.

Method of construction and materials

The method of construction adopted is essentially similar to that for residue ponds R1 to R6; only the lining is different.

The principal components of the construction are:

- . subgrade preparation;
- . installation of 1.2 mm PVC sheet;
- . application of 5 cm lean concrete on top of the PVC sheet;
- . application of 25 cm thick reinforced concrete.

One point of concern in relation to the design and method of construction is the potential risk that the concrete could crack on temperature changes; also that any construction joints may be potential weak points allowing water input to and/or output from the pond. In addition, the cadmium cake has a high sulphate content and this could affect the integrity of the concrete.

Assessment of cover materials

The ponds presently are covered with PVC sheet. However, the overall covering is inadequate because some areas are exposed to atmosphere. In addition water, from previous rainfall precipitation, was still evident (in pockets) on top of the PVC sheeting.

There is potential, therefore, for water to enter the two basins, particularly around the edges, and for leachate subsequently to overflow to adjacent surface water drainage channels. In addition, the practice of piling cadmium cake on top of the pond will aggravate the tendency for rainwater to flow to the edges of the ponds.

Provision for leak detection and control of under-drainage

An under-drainage system similar to that provided on the residue ponds is installed complete with pump sump. Any "water" collecting in the sump is transferred for re-processing.

Provision for control of surface water run-off

The control of surface water run-off is not appropriate in this case. Any excess rainwater will overflow the embankment and gravitate to an adjacent surface water ditch. If the pond was adequately covered and protected this would not be a major issue. However, with the present arrangements, contamination from leachate overflow is possible.

Figure 4.1

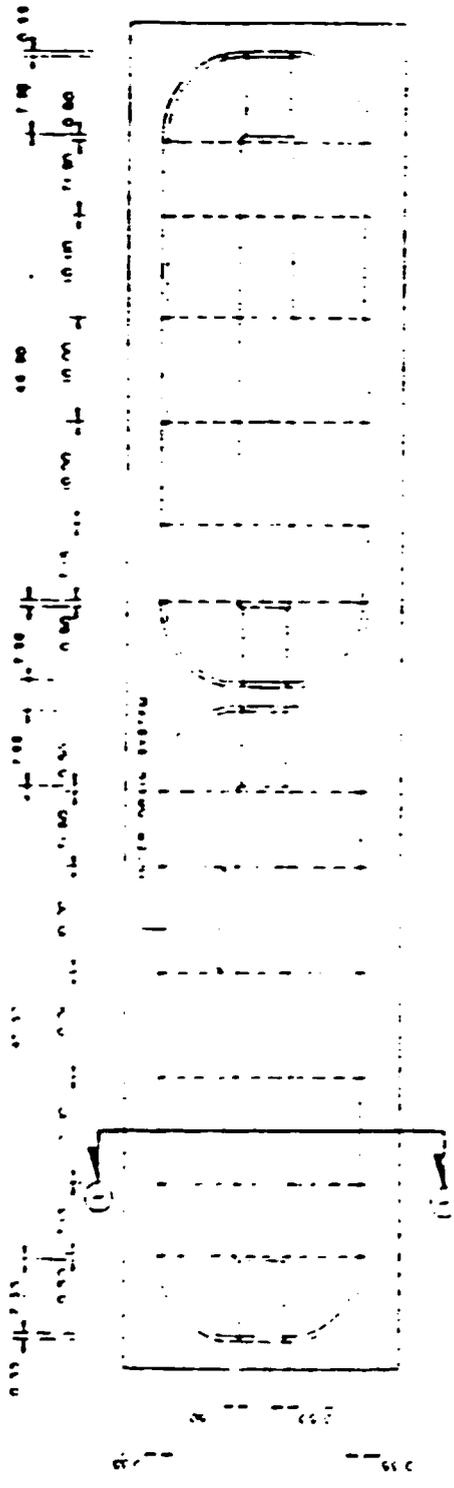
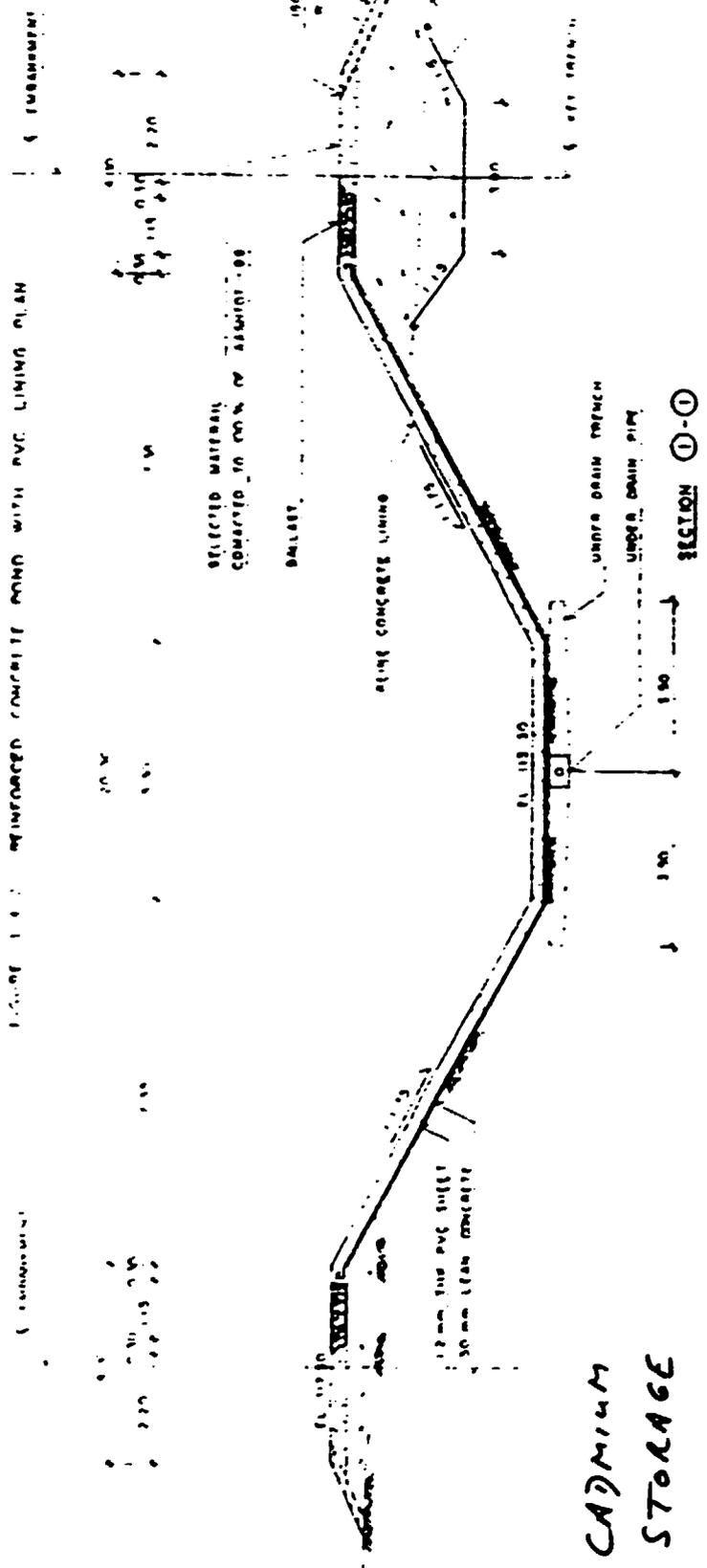


FIGURE 4.1 REINFORCED CONCRETE TANK WITH PVC LINING PLAN



CADMIUM STORAGE

SECTION 1-1

Provision for control of leachate

There are no installed procedures for collection and control of any leachate arising from the cadmium ponds.

5 CONTAINMENT OF WASTEWATER TREATMENT PLANT SLUDGES

5.1 Method of approach

5.2 Factors influencing solubility of metals

5.3 Arrangement of ponds and present status

5.4 Pond design basis and assessment of integrity

Basic design philosophy

Assessment of structures

Assessment of lining materials and method of construction

Provision for leak detection and control of under-drainage

Provision for control of leachate

5.5 Proposed combined Residue + Sludge stabilisation plan

5 CONTAINMENT OF WASTEWATER TREATMENT PLANT SLUDGES

5.1 Method of approach

Wastewaters arise principally from the basic salt circuit (Section 2 refers) and contain a range of dissolved metals, principally zinc and cadmium. Treatment comprises neutralisation of acidity and precipitation of metals using lime reagent followed by discharge to PVC-lined impoundment lagoons for settlement and containment of precipitated metals and other suspended solids.

The total volume of wastewater treated in this way presently varies between 1500 and 2000 m³/d, depending largely on the concentration of magnesium in the basic salt circuit (Section 2 refers).

After settlement the aqueous phase is transferred by pump to a radial flow gravity settler (for removal of any suspended solids carried forward from the lagoon) prior to pH correction by sulphuric acid addition and discharge.

Over a period of time the sludges retained in the storage lagoons partially dry out through evaporation. However, the overall extent of "dewatering" achieved is minimal and water inputs following precipitation essentially balance water outputs through evaporation.

5.2 Factors influencing solubility of metals

The overall effectiveness of precipitation of soluble metals as insoluble hydroxides (on alkali addition) depends on a number of factors including:

- . the range of metals present and the potential impact of co-precipitation;
- . the pH at which the neutralisation and precipitation reactions take place;
- . reaction time and ageing factors.

Figure 5.1 depicts solubilities of some metal hydroxides and oxides and this demonstrates the wide variation in pH levels to achieve optimum precipitation of individual metals.

Selection of the optimum pH for precipitation of a range of metals, for example zinc, cadmium, copper, etc is a compromise and some residual solubility could persist. Other factors discussed below include:

- . impact of carbonate formation
- . impact of excess base on re-solubilisation potential

The solid mass end product after lime precipitation of metals often fails leach tests when exposed to the atmosphere. This is because some metal hydroxides exposed to the atmosphere interact with carbon dioxide to form carbonates.

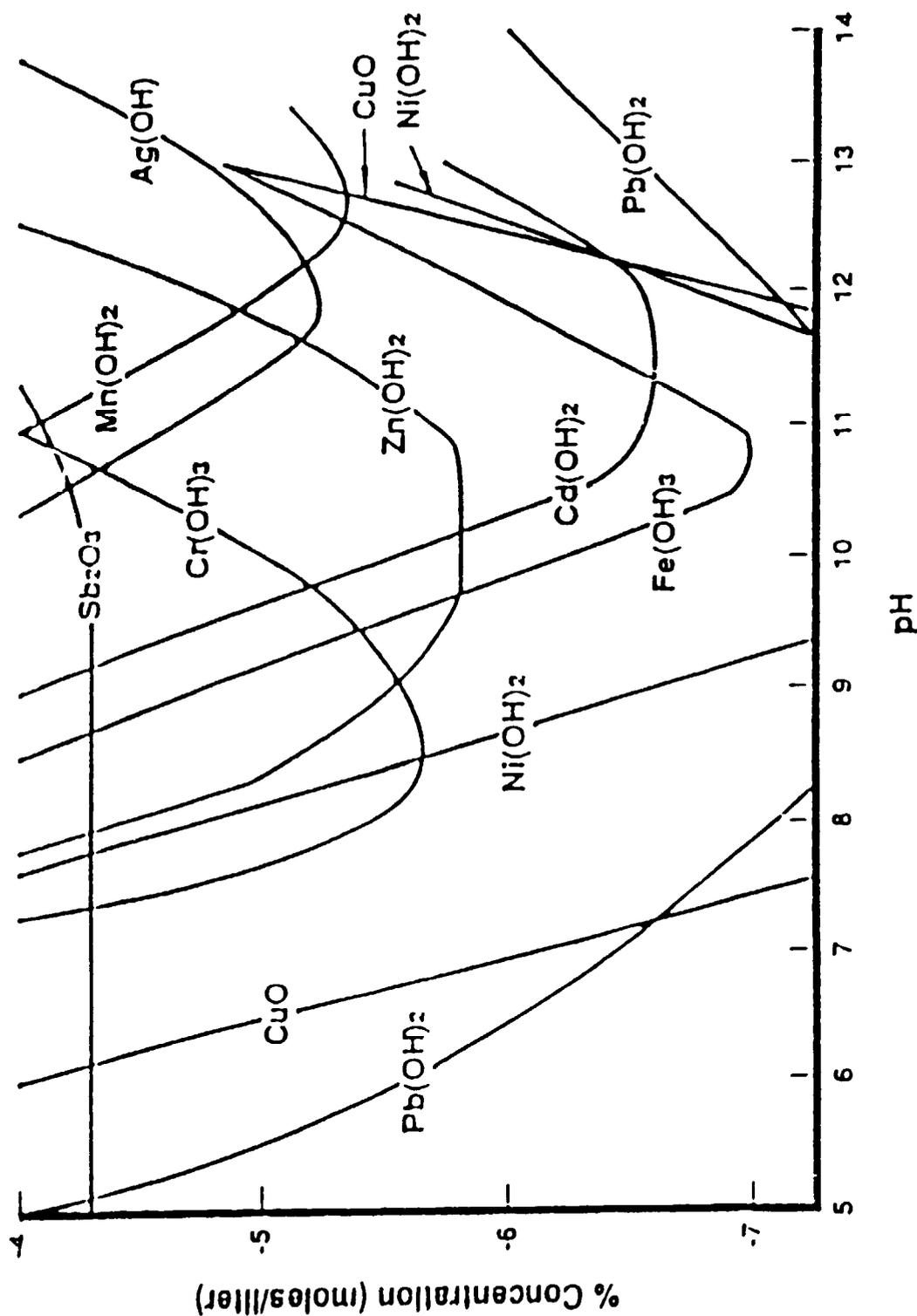
Table 5.1 - Physical sizing of wastewater sludge ponds

Pond No	Width (m)	Length (m)	Depth (m)	Volume m3	Level of embankment (m)	Level of bottom of pond (m)
N1	206.25	307.1	8.7	387364	118.5	110.5 - 111.0
N2	211	215	9.5	288496	116.25	114.0 - 107.0
N3	230	224	10.5	311400	120.75	110.0 - 115.0
N4	230	216	10.5	432079	120.75	108.0 - 110.8

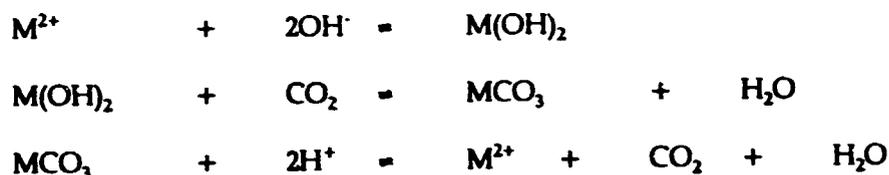
Note Pond N1 has been refurbished as Pond R6

Figure 5.1

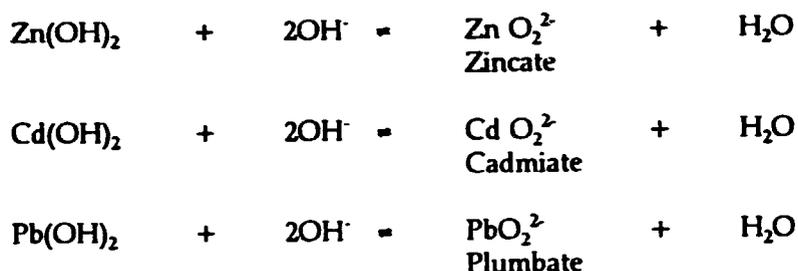
Solubilities of Some Metal Hydroxides and Oxides



Such carbonates are readily soluble in the acid used in leach tests. These reactions are represented by:



The other problem associated with this technique is that several hydroxides (Zinc, Cadmium, Lead) react with excess base to form anionic species that are extremely water soluble. These reactions are represented by:



In such cases the most effective approach is modification of the solution chemistry when the metals are precipitated into a form that does not undergo reversible reaction.

5.3 Arrangement of ponds and present status

To date four lagoons (N1 to N4) have been used for wastewater sludge containment. However, the contents of N1, originally an unlined pond, have been transferred to R3, the pond upgraded through addition of a PVC membrane and re-designated (R6) to provide future storage capacity for process residues.

Accordingly N2, N3 and N4 remain the only lagoons dedicated to the containment of wastewater treatment plant sludges and these provide a total capacity of over 1×10^6 m³ of which about 600,000 m³ (60 percent) has been used up.

The location of ponds N2 to N4 are shown in Figure 5.2. Current status and capacities are summarised below:

- N2: Capacity 288,000 m³. Full and party covered (90%) by top soil including PVC sheeting. Completion of this operation has been prevented by the inherent "liquid" properties of the sludge (see below).
- N3: Capacity 312,000 m³. Full but not covered.
- N4: Capacity 430,000 m³. Recently commissioned. Less than 10 percent full.

The nature of the wastewater treatment process is such that the majority of toxic metals discharged will be precipitated as insoluble hydroxides. However, as noted in Section 5.2 total precipitation will not occur. Also there are risks of re-solubilisation of precipitated metals caused either by carbonate reactions or reactions with excess base

to form soluble zincates and/or cadmiates or the progressive reduction of pH due to the long term influence of rainwater.

The water phase of the retained sludges could be expected, therefore, to contain some soluble metal species.

Furthermore it can be concluded that the moisture content of the retained sludges will remain high in spite of long retention to effect dewatering. This is because metal hydroxide sludges characteristically do not naturally "dewater" to any great extent and, for lagoons provided with bottom PVC membranes, the only mechanism available (after the initial draining of free water) is evaporation. For deep ponds that is 6 to 9 m, evaporation forces will only impact on the top few centimetres of the pond contents. Accordingly, it is unlikely that the average moisture content of the sludges in Ponds N2 and N3 will be less than 90 percent, that is the sludges will remain essentially liquid in nature. Long term storage therefore poses significant risk to the environment.

The fact that the sludges retained in pond N1 (now transferred to pond R3) dewatered to a friable consistency was due to the fact that under-drainage and evaporation forces were present (the pond was unlined).

5.4 Pond design basis and assessment of integrity

Basic design philosophy

The basic design philosophy for wastewater sludge ponds is similar to the design of embankment structures for residue ponds (R1 to R5).

Assessment of structures

The structural design of the wastewater sludge ponds is similar to that for the residue ponds. The detail included as Figure 3.2 therefore also applies to this case. Details of the four wastewater sludge ponds are shown in Table 5.1, although it should be noted that pond N1 has now been emptied, lined with PVC and re-numbered R6 for use in residue storage in future.

Materials used in the construction of the ponds and the actual methods of construction are similar to the residue ponds (Section 3 refers).

In conclusion, the structural integrity of the ponds is considered secure under normal conditions. However, as discussed in Section 3, no account has been taken of possible earthquake activity and under such circumstances there would be risk of embankment failure, that is the embankment could "crack" and "shear". In such an event the contents of ponds N2, N3 and N4 would "flow" because of the high water content of the retained sludges.

This phenomenon has already been observed in pond N2 when attempting to complete the covering of the pond with top soil and PVC sheet. Also, removal of the top surface of the contents of pond N3 during the time of the site survey demonstrated the inherent liquid nature of the sludge layer immediately below the zone of impact of water loss by evaporation.

Embankment failure during the unlikely event of a significant tremor therefore could result in the discharge of a toxic metal sludge, with potential high risk of reaching a watercourse.

Assessment of lining materials and method of construction

The lining material used and method of application is similar to that for the residue ponds (Section 3 refers).

Provision of leak detection and control of under-drainage

Leak detection and control of under-drainage is similar to that provided for the residue ponds (Section 3 refers).

Provision for control of leachate

There is no provision for leachate collection and control from ponds already filled with sludge.

5.5 Proposed combined Residue + Sludge Stabilisation plan

From June 1993, at the specific request of the MOI, it is proposed to lime stabilise residue in admixture with pre-thickened wastewater treatment plant sludges. To this end a clarifier/thickener is being constructed.

Embankment failure during the unlikely event of a significant tremor therefore could result in the discharge of a toxic metal sludge, with potential high risk of reaching a watercourse.

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The lining material used and method of application is similar to that for the residue ponds (Section 3 refers).

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6 ENVIRONMENTAL MONITORING

6.1 Current water management procedure

6.2 Current monitoring procedures and status

6.3 Review of monitoring data

Groundwater observation wells

Deep wells

Under-drainage pump sumps

Process wastewater discharge to Ping River

Water quality in Ping River

Heavy metal accumulation in fish located in final effluent storage pond

Heavy metal accumulation in irrigated soils

Heavy metal accumulation in irrigated soils on the PDI golf course

Heavy metal accumulation in paddy soils

Heavy metal accumulation in sediments in Ping River

Leachate tests on residue

6.4 UNIDO audit programme

Scope of sampling programme

Analysis of water samples

Analysis of soil samples

Leaching tests

6 ENVIRONMENTAL MONITORING

6.1 Current water management procedures

The management and disposal of "water" collecting on or emanating from the site can be summarised as follows:

- . Process wastewaters essentially leave the site as treated effluent discharge to the Ping River or as water used for irrigation of "green" areas immediately surrounding the refinery complex including staff residential areas and the PDI golf course.
- . Water collecting in residue or sludge storage ponds (from natural dewatering of residues and sludges and from leachate arising from precipitation) is transferred either to re-processing or to the wastewater treatment plant.
- . Surface water collecting within the main refinery process area (due to rainfall precipitation) is directed to a rainwater storage pond either for transfer to the final effluent storage pond (and discharge to the Ping River - subject to quality check) or for transfer to the wastewater treatment plant for removal of contaminants.
- . Surface water collecting from precipitation on the remainder of the site that is ponds covered with PVC sheeting and intermediate land areas, leaves the site either through seepage into the soils (and transfer to groundwater) or through discharge to watercourse via drainage ditches routed across the site. No controls are provided except for the drainage ditch to the east of residue pond R1 which is provided with a penstock valve to allow periodic water quality checks to be carried out (particularly at the start of the rainy season).

6.2 Current monitoring procedures and status

PDI currently operate the site to a high level of environmental awareness and management. An extensive quality monitoring programme and protocol is carried out on a regular basis including the following:

- . "water" quality in pond R6 from miscellaneous collection points for example under-drainage pump sumps, leachate, etc (daily);
- . "water" quality in wastewater sludge ponds N3 and N4 (daily);
- . wastewater quality after lime treatment and after primary and secondary solids clarification (daily);
- . wastewater quality after solids removal and acidification (daily);
- . final effluent quality in treated water pond (daily);
- . effluent quality discharged to Ping River (every hour during discharge);
- . "water" quality in the rainwater pond (daily);
- . "water" quality in observation wells (1 x 1 month);

- . "water" quality in deep wells (1 x 3 months);
- . "water" quality in under-drainage pump sumps (1 x 1 month);
- . water quality in the Ping River (1 x 1 month);
- . heavy metals accumulating in fish located in the final effluent pond (1 x 6 months);
- . heavy metals accumulating in irrigated soils (1 x 2 months);
- . heavy metals accumulating in soils on the PDI golf course (1 x 3 months);
- . heavy metals accumulating in paddy soils (1 x 6 months);
- . heavy metals accumulating in sediments in the Ping River (1 x 12 months);
- . leaching tests carried out on process residues (2 x 1 month).

6.3 Review of monitoring data

Groundwater observation wells

A total of 43 groundwater observation wells (OW1 to OW43) has been established by PDI (Figures 6.1 refers), of which 39 are presently operational for at least part of the time. Samples are collected for analysis at intervals of at least once every 3 months. However, in 1992 the sampling frequency was increased to a once per month basis.

The results obtained and recorded by PDI over the period 1991-92 are summarised in Table 6.1.

For each well sampled, the table shows:

- . the number of observations made, that is number of samples analysed;
- . pH range recorded over the period 1991-92, that is maximum and minimum pH values;
- . maximum and average concentrations determined for:
 - zinc
 - cadmium
 - manganese
 - lead
 - total hardness

The results do not show evidence of any significant overall contamination of groundwater. Also examination of the raw data does not show any significant variation or trend in individual results on a month by month basis, that is there is no evidence to suggest build up of contamination with time.

However, in relation to zinc, maximum concentrations of 2 mg/l and above were evident in about 15 observation wells although, with 5 exceptions, averages fell well

below 1 mg/l.

The above conclusions also were established following a hydrogeological study and groundwater quality analysis carried out by SPS Consulting Service Co Ltd in 1989/90. This study involved assessment of changes in actual groundwater levels throughout a period of 12 months, determination of the nature of groundwater flow and a detailed assessment of groundwater quality. A network of observation wells different to those used routinely by PDI was established in grid pattern across the site (Figure 6.2 refers).

The principal conclusions of the study were that:

- . The groundwater table gradually inclines from south-west to north-east with "flow" in the direction of the Ping River.
- . The groundwater flow rates is low with the flow pattern defined as "unconfined flow".
- . The difference in groundwater level between rainy season (August) and winter (November-February) generally ranges between 1 to 2 m (Table 6.12 refers).
- . The concentrations of zinc, cadmium, manganese and lead were found to be very low and well within acceptable limits.

For example, based on the collection of 125 groundwater samples over the 12 month period, the maximum concentrations determined were:

. zinc	0.322 mg/l
. cadmium	0.004 mg/l
. manganese	2.55 mg/l
. lead	0.039 mg/l

With the exception of zinc, the maximum concentrations determined during the SPS survey equate to those determined by the PDI monitoring programme.

In relation to zinc, maximum concentrations higher than 0.322 mg/l were determined in 29 of the 39 operational wells monitored by PDI, although it should be noted (Figures 6.1 and 6.2 refer) that the PDI wells generally are located much closer to the operational part of the site, thus demonstrating that some contamination, albeit minor, is taking place.

Also it shall be noted that it is unlikely that any spillages or losses of contaminated liquors such as leachate would impact significantly on groundwater quality at this stage. This is because of the high exchange capacity of most soils in relation to metals.

For example, the relative mobility of zinc in soil is determined by the same factors affecting its transport in aquatic systems that is:

- . solubility of the compound
- . soil type
- . pH of soil
- . salinity of soil

However, soil chemistry for zinc is governed primarily by the pH of the soil.

In acid soils cation exchange processes influence the fate of zinc and soluble zinc will be taken up on binding sites. When competition for such binding sites occurs, that is when the exchange capacity of the soil is exceeded, zinc would then be re-mobilised and it is at that stage that impact on groundwater quality could be significant.

In alkaline soils, the chemistry of zinc is dominated by interactions with organic ligands.

Deep wells

A total of 8 deep wells are located around the PDI site (Figure 6.1 refers) of which 7 are presently operational. Samples are collected for analysis at intervals of once every 3 months.

The results obtained and recorded by PDI over the period 1991-92 are summarised in Table 6.2 in similar form to the approach used for review of observation well data.

The results show essentially low levels of contamination although for three wells (DW2, DW3 and DW7), the maximum concentrations of cadmium determined exceeded the required standard of 0.01 mg/l. However in all cases, the averages obtained were below the standard. Similarly, the maximum concentrations of lead marginally exceeded the required standard of 0.05 mg/l for two wells (DW1 and DW3).

Examination of the raw data does not show any evidence to suggest that there is build-up of contamination with time.

Under-drainage pump sumps

A total of 22 under-drainage pump sumps are located around the PDI site (Figure 6.1 refers), of which 20 are presently operational. The pump sumps are strategically placed to collect under-drainage (and leakage) from residue ponds (R1 to R6) and wastewater sludge ponds (N2 to N4), any such drainage/leakage being transferred by pumping to pond R6 for re-processing or treatment as appropriate.

During the dry season only small amounts of "water" collect in the sumps and there is little need for pump transfer.

This indicates that leakage from ponds containing free "water" is minimal; also that the groundwater level generally is well below the base of the residue and sludge storage ponds. However, PDI confirm that during the rainy season a number of the sumps rapidly fill and "recovery" pumping has to be initiated on a more or less continuous basis.

As noted above, the increase in groundwater level between dry season and rainy season is generally within a range of 1 to 2 m. This, coupled with input of some surface water, is the main cause of "water" build up in the system.

Samples of "water" in the pump sumps are collected for analysis on a frequency basis which varies between once every 3 months to once every month depending on location. The frequency of sampling in 1992 has increased substantially over that carried out in 1991.

The results obtained and recorded by PDI over the period 1991-92 are summarised in Table 6.3 in relation to maximum and average values. The results do not show evidence of significant contamination, confirming that direct leakage from the ponds is not a serious problem. Also analysis of the raw data does not indicate any significant trends or differences between dry and rainy season conditions insofar as contamination levels are concerned.

The policy of "recovery" of "water" collecting in the sumps provides a level of environmental security which should be maintained.

Process wastewater discharge to Ping River

Treated wastewater is discharged to the Ping River, generally on a daily basis. However, when the water level in the Ping River is low, no discharge takes place.

Prior to discharge the quality of the treated effluent is checked to ensure compliance with the required standard.

Table 6.4 summarises final effluent monitoring data in terms of maximum and average concentrations (dissolved salts, zinc, cadmium and manganese) determined on a year-by-year basis between 1989 and 1992. All samples analysed fully complied with the MOI discharge standard.

Water quality in the Ping River

Water quality in the Ping River is assessed periodically as part of the PDI monitoring programme. This involves collection and analysis of samples from both upstream and downstream of the PDI outlet.

Results for the period 1991-92 are summarised in Table 6.5. The results show that the treated effluent discharge from PDI has negligible impact on the quality of water in the Ping River.

Heavy metal accumulation in fish located in final effluent storage pond

A number of species of fish are farmed in the final effluent storage pond. Samples representing the different species, and a range of sizes are analysed periodically for metal content.

Table 6.6 summarises the results of analyses for samples withdrawn in December 1991 and October 1992. The results show relatively minor take up of metals by fish.

Heavy metal accumulation in irrigated soils

Two flower beds are irrigated daily with water derived from:

- . the final effluent pond (Test bed A)
- . the Ping River (Test bed B)

Soils from each test bed are analysed periodically (about 1 x 2 months) for metal content. Table 6.7 summarises results from the period 1991-92 based on 20 determinations each for zinc, cadmium and manganese and 15 for lead. The results

show negligible differences between the metal content of the two soils.

Heavy metal accumulation in irrigated soils on the PDI golf course

Treated final effluent is used to irrigate "green" areas around the complex, including the golf course. Soil samples are analysed periodically (about 1 x 3 months) for metal content. Results for the period January to November 1992 are summarised in Table 6.8. The results do not show any evidence of significant build-up of metals in the soil.

Heavy metal accumulation in paddy soil

Paddy soils at four different location in the vicinity of the refinery are sampled periodically (about 1 x 6 months) and analysed for metal content.

Table 6.9 summarises results for the period 1986-92. These show that the metal content of the soils has remained essentially constant for a six year period.

Heavy metal accumulation in sediments in the Ping River

Samples of sediments from the Ping River are collected periodically (about 1 x 12 months) and analysed for metal content. Four sampling positions are used, including one upstream and two downstream from the pump station which equates approximately to the position of discharge of treated effluent to the Ping River.

Table 6.10 summarises results for the period 1986 to 1991. Although limited in scope, the results show that the metal content of the sediments has remained more or less the same over the period. They also show that there are minor differences only between upstream and downstream sediments.

Leachate tests on residues

Leachate tests are carried out on stabilised residues from the pan mixer and from the mixer truck on a twice per month basis. The tests are carried out in accordance with the following MOI protocol:

- . Residue ground to 0.5 to 5 mm particle size.
- . 50 g of ground residue added to 500 ml of leaching water (pH 5.8 to 6.3 adjusted with hydrochloric acid).
- . Agitate for 6 hours on a 200 rpm shaker.
- . Filter.
- . Analyse filtrate for soluble metals.

Table 6.11 summarises results as maximum and average values for zinc, cadmium, manganese and lead. The results show that the leachate complies consistently with the required standard of less than 1 and 5 mg/l for cadmium and lead respectively.

6.4 UNIDO audit programme

Scope of sampling programme

As a component part of the study a representative selection of water, soil and residue samples were taken for analysis at Chiang Mai University. In all cases, samples were split to allow check analyses to be carried out in the PDI laboratories.

In relation to "waters" a total of 6 observation well samples, 2 deep well samples and 9 under-drainage pump sump samples were taken; also samples from the treated effluent pond, standing water in the surface water discharge ditch adjacent to residue pond R1 and a water phase underlying the PVC cover sheeting on residue pond R1.

In all cases, pH was measured on-site and zinc, cadmium, copper and lead determined in the laboratory.

Three soil samples were collected for analysis representing:

- . ground conditions adjacent to the cadmium storage pond;
- . the dried out surface water ditch to the west of residue pond R1;
- . the dried out surface water ditch to the east of residue pond R1.

Finally, three samples were taken representing:

- . stabilised residue from pond R4;
- . cadmium cake from the storage impoundment;
- . wastewater sludge from pond N3.

Soil, residue and sludge samples were analysed for zinc, cadmium, copper and lead, (mg/kg on a dry weight basis). Also, residue samples were subjected to leaching tests that is the toxicity test method stipulated by MOI and the shake test method as defined in Appendix A.

Analysis of water samples

The methods used at Chiang Mai University for analysis of heavy metals in water are based on the IBP Handbook No 8 "Methods for Physical and Chemical Analysis of Fresh Waters" by HL Golterman, RS Clymo and MAM Ohnstad, Blackwell Scientific Publications, second edition 1978. Extraction procedures are documented in Appendix A of the above publication. The extraction solutions produced were then analysed by atomic absorption spectrophotometry using Varaintechtron model AA275.

The results of analyses as determined by Chiang Mai University are summarised in Table 6.13. The results of analyses as determined by PDI on the split samples are summarised in Table 6.14.

It should be noted that results produced by PDI show consistently higher concentrations of contaminants than the results produced by Chiang Mai University. The combined results show that:

A number of under-drainage pump sumps (essentially PS2, PS3 and PS14) contained concentrations of zinc or lead greater than the groundwater quality standards (of 5 and 0.05 mg/l respectively) documented by the National Environmental Board of Thailand.

A significant percentage of the under-drainage pump sumps tested (40 percent based on the Chiang Mai results but 90 percent based on the PDI results) contained concentrations of cadmium greater than the groundwater quality standard of 0.01 mg/l. (This indicates a potential for leakage or contaminated surface water run off from non-stabilised residues to enter the water system and confirms the need for the present policy of containment of any under-drainage flows with pump back to recovery or treatment.)

The observation and deep wells tested contained concentrations of zinc, cadmium, copper, manganese and lead generally lower than the groundwater quality standard, thus confirming a minimum of groundwater contamination occurring at this stage.

The water sample abstracted from under the PVC cover sheet on residue pond R1 contained high concentrations of cadmium and zinc, thus confirming the uncontrolled build up of leachate in pond R1 (because of rainwater ingress) with subsequent potential to overflow to the surface water drainage ditch(es) adjacent.

The standing water in the ditch adjacent to residue pond R1 contained significant concentrations of cadmium and zinc, thus confirming the potential for discharge of contaminated leachate from impoundment ponds containing non stabilised residue.

The water contained in the fish pond, that is treated final effluent, contained low levels of heavy metals and complied with the MOI discharge standard.

Filtrate extracted from the wastewater sludge in pond N3 contained low levels of heavy metals (when compared to the MOI discharge standard), thus confirming the basic efficiency of the lime treatment process.

Analyses of soil samples

Three soil samples, two ore residue samples and one wastewater sludge sample were analysed for heavy metal content. The analytical method used at Chiang Mai University was based on "Manual for Analytical Determination of Trace Element by Atomic Absorption Spectrophotometer" by the Southeast Asia Tin Research and Development Centre, Ipoh, Malaysia, 1983.

The results of analyses as determined by Chiang Mai University are summarised in Table 6.15. The results of analyses as determined by PDI on split samples are summarised in Table 6.16.

Again the results as determined by PDI are generally higher than those established at Chiang Mai University.

The combined results show that:

The soil sample collected about 10 m from the cadmium storage pond (at the southeast corner) had a high content of cadmium, zinc, copper and lead, thus confirming contamination external to the storage area.

Soil samples taken from the surface water drainage ditch (on opposite sides of residue pond R1) had high content of heavy metals, thus confirming the possibility of rainwater ingress to pond R1 followed by overflow of contaminated leachate to the drainage ditch located at ground level around the pond.

Leaching tests

Two test methods have been used in assessing the potential for leaching of metal from:

- stabilised residue
- cadmium cake
- wastewater treatment plant sludge

The first method is the toxicity test carried out in accordance with the leach test method issued by the MOI. The second method is the maximum concentration method according to shake test. The two tests are similar to the test performance by Chulalongkorn University and summarised in Appendix A.

The results of the leaching tests carried out by Chiang Mai University are summarised in Tables 6.17 to 6.19.

Table 6.17 shows the pH of solution after extraction. It can be seen that pH of solution increases on samples of ore residue (R4) and sludge residue (N3). This is due to extraction of lime. On the contrary, cadmium residues which are not lime stabilised give only a marginal increase in pH of solution after extraction.

In the case of the cadmium cake residue the above test results in high concentrations of cadmium being leached out but not copper or zinc.

A leaching test by the maximum concentration shake method was carried out and the results are summarised in Table 6.19. For ore residue, after 7 days of leaching, the pH of the extract reduced from 10.30 to 9.90. However, there was no evidence of substantial leach out of heavy metals, although concentrations of cadmium would have exceeded the groundwater quality standard of 0.01 mg/l. and increasing amounts of metals were being leached out with time. For example, copper could be leached out from 0.027 to 0.130 mg/l after 7 days of leaching. Similarly, cadmium could be leached out from 0.008 to 0.051 mg/l after 7 days and zinc from 0.049 to 0.442 mg/l after 7 days. Leaching from sludge residues also followed a similar pattern.

For cadmium residue, cadmium metal could be leached out easily, thus confirming the hazardous nature of this particular wastestream.

The results of leaching tests carried out by PDI on split samples of stabilised ore residue from wastewater sludge residue are documented in Table 6.20.

In overall terms it can be concluded that lime-stabilised silicate ore residue and lime-treated wastewater treatment plant sludges are very stable, with minimum potential for leaching. However, there is evidence to suggest that leaching of metals could take place over an extended period particularly as the pH of the leach liquor varies following prolonged exposure to precipitation. This confirms the importance of providing final covering of ponds to prevent rainwater ingress. Alternatively, a long term leachate management programme would be necessary.

RESULTS OF PDI MONITORING PROGRAMME 1991-92

Table 6.2 - Deep wells (DW1 to DW8)

Location	No of Observ	pH Range	TH *		Zinc		Cadmium		Manganese		Lead	
			Max	Av	Max	Av	Max	Av	Max	Av	Max	Av
DW1	8	7.25 to 8.42	400	347	0.35	0.08	0.01	0.006	0.045	0.016	0.056	0.015
DW2	8	6.46 to 7.87	344	311	1.75	0.7	0.03	0.009	0.037	0.015	0.046	0.016
DW3	8	6.64 to 7.46	450	409	0.32	0.125	0.01	0.006	0.13	0.045	0.065	0.02
DW4	8	7.19 to 8.65	349	331	2.26	1.14	0.02	0.008	0.07	0.0038	0.037	0.015
DW5	8	7.30 to 8.55	397	353	0.71	0.149	0.01	0.006	0.29	0.11	0.028	0.011
DW7	8	6.55 to 8.23	370	308	2.008	0.954	0.04	0.011	0.36	0.279	0.028	0.001
DW8	4	7.20 to 8.21	368	325	2.95	1.795	0.01	0.007	0.11	0.056	0.01	0.01
DRINKING WATER STANDARD		6.9 to 9.2	300 - 500		5 - 15		0.01		0.3 - 0.5		0.05	

* Total hardness mg/l as CaCO₃

RESULTS OF PDI MONITORING PROGRAMME 1991-92

Table 6.3 - Underdrainage pump sumps (PS1 to PS22)

Location	No of Observ	pH Range	TH *		Zinc		Cadmium		Manganese		Lead	
			Max	Av	Max	Av	Max	Av	Max	Av	Max	Av
PS1	15	7.06 to 7.94	554	328	5	3.544	0.02	0.011	0.56	0.258	0.03	0.03
PS2	12	6.91 to 7.84	700	624	1.09	0.248	0.02	0.011	0.27	0.103	0.03	0.03
PS3	12	7.09 to 7.85	698	541	1.4	0.41	0.01	0.01	0.1	0.034	0.03	0.03
PS4	6	7.45 to 8.28	400	308	0.66	0.305	0.01	0.01	0.08	0.025	0.03	0.03
PS5	6	8.02 to 8.27	816	637	0.35	0.105	0.01	0.01	0.03	0.015	0.03	0.027
PS6	5	7.53 to 8.00	620	558	1.68	0.45	0.32	0.076	0.18	0.06	0.03	0.03
PS7	5	7.20 to 8.42	740	335	0.22	0.138	0.03	0.014	0.05	0.026	0.03	0.03
PS8	6	7.20 to 8.85	740	507	0.72	0.26	1.95	0.333	0.15	0.105	0.03	0.03
PS10	6	7.07 to 8.42	1280	647	2.41	0.462	0.01	0.01	1.36	0.243	0.03	0.03
PS11	13	7.01 to 7.88	480	290	0.35	0.113	0.01	0.01	0.96	0.173	0.03	0.03
PS13	6	6.74 to 8.29	750	413	0.45	0.142	0.11	0.028	7.3	2.905	0.03	0.03
PS14	14	7.04 to 8.10	400	269	1.2	0.395	0.01	0.01	0.52	0.159	0.03	0.03
PS15	9	7.05 to 7.88	510	316	2.34	0.748	0.01	0.01	0.45	0.133	0.03	0.03
PS16	6	6.77 to 8.11	240	179	0.38	0.09	0.02	0.012	0.08	0.043	0.03	0.03
PS17	6	7.33 to 8.68	660	308	1.7	0.743	0.03	0.02	0.19	0.09	0.03	0.03
PS18	7	7.35 to 8.04	420	306	1.51	0.266	0.02	0.011	0.39	0.094	0.03	0.0267
PS19	7	6.89 to 8.05	510	380	2.63	0.527	0.09	0.031	5.45	1.363	0.03	0.0267
PS20	9	5.70 to 8.34	900	688	5.9	3.61	0.02	0.011	0.9	0.468	0.03	0.026
PS21	7	7.62 to 8.13	650	426	2.37	0.893	0.02	0.011	0.35	0.069	0.03	0.0133
PS22	2	7.51 to 8.10	470	460	0.47	0.36	0.01	0.01	0.05	0.03	0.03	0.02
STANDARD					5.0		0.01		0.3		0.05	

* Total Hardness (mg/l as CaCO₃)

RESULTS OF PDI MONITORING PROGRAMME 1991-92

Table 6.3 - Ping River Water Quality

Location	No of Observ	pH Range	Results in mg/l									
			TH *		Zinc		Cadmium		Manganese		Lead	
			Max	Av	Max	Av	Max	Av	Max	Av	Max	Av
U6000	4	7.17 to 8.19	100	89	0.345	0.107	0.005	0.003	0.04	0.028	0.01	0.006
U2000	7	7.67 to 8.35	100	82	0.31	0.12	0.03	0.007	0.19	0.06	0.01	0.005
U200	6	7.58 to 8.31	90	78	0.52	0.128	0.005	0.003	0.046	0.026	0.01	0.005
D200	7	7.45 to 8.23	300	174	0.42	0.139	0.007	0.004	0.296	0.09	0.01	0.003
D2000	7	7.73 to 8.29	170	108	0.57	0.102	0.005	0.003	0.051	0.028	0.01	0.004
D4000	7	7.85 to 8.34	130	93	0.32	0.075	0.005	0.002	0.075	0.035	0.01	0.003
D6000	7	7.92 to 8.42	92	78.4	0.29	0.075	0.008	0.003	0.045	0.03	0.01	0.005

U2000 Upstream 2000m

D6000 Downstream 6000m

RESULTS OF PDI MONITORING PROGRAMME

Table 6.4 - Process Wastewater - after treatment 1989 - 92

	No of Observ	pH Range	Results in mg/l							
			Dissolved Salts		Zinc		Cadmium		Manganese	
			Max	Av	Max	Av	Max	Av	Max	Av
1989	28	6.6 to 8.25	3600	2590	1.55	0.46	0.02	0.01	0.23	0.08
1990	25	7.1 to 8.9	3050	2575	0.47	0.25	0.01	0.01	0.09	0.03
1991	24	6.5 to 8.6	2820	2623	0.26	0.11	0.01	0.01	0.06	0.02
1992	16	6.9 to 7.9	3110	2666	0.09	0.06	0.01	0.01	0.08	0.02
MOI Discharge Standard		5 - 9	5000		5.0		0.03		5.0	

RESULTS OF PDI MONITORING PROGRAMME

Table 6.6 - Heavy metal accumulation in fish located in final effluent storage pond (1991-92)

Date	Name	Size	Part of Body	Heavy Metal in mg/Kg (wet weight)		
				Zn	Cd	Mn
Dec 1991	Nil	Big	Meat	16.94	0.28	0.37
		Medium		6.91	0.1	0.29
		Small		14.64	0.28	0.19
		Smallest		16.54	0.1	0.29
Oct 1992	Cat fish	Big	Meat	7.8	0.96	0.41
		Medium		9.18	0.6	0.42
		Small		9.8	0.52	1.6
		Smallest		10.82	0.54	1.33
Food Standard						
- Food Standard of Public Health Ministry				100	-	-
- Food Standard of Australia				-	5.5	-

RESULTS OF PDI MONITORING PROGRAMME

Table 6.7 - Heavy metal accumulation in irrigated soils 1991-92

	Results in mg/Kg (dry weight)							
	Zinc		Cadmium		Manganese		Lead	
	A	B	A	B	A	B	A	B
Average	71.32	76.4	1.08	0.79	281	290	27	28
Maximum	96.6	110	11	4.8	424	432	46	40
Minimum	36.4	34.2	0.15	0.15	210	154	0.2	0.2

A Using treated process wastewater from PD1

B Using water from the Ping River

Total no. of observations for Zinc, Cadmium, Manganese 20

Total no. of observations for lead 15

RESULTS OF PDI MONITORING PROGRAMME

Table 6.8 - Heavy metal accumulation in irrigated soils on the PDI golf course 1992

	Results in mg/Kg (dry weight)							
	Zinc		Cadmium		Manganese		Lead	
	Jan	Nov	Jan	Nov	Jan	Nov	Jan	Nov
Hole 2	60	43	1.31	0.2	485	333	13.4	31.3
Hole 7	50	89	2.47	0.4	551	429	12.1	24
Hole 9	111	43	0.22	0.2	516	432	8.1	22

RESULTS OF PDI MONITORING PROGRAMME 1991-92

Table 6.9 - Heavy metal accumulation in paddy soil 1986-91

Location	Results in mg/Kg (dry weight)					
	Zinc		Cadmium		Manganese	
	1986	1991	1986	1991	1986	1991
A	75	56	<1.0	<0.2	546	406
B	75	59	<1.0	<0.2	620	390
C	73	87	<1.0	<0.2	880	1200
D	67	71	<0.5	<0.2	600	820

A Ban Pra Dang

B Ban Sob Yom

C Ban Tha Mai Dang

D Ban Tha Ta Kaw i

RESULTS OF PDI MONITORING PROGRAMME

Table 6.10 - Heavy metal accumulation in sediments in Ping River 1986-92

Location	Results in mg/Kg (dry weight)					
	Zinc		Cadmium		Manganese	
	1986	1991	1986	1991	1986	1991
U6000	37	11	<0.1	<0.2	485	204
Pump Station	-	65	-	<0.2	-	994
D200	87	53	<0.5	<0.2	619	494
D6000	-	68	-	<0.2	-	596

RESULTS OF PDI MONITORING PROGRAMME

Table 6.11 – Leachate tests on residues 1992

	No of Observ	pH Range	Results in mg/l							
			Zinc		Cadmium		Manganese		Lead	
			Max	Av	Max	Av	Max	Av	Max	Av
Pan mixer 1/2	44	8.4 to 12.1	0.82	0.23	0.01	0.01	0.13	0.03	ND	ND
Pan mixer 3/4	44	8.74 to 11.7	0.61	0.22	0.01	0.01	0.63	0.03	ND	ND
Mixer truck 1	44	9.42 to 12.0	0.84	0.25	0.07	0.01	0.58	0.03	ND	ND
Mixer truck 2	44	9.54 to 12.0	0.85	0.27	0.05	0.01	0.14	0.03	ND	ND

ND Not detected

SPS CONSULTING SERVICES - HYDROGEOLOGICAL STUDY

Table 6.12 - Groundwater level measurement (Typical)

Well No	Water level (m. MSL)								
	5/8/89	7/9/89	16/11/89	27/12/89	1/2/90	26/3/90	11/6/90	16/7/90	13/8/90
A2	110.494	109.944	111.724	111.214	110.804	110.344	110.514	110.146	110.124
A3	110.296	109.696	110.946	109.746	109.296	108.946	109.796	109.146	109.016
A6	103.525	103.425	103.695	102.945	103.165	103.515	103.695	103.793	103.295
B3	111.433	111.273	111.673	111.523	111.353	111.123	111.263	111.223	110.993
B4	106.242	106.242	107.542	106.742	106.172	105.822	106.492	105.892	105.492
B5	105.705	105.616	105.765	105.415	105.015	104.565	105.615	105.265	105.015
D5	104.296	104.026	104.576	104.176	104.046	103.976	104.426	104.026	103.926
D6	104.242	104.242	104.652	103.992	103.912	103.992	104.042	103.892	103.842

UNIDO AUDIT PROGRAMME

Table 6.13 - Results of analysis of water samples (Chiang Mai University)

Sample	Field pH	mg/l			
		Cu	Cd	Pb	Zn
PS-1	7.67	<0.005	<0.002	<0.005	0.684
PS-2	7.73	<0.005	0.162	<0.005	5.073
PS-3	7.06	<0.005	0.182	0.010	4.870
PS-10	7.75	<0.005	0.014	0.008	1.320
PS-11	8.90	<0.005	0.006	0.007	0.231
PS-14	7.43	<0.005	0.198	0.008	3.255
PS-17	7.90	<0.005	<0.002	0.006	0.130
PS-19	6.70	<0.005	<0.002	<0.005	0.234
PS-21	6.81	<0.006	<0.002	<0.005	3.077
PS-22	7.90	<0.005	<0.002	0.008	0.211
OW-9	7.30	<0.005	<0.002	0.006	0.117
OW-15	7.14	<0.005	<0.002	0.005	0.178
OW-16	7.77	<0.005	<0.002	0.006	0.122
OW-28	8.99	<0.005	<0.002	<0.005	0.081
OW-33	8.03	<0.005	<0.002	0.008	0.028
OW-40	7.20	<0.005	<0.002	0.006	0.081
DW-5	7.30	<0.005	<0.002	<0.005	0.012
DW-7	7.80	<0.005	<0.002	<0.005	0.215
Water under PVC (R1)	6.02	<0.005	10.532	0.140	55.80
Fish pond	8.25	<0.005	<0.002	<0.005	0.101
Ditch adjacent R1	7.40	<0.005	0.625	0.005	18.47
Filtrate from Sludge residue	12.00	<0.005	0.003	<0.005	0.142
Ground water quality standard	7.05-8.5	1.00	0.01	0.05	5.00
Effluent standard	5-9	1.00	0.10	0.20	5.00

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Table 6.14 – Results of analysis of water samples (PD1)

Sampling point	pH	Tot Hardness (mg/LasCaCO ₃)	mg/l			
			Zn	Cd	Mn	Pb
PS-1	7.83	230	1.93	0.074	0.400	0.011
PS-2	7.50	1550	9.63	0.190	0.900	0.034
PS-3	7.43	1780	30.70	0.270	0.280	0.034
PS-10	7.33	1930	1.89	0.290	0.830	0.029
PS-11	7.64	1740	0.34	0.280	0.080	0.011
PS-14	7.18	1800	5.46	0.130	0.490	0.029
PS-17	7.40	1400	0.40	0.024	0.072	0.034
PS-19	6.88	450	0.46	0.016	0.330	0.040
PS-21	6.78	700	3.55	0.032	1.250	0.034
PS-22	7.38	1040	0.27	0.006	0.160	0.034
OW-9	7.36	800	0.30	0.028	0.380	0.034
OW-16	7.78	300	0.37	0.012	6.300	0.190
OW-28	8.02	510	0.28	0.012	2.430	0.017
OW-33	7.53	640	0.12	0.008	0.052	0.029
OW-40	7.34	880	0.52	0.008	0.830	0.250
DW-5	7.41	610	0.18	0.008	0.240	0.017
DW-7	7.53	560	0.41	0.014	0.030	0.011
Ditch adjacent R1	7.14	2530	24.00	0.67	6.670	0.034
Water under PVC (R1)	5.94	4580	1566.00	23.80	174.800	0.017
Fish pond	7.48	1880	0.21	0.012	0.12	0.029

UNIDO AUDIT PROGRAMME

Table 6.15 – Results of analyses of soil and residue samples (Chiang Mai University)

Sample	Total (mg/Kg)			
	Zn	Cd	Cu	Pb
Soil near Cd pond	543.66	12.030	4.940	53.490
Soil from drainage ditch (R1 - West)	2609.58	29.170	0.940	12.280
Soil from drainage ditch (R1 - East)	5324.88	284.680	19.680	153.550
Stabilised residue (R4)	14578.77	150.210	11.550	801.150
Cadmium residue	169533.31	97794.020	34075.000	7671.380
Sludge residue (N3)	12448.52	0.010	1899.530	0.008

Table 6.16 – Results of analyses of soil samples (PD1)

Sampling point	mg/Kg			
	Zn	Cd	Mn	Pb
Soil near Cd pond	1088	29.6	540	107.3
Soil from drainage ditch (R1 - West)	9600.00	286.80	1890.00	167.10
Soil from drainage ditch (R1 - East)	25880.00	256.80	944.00	53.00

UNIDO AUDIT PROGRAMME

Table 6.17 - Leaching tests (Chiang Mai University)

(1) pH of solution from toxicity test

	pH before extraction			pH after extraction		
	1	2	Average	1	2	Average
Ore residue (F4)	6.00	6.00	6.00	10.58	10.54	10.56
Cd residue	6.00	6.00	6.00	7.80	7.84	7.82
Sludge residue (N3)	6.00	6.00	6.00	10.82	10.80	10.81

Table 6.18 - Leaching tests (Chiang Mai University)

(2) Heavy metal concentrations in solution after extraction from toxicity tests

	Cu (mg/l)			Cd (mg/l)			Zn (mg/l)			Pb (mg/l)		
	1	2	Avg	1	2	Avg	1	2	Avg	1	2	Avg
Ore residue (F4)	<0.005	<0.005	<0.005	0.008	0.007	0.007	0.415	0.427	0.421	0.017	0.019	0.018
Cd residue	0.022	0.024	0.023	65.000	64.020	64.510	0.902	0.858	0.880	0.200	0.180	0.180
Sludge residue (N3)	<0.005	<0.005	<0.005	0.082	0.086	0.074	0.080	0.088	0.089	<0.005	<0.005	<0.005

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Table 6.19 - Leaching tests (Chiang Mai University)

(3) Leaching tests by maximum concentration shake method

Sample	Extraction No	pH of solution				
			Cu	Pb	Zn	Cd
Ore residue (R4)	1	10.30	0.027	0.049	<0.005	0.008
	2	10.23	0.033	0.071	<0.005	0.011
	3	9.90	0.044	0.080	<0.005	0.016
	4	10.00	0.059	0.140	<0.005	0.023
	5	9.98	0.081	0.204	<0.005	0.036
	6	9.85	0.108	0.362	<0.005	0.044
	7	9.90	0.130	0.442	<0.005	0.051
Cd residue	1	7.72	0.067	0.717	<0.005	66.750
	2	7.91	0.073	1.110	<0.005	83.250
	3	7.75	0.094	1.530	<0.005	126.940
	4	7.34	0.135	3.520	0.006	133.980
	5	7.34	0.155	4.000	0.016	137.140
	6	7.32	0.178	4.680	0.029	162.120
	7	7.30	0.185	5.250	0.041	132.110
Sludge residue (N3)	1	10.89	<0.005	0.089	<0.005	0.031
	2	11.63	<0.005	0.140	<0.005	0.055
	3	10.66	0.005	0.150	<0.005	0.068
	4	10.00	0.014	0.156	<0.005	0.094
	5	9.60	0.014	0.164	<0.005	0.107
	6	9.70	0.019	0.170	<0.005	0.135
	7	9.68	0.021	0.175	<0.005	0.157

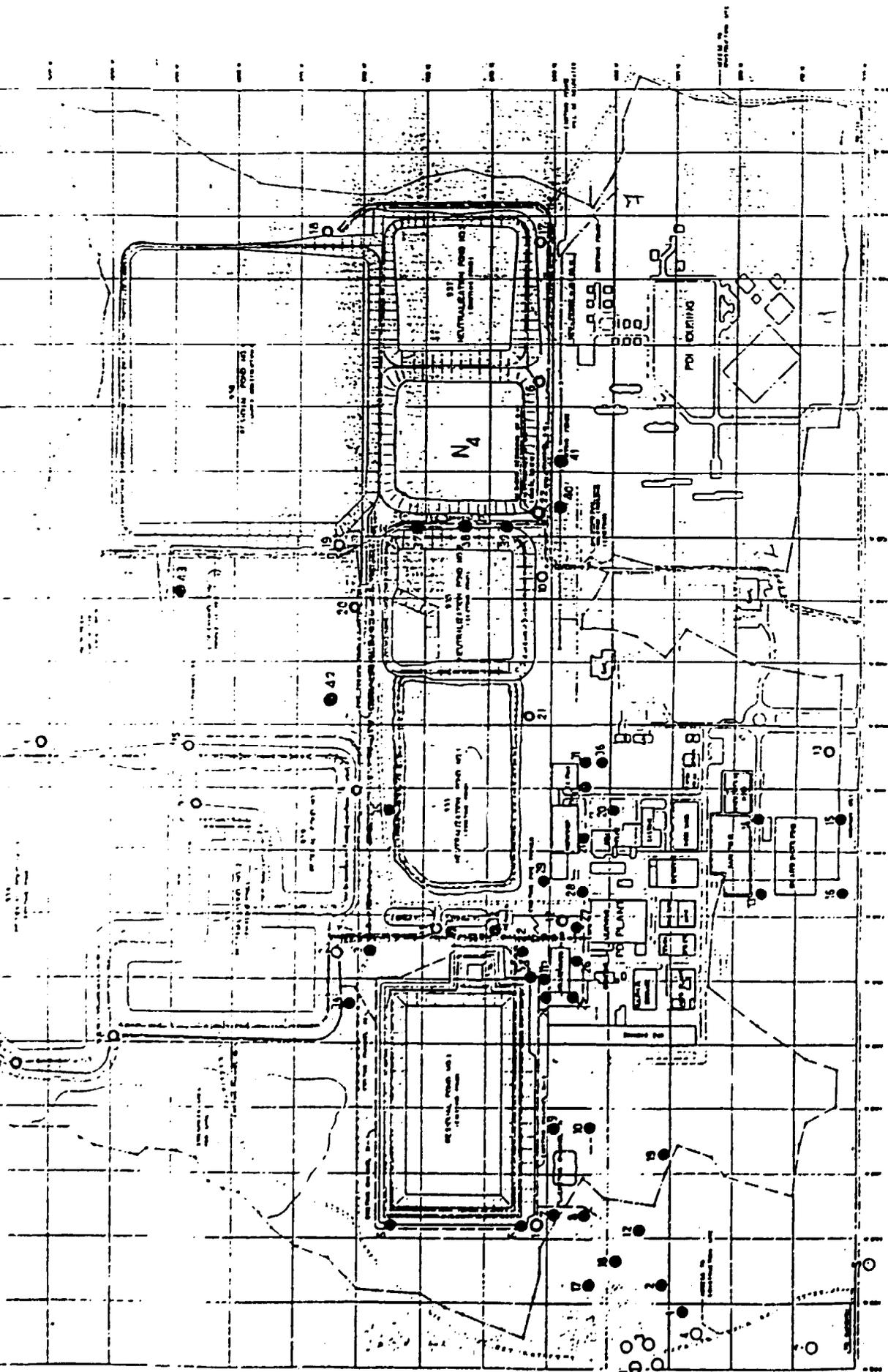
Note initial pH of extract solution = 4.0

UNIDO AUDIT PROGRAMME

Table 6.20 - Leaching tests (PDI)

Sampling Point	pH	mg/Kg			
		Zn	Cd	Mn	Pb
Ore residue (R4)	9.31	0.050	0.020	<0.01	<0.03
Sludge residue (N3)	9.75	0.070	0.010	0.010	<0.03

Figure 6.1



- Pump sump
- Observation well
- Drinking well

Figure 6.1 - Utility and Water Supply System Layout Plan

Figure 6.2

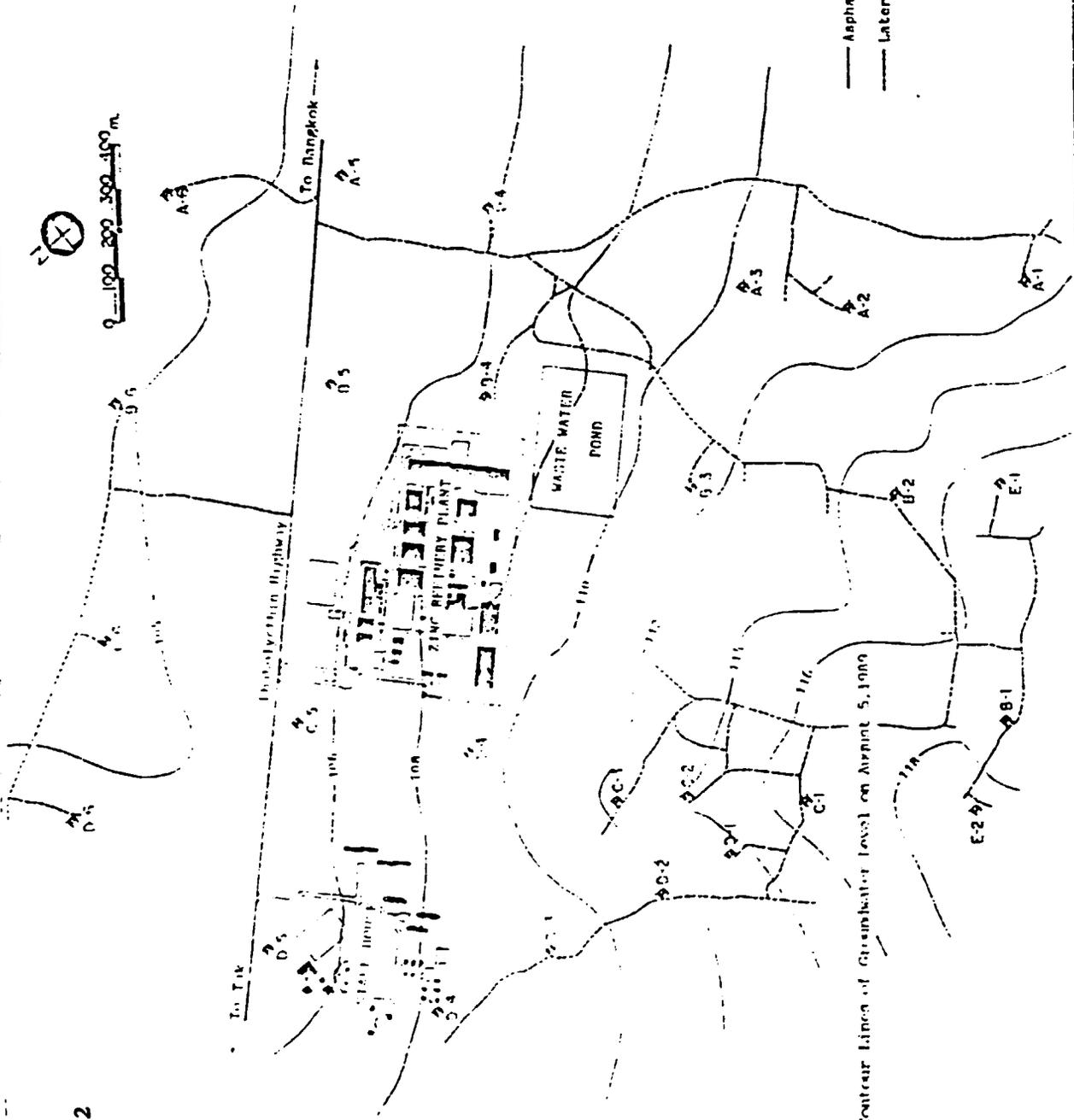
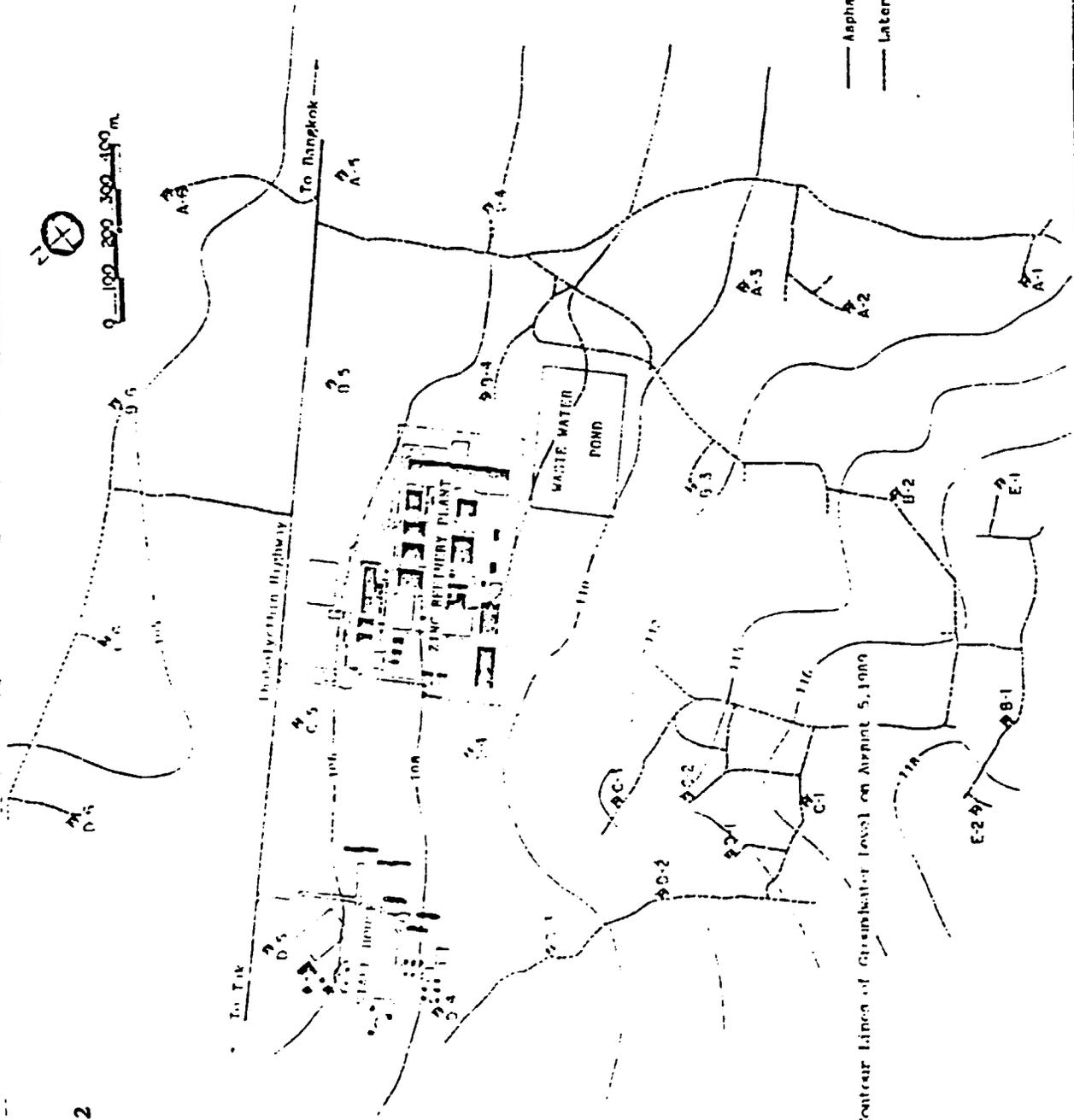


Figure 1 Contour Lines of Groundwater Level on August 5, 1980



7 LEGISLATION AND STANDARDS

7.1 Relevant Thailand legislation

Existing
Proposed

7.2 Relevant international standards and codes of practice for hazardous waste containment

General design considerations
Experience overseas

7 LEGISLATION AND STANDARDS

7.1 Relevant Thailand Legislation

Existing

Existing Thailand legislation relevant to the PDI refinery at Tak includes:

- . Industrial Effluent Standards and Regulations
- . Solid Waste, Nightsoil and Hazardous Wastes Management in Factories

The Industrial Effluent Standards and Regulations were ratified by the Ministry of Industry (MOI) in 1978 and 1982. As a result the effluent from any industrial activity should comply with the standard specified.

Standard (expressed as maximum concentrations) relevant to PDI for discharge to the Ping River include:

. Zinc	3.0 mg/l
. Cadmium	0.1 mg/l
. Lead	0.2 mg/l
. Manganese	5.0 mg/l
. Nickel	0.2 mg/l
. Silver	0.02 mg/l
. Total dissolved salts	2000-5000 mg/l

Current standards relevant to the landfilling of hazardous wastes include the following:

- . Side and bottom lining must be provided to prevent contamination of groundwater from leachate.
- . The liner must be physically strong and thick enough for weight and pressure and may be either a synthetic material or a natural material such as clay with a permeability less than 10^{-7} cm/sec or a combination.
- . The bottom of the landfill must be not less than 5 ft above the groundwater table.
- . Leachate collection and leachate treatment system must be provided or leachate must be taken for treatment outside.
- . After landfill operation is completed the landfill should be finally covered with impermeable material and soil for planting respectively. An adequate drainage system shall also be provided.
- . Material used for the final cover and bottom liner must be identical. The thickness of soil for planting must be not less than 150 cm and a sand layer may be provided between final cover and top soil.

The ground cover plants must be short-root plants or have the longest roots less than 150 cm.

Monitoring wells must be installed for groundwater sampling. The number and sizing of monitoring wells should be followed as approved by the Department of Industrial Works. Groundwater quality must meet or exceed the following criteria:

-	Arsenic (As)	0.05 mg/l
-	Cadmium (Cd)	0.01 mg/l
-	Chromium (Cr)	0.05 mg/l
-	Lead (Pb)	0.05 mg/l
-	Mercury (Hg)	0.001 mg/l
-	Nickel (Ni)	0.05 mg/l
-	Manganese (Mn)	0.3 mg/l
-	Copper (Cu)	1.0 mg/l
-	Zinc (Zn)	5.0 mg/l

Proposed

The Ministry of Industry (MOI) at present is in the process of establishing a new regulation for hazardous waste landfill operation. This will be based on the design to be used by the MOI for the new secured landfill waste disposal centre to be built near Bangkok.

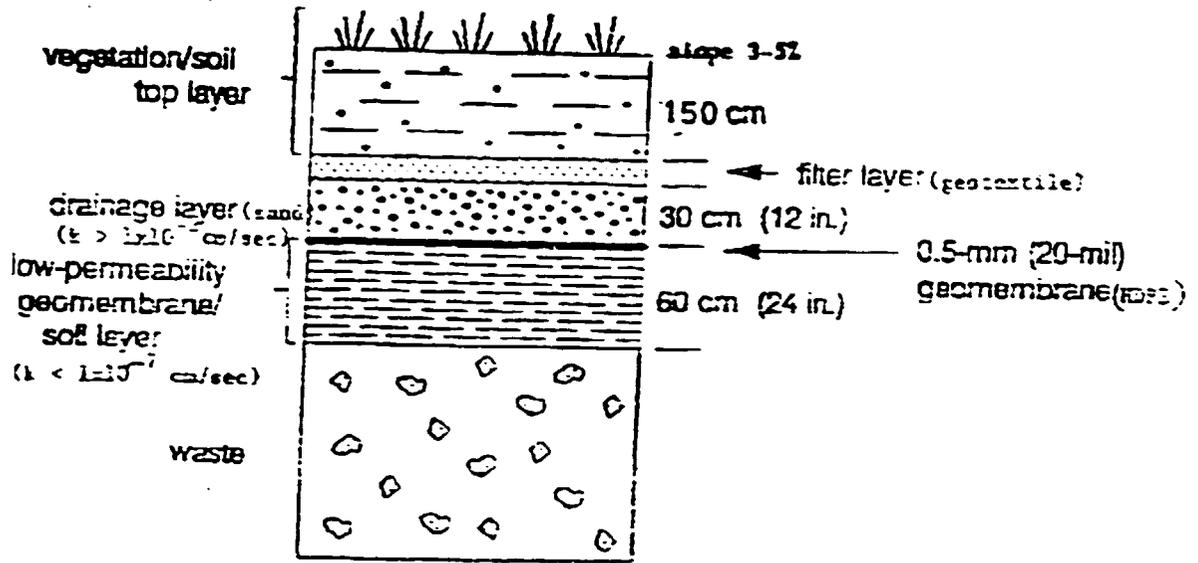
The design will include double layers of plastic membrane, with impermeable clay and with leachate collection and observation wells. A cross-section of the proposed landfill is shown in Figure 7.1.

The site will be first lined with composite geomembrane and soil with low permeability ($k < 1 \times 10^{-7}$ cm/sec) followed by a geomembrane (HDPE 0.75 mm thickness). Drainage pipes will then be installed to provide for leak detection. These pipes will be connected to a pumping station and leakage monitoring well. A further layer of geomembrane (HDPE 0.75 mm thickness) will then be added followed by a series of drain pipes installed within a soil layer. These pipes will collect leachate for further treatment. (A special "filter" layer being included so that water will flow to the leachate collection system.)

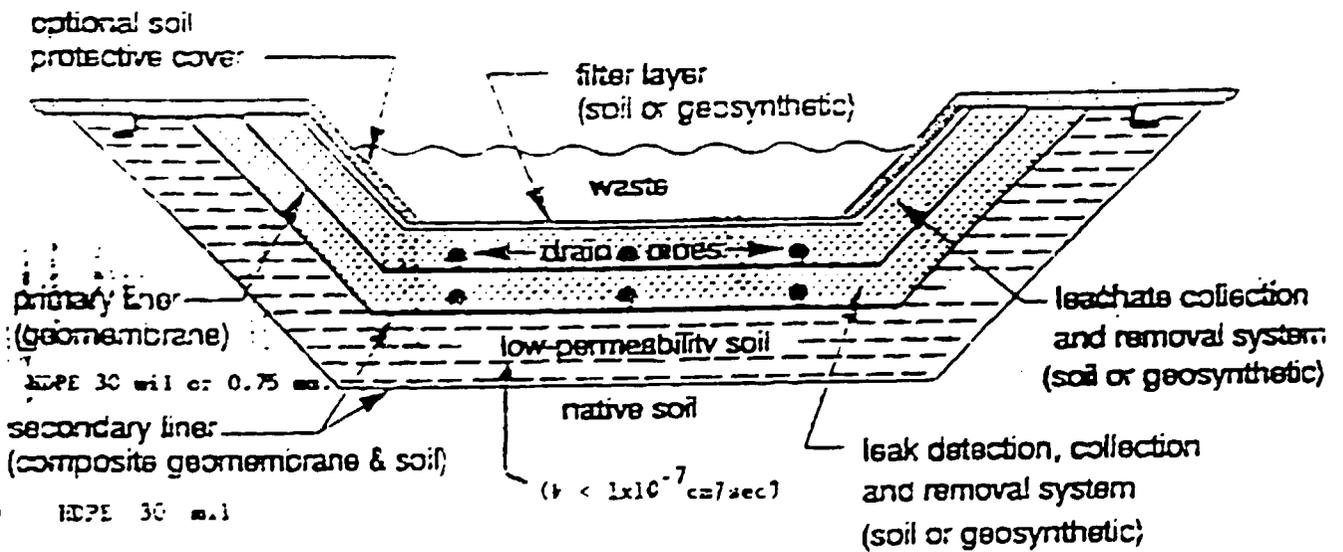
After completion of waste dumping, the site will be covered with low permeability geomembrane and soil ($k < 1 \times 10^{-7}$ cm/sec) and then at a later stage, with HDPE 0.5 mm thickness. A 30 cm drainage layer (sand $k > 1 \times 10^{-2}$ cm/sec) will be installed on top of the HDPE followed by a filter layer (geotextile) and then 150 cm of top soil (with a surface slope of 3 to 5 percent). Finally vegetation will be planted.

It is proposed that this type of landfill design will be used as the basis for a new regulation concerning the safe storage of hazardous waste. It is believed that this new regulation will be introduced within the next 12 months or so.

Figure 7.1



Landfill Cover Design for Hazardous Wastes



Schematic of Double Liner System
for Hazardous Wastes

7.2 Relevant international standards and codes of practice for hazardous waste containment

General design considerations

A hazardous waste landfill must be designed and constructed so that it becomes the final repository for the waste materials. At the same time the landfill must control any release of contaminants into the surrounding environment that could degrade its quality to a point that would impair the ongoing use of lands (or water) near the facility.

In engineering containment systems reliance is placed on engineered facilities to protect the environment. Typically, landfills designed using this approach combine engineered liners and covers and leachate collection and treatment systems to control the release of contaminants to the environment.

While engineered containment reduces the potential risks associated with contaminant migration into the environment, questions remain concerning the integrity and functionality of such systems over the long term, particularly in relation to liner materials, the integrity of drainage systems etc for leachate collection and control. The additional cost and responsibility associated with the long term maintenance and operation of such systems have to be fully accounted for.

Experience overseas

The double flexible liner system (with fully engineered leachate collection and transfer, under-drainage and top cover) has become the standard method of approach for hazardous waste containment. The design of such systems is detailed in two documents enclosed as Appendices B and C.

- US EPA: Guide to Technical Resources for the Design of Land Disposal Facilities
- Environment Canada: National Guidelines for the Landfilling of Hazardous Waste

Particular points to note are that:

- a minimum safety factor of 1:4 is recommended for interior cell slopes;
- due account should be taken of settlement and heave factors because they can cause stress and, hence, adversely affect the integrity and performance of liner materials and leachate collection systems;
- a double flexible liner system is considered mandatory for hazardous waste containment;
- the actual choice of liner systems is still the subject of considerable debate and although HDPE appears to be the preferred material over alternatives such as PVC, there is as yet no uniform consensus on this matter;

- an engineered leachate collection, removal and monitoring and, if necessary, treatment system is mandatory for hazardous waste landfill sites;
- an engineered cover system also is mandatory for hazardous waste landfill particularly to control surface water infiltration (and hence liquid migration and leachate generation) but also to sustain vegetation growth;
- seismic analysis is critical when there is potential for liquifaction to occur;
- the construction of continuous watertight, flexible membrane liners, (bottom or cover) is critical and is heavily dependent on the construction of the seams bonding the sheeting together, the seams being the most likely source of failure on a flexible membrane liner (for site installed seams, constant inspection is necessary to ensure integrity).

8 ANTICIPATED PROCESS CHANGE TO CALCINE FEED MATERIAL

8.1 Background and timing

8.2 Anticipated production level and preliminary materials balance

8.3 Consideration of proposed process technology

8.4 Alternative process options to minimise environmental impact

8 ANTICIPATED PROCESS CHANGE TO CALCINE FEED MATERIAL

8.1 Background and timing

The silicate ore body presently mined at Mae Sot is expected to run out around mid-1994. At that time it is planned to convert the refinery to an imported sulphide ore body 'feedstock' following its conversion to oxide (calcine) in a new sinter plant to be constructed on the Maptaphut industrial estate at Rayong, 200 km east of Bangkok. The calcine produced at the new plant will be transferred to Tak by road transport for conversion to zinc metal based on the "Jarosite" process.

8.2 Anticipated production level and preliminary materials balance

It is intended to maintain an overall production level of 77,000 t/a of product zinc (231 t/d). This will require a feed input of 165,000 t/a (450 t/d) of calcine with a zinc content of 55 percent. Other products will include cadmium at a production level of 1 t/d (compared to 1.5 t/d presently) and a copper/cobalt residue (2 t/d) which will be returned to Rayong for pyrometallurgical recovery of copper.

Because of high zinc content in the feed material, the quantity of residue produced will be substantially less than that produced presently, that is about 400 t/d with a moisture content of 50 percent compared to 2000 t/d presently (also assuming a 50 percent moisture content).

In volumetric terms this implies a reduction in required residue storage volume from about 500,000 m³ per annum as at present to about 80,000 m³ per annum.

The process residues essentially will comprise unreacted ore together with "Jarosite" precipitate which is produced at a pH within the range pH 1.7-2.5. The chemical formulation of Jarosite precipitate is $R^+Fe_3(OH)_6(SO_4)_2$ where R^+ is Na^+ , K^+ or NH_4^+ . In addition the residue is expected to contain about 33 kg/d silver and about 7 t/d of lead, the latter being on the basis that lead sulphate ($PbSO_4$) does not readily dissolve in the leaching process.

In addition to substantially reduced quantities of process residue, it is expected that wastewater volumes (presently ranging between 1500 to 2000 m³/d depending on the magnesium content of the silicate ore body) will be reduced to about 100 m³/d.

8.3 Consideration of proposed process technology

The "Jarosite" process involves the use of a 3 step leaching process (neutral leach, acid leach and hot acid leach) to improve the recovery of zinc, cadmium and copper over that normally achieved by conventional single step leaching and purification technology. This results in a significant quantity of iron going into solution and this is precipitated subsequently, as noted above, as $RFe_3(OH)_6(SO_4)_2$.

Jarosite residues generally are now classified as hazardous mainly because they contain low concentrations of lead and cadmium that originate from the calcine used to neutralise the hydrolysis acid produced during Jarosite production. As a result purpose-designed "secure" storage ponds are required for its long term storage.

Also it should be noted that the relatively low bulk density of the residue increases the effective storage capacity required.

As described in Section 7, the long term storage of waste classified as hazardous in Thailand will, in the future, require provision of double membrane type storage ponds with under-drainage, leachate collection etc.

Accordingly such requirements should be taken into account at this stage in establishing the commercial and environmental viability of the proposed process change.

Also the practicability of long term storage of such wastes presently is being questioned and increasing environmental pressures may force the Industry as a whole to consider alternative processes. For example, processes what not only increase the recovery of zinc, cadmium and copper (and perhaps other metals such as lead and silver) but which also convert the process residues, particularly the iron, to a less hazardous (preferably saleable) form or which generate substantially reduced volumes for "secure" disposal. In addition, a range of pyrometallurgical processes are being developed which would convert the Jarosite residue, once formed, into an inert material or potential by-product of value.

8.4 Alternative process options to minimise environmental impact

Possible alternative processes include the *Goethite* process which precipitates iron from solution as a crystalline form of $\text{FeO}(\text{OH})$. This form of precipitate has been found to be reasonably easy to filter and wash before impoundment. Furthermore the volume of residue produced by this process is about 30 percent less than that produced by the Jarosite process. However, the residue would still be classified as "hazardous".

Another possible alternative process is the *hematite* process which produces a residue (Fe_2O_3). This is the closest to being consumable by other industries or which is inert and directly disposable without costly impoundment.

Possible hydrometallurgical processes for converting Jarosite to hematite include:

- . direct conversion at elevated temperatures (greater than 200 deg C) in weakly acidic sulphuric acid media;
- . dissolution at low temperatures in concentrated sulphuric acid media followed by re-treatment of the iron-bearing solutions;
- . decomposition in ammoniacal media followed by precipitation of Fe_2O_3 at temperatures of greater than 100 deg C and evaporative crystallisation of ammonium sulphate.

Possible pyrometallurgical processes (presently in development) for conversion of Jarosite type residues include:

- . smelting in an electric furnace to produce by-products, lead bullion and zinc/lead dust together with an inert "slag" type waste material (DetNorske Zinc/Boliden);
- . electrosmelting to produce zinc/lead dust and an inert "slag" waste material (RWTH-Aachen).

In addition, a wide range of pyrometallurgical processes has been or are being developed for conversion of neutral leach liquor (NLR) to a combination by-product of value and inert waste material and a number of these may have relevance in this case.

In view of the cost implications concerning the long term storage of hazardous wastes that is double membrane systems, leachate collection and control, etc, it is appropriate, therefore, at this stage to consider the following alternatives:

- . lime stabilisation of Jarosite residues (if practicable) in order to substantially reduce the potential for leaching and thereby allow long term storage in lower cost single membrane type ponds;
- . hydrometallurgical conversion of Jarosite to hematite;
- . pyrometallurgical conversion of Jarosite to inert end product or by-product of value.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

Environmental management generally
Environmental monitoring
Residues management
Wastewater sludges management
Cadmium cake management
Proposed process changes (calcine feed)

9.2 Recommendations

Monitoring
Residues management
Wastewater sludges management
Cadmium cake management
Proposed process changes

9^o CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

Environmental management generally

PDI essentially operate the site to a high level of environmental awareness and management. Substantial "green" areas, including a golf course, have been established around the refinery complex using treated effluent for purposes of irrigation. Housekeeping practices in and around the principal processing areas are of a high standard.

Environmental monitoring

PDI operate an extensive monitoring protocol and programme covering loss of heavy metals to the environment. This is carried out on an on-going basis and includes analysis of groundwaters, under-drainage pump sump contents, process wastewaters, river water, various soils irrigated with final effluent, river sediments, etc. The overall conclusion based on a detailed examination of results, particularly over the period 1991-92, is that release/migration of heavy metals such as zinc, cadmium, manganese and lead to the environment is very low. This was confirmed by the independent tests carried out during the study. However, it should be noted that:

- . It is unlikely that any spillages or losses of contaminated leachate to ground would impact significantly on groundwater quality at this stage because of the natural exchange capacity of the soils. However, in the longer term such impacts could become significant.
- . The under-drainage systems associated with residue ponds and wastewater sludge ponds appear to be effective in containing minor leakages.
- . The company's monitoring procedures are not subject currently to independent audit.

Residues management

Long term storage of "stabilised" silicate-based residues in existing single membrane ponds can be regarded as a secure and environmentally safe operation because:

- . the structural integrity of the deposits probably would be maintained in the unlikely event of failure of the containment embankments;
- . risks of generating leachate contaminated with dissolved metals would remain low on a long term basis although a cover system should be provided to minimise potential for infiltration of surface water and, hence, leachate generation (a leaching test based on the maximum concentration shake method demonstrated that small but increasing amounts of metals could be leached out with time).

Long term storage of non-stabilised silicate based residues in existing single membrane ponds can be regarded as satisfactory in relation to structural integrity. However, there are significant risks associated with generation of leachate contaminated with dissolved metals (100 percent sealing of ponds cannot be guaranteed and any

rainwater ingress will give rise to build-up of substantial quantities of contaminated leachate, as confirmed in pond R1, and at present there is no provision for its collection, transfer and treatment).

There is evidence of contaminated leachate release/migration from residue pond R1 as determined by analysis of soils in the vicinity of the pond and also by analysis of standing water in the surface water drainage ditch adjacent to the pond.

Stabilised residues would appear to have substantial by-product value (after further processing) as building bricks or some other form of construction material (based on reports made available from various sources).

Wastewater sludges management

Long term storage of wastewater treatment sludges in ponds N2, N3 and N4 is not satisfactory because of the "liquid" characteristics of the low solids content sludges (which would almost certainly flow as a mud in the event of an embankment failure) and because of the long term risks associated with the generation of leachates containing dissolved metals.

The proposal to jointly stabilise wastewater sludges with process residues (due to be effective as from June 1993) will substantially reduce environmental risks associated with the handling and storage of the former.

Cadmium cake management

The present method of containment of cadmium cake is unsatisfactory because of the risk that rainwater will enter the ponds and that contaminated leachate will be produced. Control of such leachate presently is entirely dependent on manual intervention.

Processing the cake to cadmium metal and, thereby, eliminating the need to store cadmium cake on site is the preferred PDI strategy. However, assuming a start date of mid-1993 and taking into account the additional refining capacity available after mid-1994, it will take at least five and possibly six years to clear the backlog.

Under these circumstances additional action is required to protect the integrity of the system for a five to six year period.

Proposed process changes (calcine feed)

Jarosite residues (from processing of calcine feed material) generally are classified as hazardous, mainly because they contain lead and cadmium.

In view of the proposed changes in legislation relating to the containment of hazardous wastes in Thailand, the long term storage of jarosite residues in single membrane ponds is unlikely to prove satisfactory.

9.2 Recommendations

Monitoring

The PDI monitoring protocol should be extended to include analysis of soils within surface water drainage ditches not connected to the existing recovery system.

The integrity of the under-drainage collection and transfer systems should be fully maintained particularly during the rainy season.

PDI monitoring procedures and results should be subject to independent audit on a once per year basis.

A post closure environmental monitoring and management plan should be put into place and funds allocated as appropriate.

Residues management

Facilities for leachate collection, transfer and treatment should be provided on all existing storage ponds containing non-stabilised silicate residues.

Storage ponds containing stabilised residues should be covered to minimise potential for infiltration of surface water.

Further studies and investigations should be carried out to achieve an "approved" end use of stabilised silicate residues (after further processing as necessary). UNIDO should consider providing technical support to PDI in this regard.

Wastewater sludges management

Wastewater sludges contained in ponds N2 and N3 should be removed for dewatering and possible stabilisation in admixture with silicate-based residues. This should take place over the period remaining for processing of silicate ores.

Cadmium cake management

Cadmium cake presently stored on site should be processed to cadmium metal as soon as possible

On the basis that a minimum of five to six years will be required to effect re-processing, a basic building structure should be provided around the existing storage points to prevent airborne dusts from being generated and to minimise potential for penetration of surface water and generation of leachate.

Proposed process changes

Jarosite residues should be contained in double membrane storage ponds designed in accordance with the proposed new MOI regulation for hazardous waste containment (unless stabilised to the extent necessary to permit consideration of the single membrane option).

Alternative hydrometallurgical and/or pyrometallurgical processes should be considered to convert Jarosite to hematite or other inert end product/by-product of value. UNIDO should consider providing technical support to PDI in this regard.

APPENDIX A

RESIDUE STABILISATION

**REVIEW OF REPORT OF MATERIALS SCIENCE RESEARCH INSTITUTE
OF CHULALONGKORN UNIVERSITY**

- A1 Objectives**
- A2 Characteristics of ore and ore residue**
- A3 Stabilisation of ore residue**
- A4 Leaching test on stabilised ore residue**

Toxicity test
Shake test
Slow shake test
Results

APPENDIX A

RESIDUE STABILISATION

REVIEW OF REPORT OF CHULALONGKORN UNIVERSITY

A1 Objectives

A report from Metallurgy and Material Science Research Institute of Chulalongkorn University (1989) has been reviewed. This report was a contract research between PDI and Chulalongkorn University, the objective being to find the most economic way of stabilising process residue from the zinc refinery (using lime or cement).

A2 Characteristics of ore and ore residue

Physical and chemical properties of ore residue were analysed. Physical characteristics of ore residue received from PDI in November 1987 are shown in Table A1. The average moisture content of ore residue was about 80-90 percent by weight. Liquid limit was about 49.9 percent and the residue was non-plastic which means the material can flow at high moisture content. The specific gravity of the residue was 2.70. Maximum dry density of ore residue was 1.234 t/m^3 at the optimum moisture content of 41.6 percent. The unconfined compressive strength by using cylindrical sample when obtaining maximum comparison was 2.39 kg/cm^2 .

Chemical characteristics of ore residue were as follows:

pH	5.6
organic matter	0.03%
cation exchange capacity	5.7 meq/100 gm of dry sample

Chemical composition of ore residue and original ore obtained from PDI were also analysed using x-ray fluorescence analysis by Energy Dispersive x-ray Fluorescence Spectrometer model EDXRF XR-200 and shown in Table A2.

Zinc ore contains ZnO at about 24.33 percent while SiO_2 is the major composition of the ore at about 40.95 percent. The Al_2O_3 content was about 9.70 percent. After processing, the ore residue consisted of ZnO about 1.37-3.01 percent while SiO_2 was about 37.10-55.80 percent. S became higher at about 7.23-16.47 percent. The other elements were similar to the zinc ore.

A3 Stabilisation of ore residue

The study was performed by mixing ore residue with different quantities of lime and/or cement and compacting to obtain higher density. Samples were tested for maximum dry density and optimum moisture content and then prepared at maximum dry density to determine the optimum lime or cement content for stabilisation of ore residue. The samples were tested for compressive strength using the TASTMD 2166 method.

The result of the test is shown in Table A5. The result indicates that, at lime content less than 3 percent, increase in strength with curing time is not significant. However, at a lime content higher than 4 percent the strength increased in proportion to the lime addition. At lime content higher than 10 percent the compressive strength again became a constant. The report concluded that a lime content of 4 percent would be sufficient to stabilise the process residuals. However, to obtain full solidification the lime content would have to be increased to 10 percent.

A4 Leaching test of stabilised ore residue

Leaching tests were carried out to identify the stability of stabilised ore residue of PDI waste. Three different methods of test were performed:

- Toxicity test method issued by Ministry of Industry (MOI)
- Shake test developed from Standard Leaching Test of EPA
- Slow shake test development from method of Johnson, Lancione and Sanning.

Toxicity

The first method is the toxicity method which was issued under the Ministry of Industry No 25 BE 2531 (1988). The extract procedures and method of analysis of pollutants are as follows:

- Grind and sift to reduce size of waste particles to between 0.5-5 mm.
- Add 50 g of sample into solvent ($H_2O + HCl$ at pH 5.8-6.3). Ratio of solution is 10 times (ml) to weight (g) of sample.
- Shake sample on agitator for 6 hours (200 cycle/min 5 cm stroke length).

Filter solution with asbestos paper (pore size 1 micron).

Analyse filtrate by AA method.

Shake test

There are two shake test methods, namely maximum concentration and maximum release. The methodology is compared in Table A4.

Slow shake test

The procedure of this method is as follows:

- Cut stabilised ore residue into a cylindrical shape of 7 cm dia x 2.3 cm thick. Leave in open air situation for 7 days. Drill a small hole at centre.
- Hang up this specimen in a 2 l beaker, fill the beaker with solvent at pH 4 using 10 times the amount of specimen.
- Stir continuously by magnetic stirrer for a period.
- Filter through glassfibre filter paper (size 1 micron).
- Submit filtrate for pH measurement and AA analysis.
- Repeat above procedure until the concentration of heavy metals in water are constant.

Results

The results of the four tests are shown in Tables A5 to A8.

From Table A5 the result of toxicity tests of the 4 percent lime-stabilised PDI ore residue showed that the residue leached out very small amounts of heavy metal when compared to the leaching standard issued by MOI. The residue could be classified as non-hazardous waste according to the MOI.

From Tables A6 and A7, the result also indicated similarly that leaching from 4 percent lime stabilised ore residue is very small compared to the MOI standard.

Table A.1 – Physical Characteristics of ore residues (November 1987)

1) Moisture Content	80 – 90 % by weight	ASTM-D 2216 : Laboratory determination of moisture content of soil
2) Liquid Limit and plastic Limit	L.L. = 49.9 % PL. = NP (non . plastic)	ASTM-D 4318 : Test method for liquid limit plastic limit and plasticity index of soil
3) Specific gravity	2.70	ASTM-D 854 : Test method for gravity of soils
4) Dry density	Max dry density = 1.234 ton/m ³ Optimum moisture content = 11.6 %	ASTM-D 698 : Moisture – density relations of soils and soil aggregate mixtures using 5.516 rammed 12 in drop
5) Unconfined compressive strength	2.39 kg/cm ²	ASTM-D 2166 : Test method for unconfined compressive strength of cohesive soil

Table A.2 – Chemical Composition of Ore Residue and Ore

Composition	Ore residue as received in		Ore material
	May 1989	Nov 1987	received on September 1987
SiO ₂	37.1	55.8	40.95
Al ₂ O ₃	7.15	9.83	9.70
CaO	13.78	8.9	4.94
K ₂ O	1.54	1.51	0.85
TiO ₂	0.28	0.03	0.19
MgO	1.06	-	3.08
S	16.47	7.23	0.41
MnO ₂	0.7	0.78	4.41
Fe ₂ O ₃	6.63	7.02	24.33
ZnO	3.01	1.37	0.19
PbO	0.33	0.31	-
ZrO ₂	-	0.03	-
SrO	0.01	<0.02	-
Na ₂ O	-	-	-
CuO	0.08	-	-

Table A.3 – Compressive strength test of stabilised residue with time

	Compressive strength (kg/cm ²) at 0 to 90 days curing time					
	0 day	7 Day	14 day	30 day	60 day	90 day
0	3.80	4.14	4.59	5.60	7.00	7.75
1	3.70	4.43	5.10	6.67	7.23	7.80
2	3.76	4.65	5.77	6.56	7.12	7.90
3	3.56	5.83	6.67	7.29	7.35	8.00
4	3.76	8.30	8.69	10.60	11.25	12.22
6	3.42	12.73	17.44	17.94	20.13	20.25
8	3.76	19.82	26.74	30.61	33.64	32.24
10	3.98	30.27	36.44	42.44	42.89	42.61
12	3.27	31.62	37.42	42.05	42.05	42.61

Table A.4 – Comparison of shake test methods

Maximum Concentration Test I	Maximum Release Test (II)
1) Grind and sift to reduce size of waste particles to 0.5 - 1.65 mm	1) Same as I
2) Using distilled water adjusted to pH 4 with HCl	2) Same as I
3) Ratio of waste particle (g) to volume of solvent (ml) is 1:10	3) Same as I
4) Shake for 24 hrs (200 cycle/min 5cm. stroke length)	4) Same as I
5) Allow sedimentation for 1 hour. Filter through fibre glass paper (pore size 1 micron)	5) Same as I
6) Take part filtrate sample for pH measurement and heavy metal analysis by AA	6) Take all filtrate samples for pH measurement and heavy metal analysis by AA
7) Measure volume of remaining filtrate, add sample powder by 1:10 ratio	7) Dry sediment at 60 °C for 15 hrs. Add solvent (ratio 1:10)
8) Shake as before for 24 hrs, filter, take sample and analyse. Follow the same procedure 7 times	8) Shake as before for 24 hrs, filter, submit filtrate sample for analysis and follow the same procedure 7 times.

Table A.5 – Results of Toxicity Test

	pH after leach	Heavy metal concentration (mg/l)						
		Zn	Cd	Mn	Pb	Cr	As	Hg
1) Stabilised Ore residue 0.5 – 5 mm	9.08	0.056	0.007	<0.004	<0.02	<0.1	<0.01	<0.0002
2) Stabilised Ore residue 0.5 – 5 mm. mixed with size 0.5 – 1.0 mm	9.20	0.07	0.006	<0.004	<0.02	<0.1	<0.01	<0.0002
3) Silicate Ore	7.80	0.38	0.06	0.008	0.02	<0.1	<0.01	<0.0006
4) Non stabilised residue	6.54	360	3.6	8	0.02	<0.1	<0.01	<0.0008
MOI Leaching standard		-	1	-	5	5	5	0.2
Public Health drinking water standard		5	0.01	0.05	0.05	0.05	0.05	0.002

Note : Tests carried out at room temperature (26°C)

Table A.6 – Result from Shake Test

Leach No	Samples	pH after leach	Zn	Cd	Mn	Pb
			Conc mg/l	Conc mg/l	Conc mg/l	Conc mg/l
1	A	9.08	0.006	<0.002	<0.004	<0.02
	B	6.75	1100	14.7	27.1	0.13
2	A	9.21	0.01	<0.002	<0.004	<0.02
	B	6.67	2350	29.5	50.9	0.25
3	A	9.61	0.03	<0.002	<0.004	<0.02
	B	6.63	3440	43.1	73.7	0.25
4	A	9.77	0.045	<0.002	<0.004	<0.02
	B	6.60	4170	54.6	96.8	0.38
5	A	9.50	0.068	<0.002	<0.004	<0.02
	B	6.41	5900	68	134	0.38
6	A	9.58	0.052	0.002	<0.004	<0.02
	B	6.45	6970	79.4	158	0.38
7	A	9.64	0.062	0.002	<0.004	<0.02
	B	6.44	7940	93.6	200	0.38

A : Stabilised ore residue

B : Non stabilised ore residue

Table A.7 - Result from shake test

Leach No	Samples	pH after leach	Zn		Cd		Mn		Pb	
			Conc mg/l	% Leach	Conc mg/l	% Leach	Conc mg/l	% Leach	Conc mg/l	% Leach
1	A	9.15	0.01	0.0007	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	6.59	1005	74.4	12	85.7	22.4	7	0.1	0.06
2	A	9.84	0.015	0.001	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	6.87	152	11.2	1.1	7.86	3.1	0.97	0.02	0.01
3	A	9.22	0.025	0.0018	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	7.14	46.2	3.4	0.87	6.21	0.82	0.26	0.02	0.01
4	A	8.92	0.02	0.0015	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	7.09	22.5	1.67	0.45	3.21	0.42	0.13	0.02	0.01
5	A	8.63	0.017	0.0012	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	7.15	12.9	0.95	0.23	1.64	0.19	0.06	0.02	0.01
6	A	8.90	<0.002	<0.0001	<0.002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	7.25	8.28	0.61	0.15	1.07	0.13	0.04	0.02	0.01
7	A	8.90	<0.002	<0.0001	0.0002	<0.014	<0.004	<0.001	<0.02	<0.01
	B	7.49	5.08	5.08	0.12	0.86	0.1	0.03	0.02	0.01
% of heavy metal leached compared to original amount		A	<0.007		<0.098		<0.007		<0.07	
		B	92.6		106.6		8.49		0.12	

A : Stabilised ore residue

B : Non stabilised ore residue

Table A.8 - Result from Shake Test

Period	pH after leach	Heavy metal concentration (mg/l)			
		Zn	Cd	Mn	Pb
2	8.48	0.010	0.014	0.020	<0.02
4	8.95	0.023	0.004	<0.004	<0.02
6	8.77	0.013	0.002	<0.004	<0.02
8	8.51	0.011	0.002	0.004	<0.02
9	8.55	<0.002	0.004	0.004	<0.02
10	8.63	0.009	<0.002	<0.004	<0.02
13	8.60	<0.002	<0.002	0.004	<0.02
15	8.36	0.016	<0.002	0.004	<0.02
17	8.29	<0.002	<0.002	0.004	<0.02
22	8.65	0.013	<0.002	0.004	<0.02
27	8.53	0.015	<0.002	0.004	<0.02
34	8.51	0.017	0.002	0.010	<0.02
41	8.43	0.009	0.003	0.009	<0.02
49	8.36	0.004	0.002	0.009	<0.02