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THE CHARACTERISATION AND LEACHING BEHAVIOUR OF COAL WASHERY TAILINGS

A thesis submitted in partial fulfilment of the requirements for the award of the degree

MASTERS OF SCIENCE (HONOURS)

from

THE UNIVERSITY OF WOLLONGONG

by

PETER M^{C}GLINN, B. Sc.

DEPARTMENT OF GEOLOGY

1992

ABSTRACT

This work investigates the ultrafine component of the reject stream from West Cliff Colliery, near Appin, on the NSW South Coast. The tailings studied were less than 118µm in size. The tailings were characterised mineralogically and elementally, using analytical techniques such as XRD, SEM, γ-Spectrometry and ICP. A series of standard and modified leaching tests, based on the BEOP-31 standard, was used on the tailings to determine the release of four of the primary elements, and ten heavy metal elements, under different leaching conditions.

The tailings were found to consist mainly of kaolinite, siderite, including a magnesium-bearing siderite, calcite and quartz, with lesser amounts of illite and magnetite. Kaolinite was considered to be the primary source for aluminium in the leachates, siderite for iron, calcite for calcium, and the magnesium-bearing siderite for magnesium.

The release of calcium and magnesium was relatively high, saturating the leachates, and accounting for the alkalinity. The pH of the leachates increased rapidly from 4 of the initial leaching solution to 9. The release of the heavy metals was very low. The leaching of manganese differed from the other heavy metal elements, and appeared to parallel that of magnesium and calcium for at least some of the leaching time.

The release of the heavy metals from the tailings was generally much less than the concentrations recommended for potable water by the SPCC.

Geochemical modelling of the leaching system was able to predict pH and magnesium and calcium concentrations in the leachates reasonably well. Modelling of the dissolution of siderite and kaolinite was not successful probably due to the complex behaviour of these minerals in aqueous systems.

ACKNOWLEDGEMENTS

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TABLE OF CONTENTS

APPENDICES

CHAPTER 1

INTRODUCTION

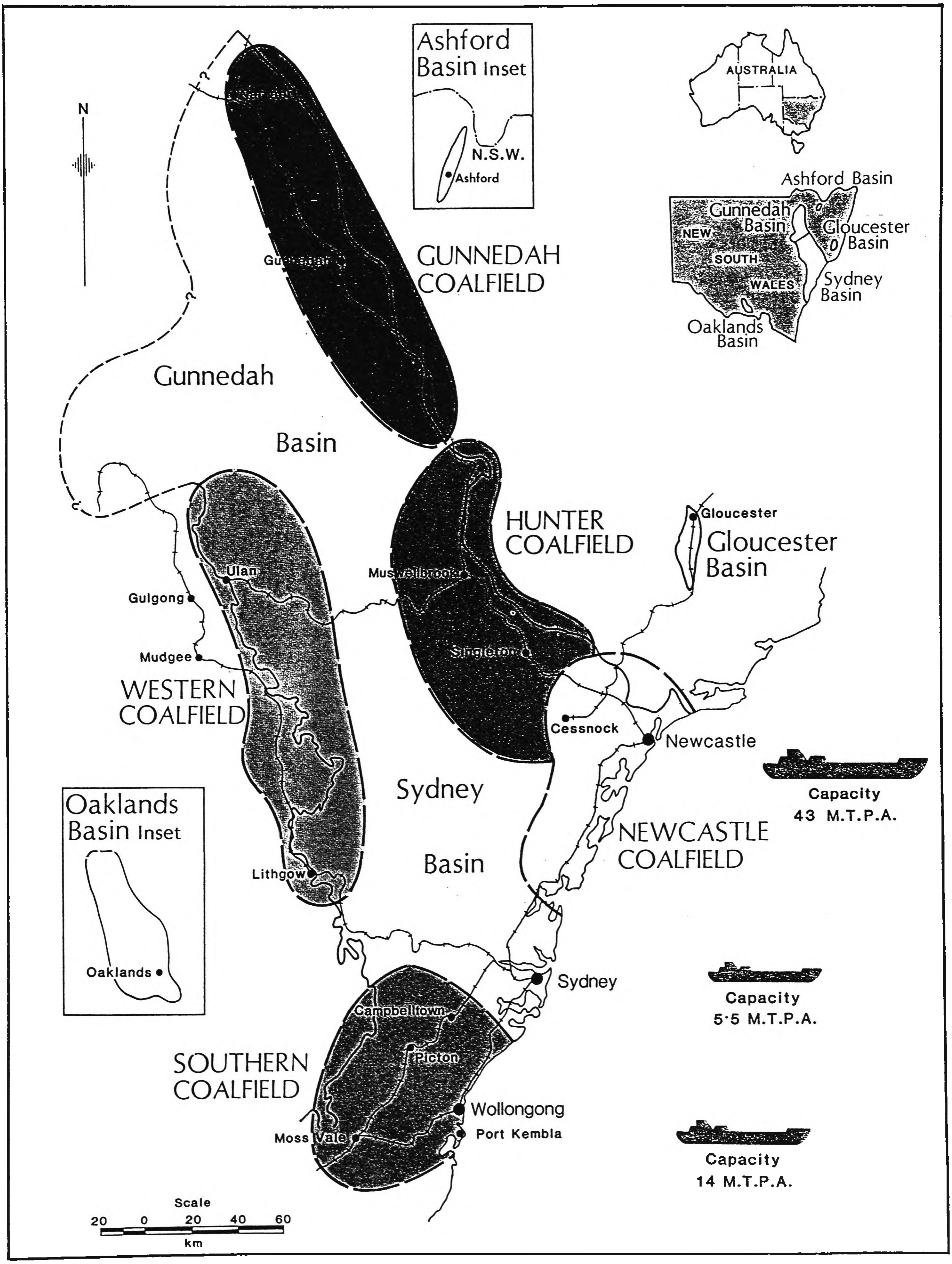
Coal mining is the principal mineral resource industry of New South Wales and one of the most important in Australia. Figure 1.1 shows the major coal mining districts in New South Wales. The South Coast region of New South Wales is one of the oldest coal mining districts in the State and accounts for 20% of the total state coal production (Joint Coal Board, 1990). There are 17 mines in this area (see Figure 1.2) primarily mining the Bulli and Wongawilli seams (see Figure 2.3, Chapter 2, for stratigraphic details). The Bulli Seam is the most important and is mined by the majority of the mines.

All aspects of the coal industry have some impact on the environment. Coal exploration, evaluation and development programs, and coal utilisation can have significant impact on the physical, chemical and biological environment in many areas. The various impacts on the environment are summarised in Figure 1.3.

Coal, by its very nature, is a heterogeneous material, and is defined as a sedimentary formation of combustible, organic material containing inorganic rock and mineral matter (Speight, 1983). Coal produced from operating mines is even more variable due to the incorporation of non-coal bands, mineral aggregates and a certain amount of roof and floor rock in the output material. The introduction of mechanised, high productivity extraction methods such as the longwall has resulted in run-of-mine coals that are finer, wetter and dirtier than in the past, and given rise to an increasing need to prepare or clean the material in some way before use.

Washing of mined coal is carried out to improve coal quality. Coal washing removes a high proportion of the extraneous mineral matter making the

Figure 1.1 Major Coal Mining Districts of New South Wales (Source - NSW Department of Minerals and Energy, 1989)



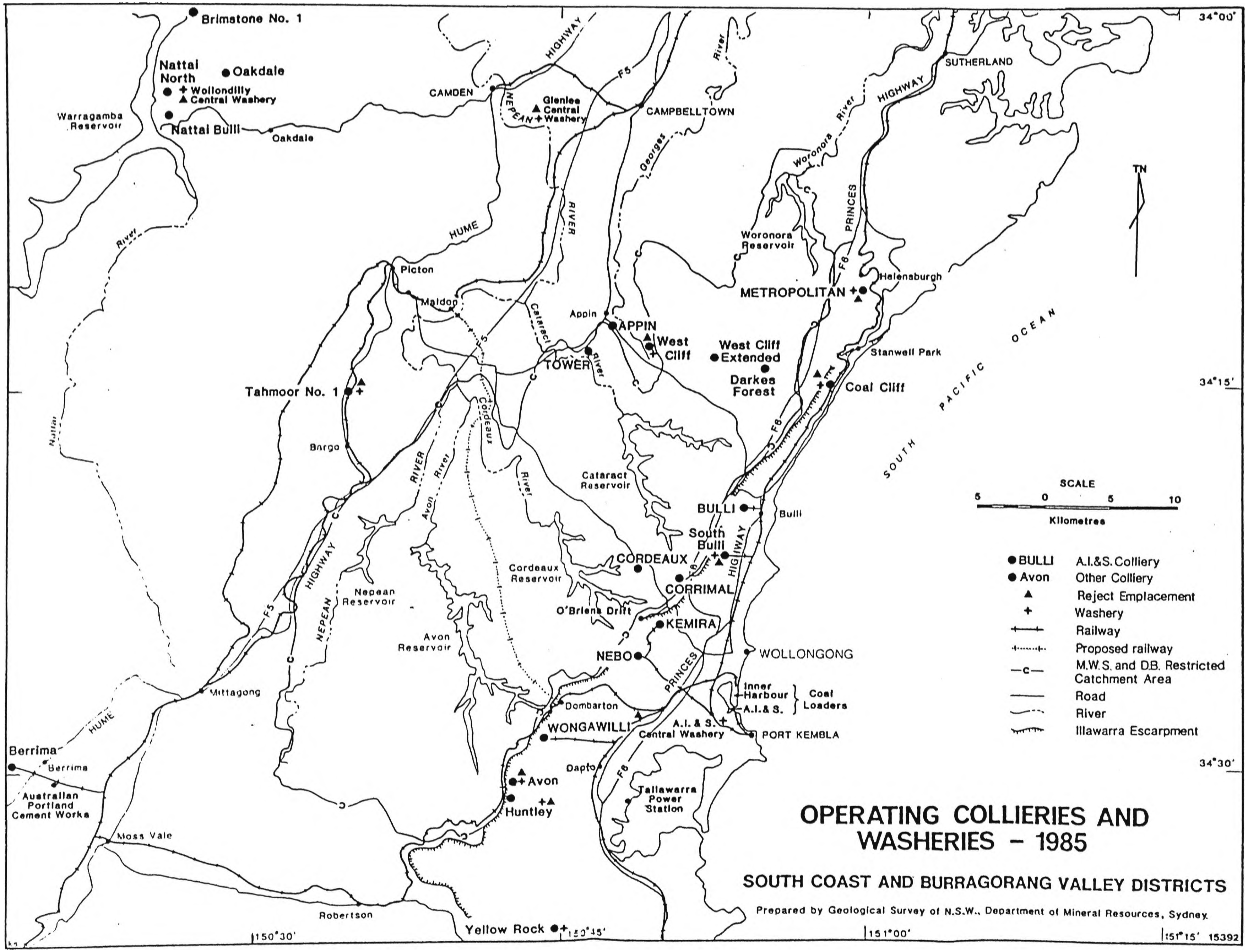


Figure 1.2 Coal Mines of the Illawarra District (Source - NSW Department of Minerals Resources, 1984)

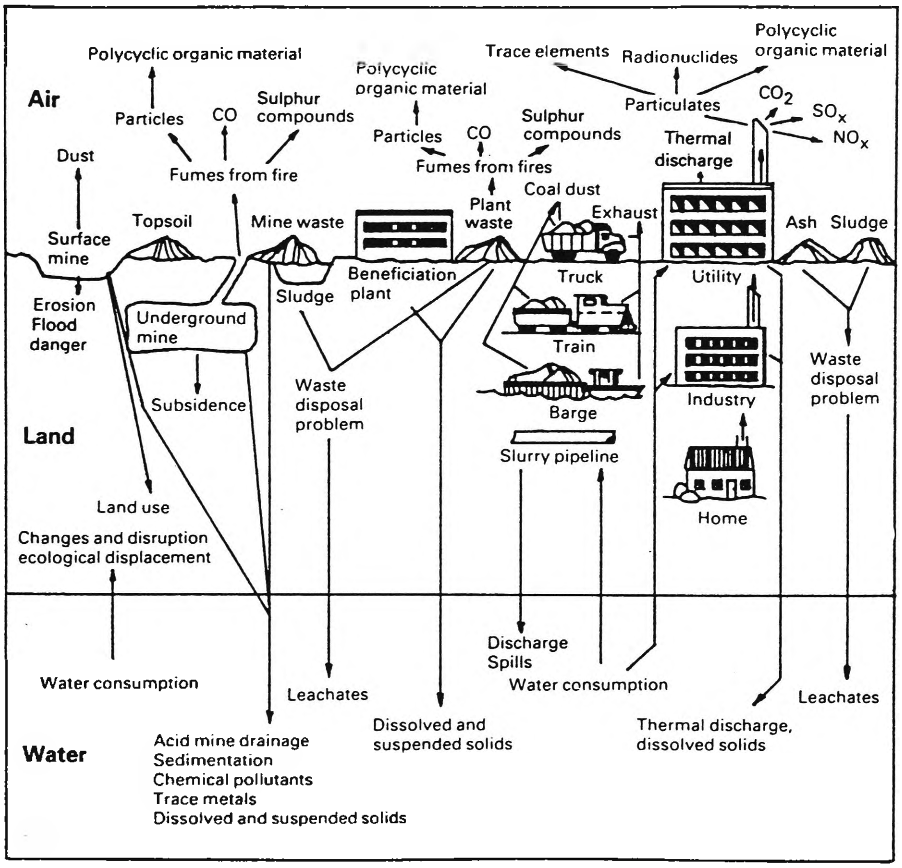


Figure 1.3 Environmental Impacts of Coal Mining, Transportation and Utilisation (Source - Ward, 1984)

coal more amenable for utilisation e.g. in power generating facilities and for steel making. This is particularly important for the coal export industry where severe penalties may be incurred by coal producers for supplying coal below contract specifications. Buyers' specifications for the level of mineral matter in coking coal are generally more stringent than those for steaming coal.

Coal washing produces not only coal for utilisation but solid waste material. There are three basic types of solid waste, distinguished on the basis of particle size:

- Coarse reject, with a particle size ranging from 12.7 to 127mm.
- Medium-sized reject, with a particle size ranging from 12.7 mm to 0.5 mm.

- Fine rejects, more commonly known as tailings, with a particle size less than 0.5 mm.

The annual production of coal washery rejects in New South Wales has increased substantially in the last 30 years - from approximately two million tonnes to 13 million tonnes (Joint Coal Board, 1990). In fact, the production of coal washery rejects has increased at a faster rate than the production of coal due to more stringent market demands for lower ash coal, more efficient mining techniques which allow for the economic recovery of higher ash coal, and greater efficiencies in coal preparation. It has been estimated that the growth rate for coal demand in New South Wales will increase by 2.6% per year to the year 2000 (Department of Resources and Energy, 1986).

A study carried out by Stockton (1979) surveyed fine rejects disposal in Australia. The results showed that tailings produced by New South Wales and Queensland collieries accounted for 18% of total rejects production. Stockton refers to estimations by Edwards (1976) that 30% of world coal production is rejected and, on this basis, in excess of 550 million tonnes of waste are produced annually. Colliery waste disposal, therefore, is a significant problem.

During the physical cleaning of coal, naturally-occurring elements in the coal and associated mineral matter partition among the clean coal, the coal waste and the process water used for cleaning. The coal fraction is generally depleted in trace elements whilst the waste is enhanced in trace elements (Swaine, 1985).

An inherent problem in the disposal of solid waste on land is the possibility of groundwater contamination, and the contamination of natural surface waters, by the leachates from the waste. In the United States and Britain, groundwater infiltration of coal washery wastes has led to pollution problems associated with the generation of acid mine drainage contaminated with heavy metals leached from the tailings. In Australia little work has been carried out on the leaching of solid wastes to determine if this is true for local coal mining regions.

This thesis addresses the lack of information on the environmental impact of disposal of Australian coal washery tailings by assessing the source term for releases of trace elements from the tailings. This has been done by leaching the tailings over time, analysing the leachates and studying the accompanying changes in the mineralogy of the tailings. Knowledge of the leaching behaviour of the tailings will be important in determining the proportion of the elements present in the residue that can be removed by leaching, and in determining the behaviour of a dump of this material when exposed to the environment. The experimental results coupled with computer model simulations can be used to determine the effect of leaching on other, coarser waste material, dumped under similar conditions.

In particular, this thesis investigates tailings produced at West Cliff Colliery, near Appin, in the Illawarra region of New South Wales (see Figure 1.2 for location). West Cliff Colliery mines the Bulli Seam at a depth of 400 to 500 metres and produces a premium grade coking coal. The New South Wales Coal Yearbook 1989-90 (Joint Coal Board) shows that West Cliff produced 237,400 tonnes of washery rejects (15% of raw coal production) during that year, of which 2% were ultrafine tailings. Of the 17 operating South Coast/Illawarra coal mines West Cliff is the third largest producer of washery reject material. All solid waste from West Cliff Colliery, including tailings, are disposed of on site.

This work investigates the mineralogy of the tailings component of coal preparation wastes from West Cliff Colliery, and the leaching of heavy metals from the tailings, especially those heavy metals which are more commonly considered to cause environmental problems, viz. mercury, chromium, copper, zinc, manganese, cadmium, arsenic and lead. These metals, in sufficiently high quantities, may be a hazard to certain animal life and vegetation.

CHAPTER 2

BACKGROUND

The geology of the Bulli coal seam and the procedures used to clean the coal and dispose of the tailings, at West Cliff, are detailed below.

2.1 Geology

The world's most extensive and valuable coal measures were laid down shortly after the evolution and rapid propagation of land plants in the late Devonian period, about 345 million years ago. It was termed the Carboniferous period by European geologists because it marked the appearance of vast accumulations of productive coal measures (Whitmore, 1979). However, in Australia, the occurrence of coal in the carboniferous sequence is insignificant, prolific deposits only forming in the subsequent Permian period with further accumulations occurring in the Triassic, Jurassic and Cretaceous times. Figure 2.1 shows an approximation of the geological age of the world's coal resources.

A comparison between the northern hemisphere's carboniferous coals and those of the Australia's Permian coals show that the Carboniferous representatives are generally lower in mineral matter content, and that the range in variation of ash of the individual Carboniferous coal types is more restricted than the corresponding Permian types (Marshall, 1967).

Although the inorganic impurities in coals of the two periods are normally represented by the same principal groups of minerals - with clays, quartz, feldspar, carbonates and sulphides predominating - differences arise in the total content of impurities and the proportional representation of the particular categories of mineral matter. Quartz, for example, is a ubiquitous mineral. It generally occurs in higher proportions in the washery refuse

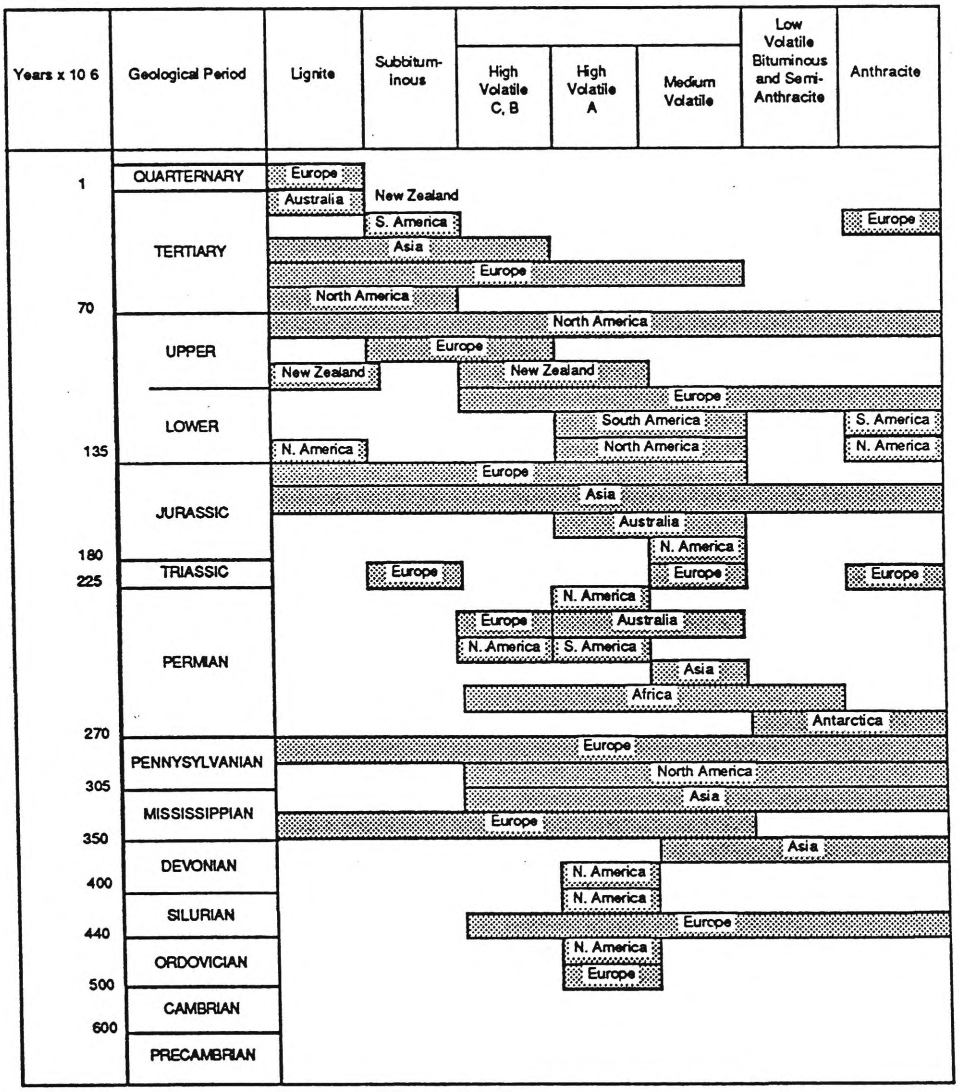


Figure 2.1: Approximation of the Geological Age of the World's Coal Resources (Source - Pretor, 1986)

than in the coal itself, or the intraseam clay bands, as there is usually significant contamination from the roof and floor strata (Ward, 1980).

West Cliff Colliery lies in the Southern Coalfields of New South Wales (see Figure 1.2, Chapter 1). These coalfields form part of the Sydney Basin, stratigraphically shown in Figure 2.2. West Cliff mines the Bulli Seam which forms the uppermost part of the Permian Illawarra Coal Measures. These coal measures occupy the southeastern segment of the Sydney Basin and lie conformably upon the Shoalhaven Group. The Triassic Narrabeen Group, likewise, lie conformably upon the coal measures. Figure 2.3 shows the stratigraphic sequence of the Illawarra Coal Measures.

GROUP	SUBGROUP	FORMATION
WIANAMATTA GROUP		Bringelly Shale Minchinbury Sandstone Ashfield Shale
		Mittagong Formation
		Hawkesbury Sandstone
NARRABEEN GROUP	Gosford Subgroup	Newport Formation Garie Formation
	Clifton Subgroup	Bald Hill Claystone Bulgo Sandstone Stanwell Park Claystone Scarborough Sandstone Wombarra Claystone Coalcliff Sandstone
ILLAWARRA COAL MEASURES	Sydney Subgroup	Bulli Coal Eckersley Formation Wongawilli Coal Kembla Sandstone Allans Creek Formation Appin Formation Tongarra Coal Wilton Formation
	Cumberland Subgroup	Erins Vale Formation Pheasants Nest Formation
SHOALHAVEN GROUP		Broughton Formation Berry Siltstone Nowra Sandstone Wandrawandian Siltstone
	Conjola Subgroup	Snapper Point Formation Pebbley Beach Formation Wasp Head Formation
CLYDE and YARRUNGA COAL MEASURES		
TALATERANG GROUP		Tallong and Yadboro Conglomerates Pigeon House Creek Siltstone

Figure 2.2: Stratigraphy and Depositional Environments of the Southern Sydney Basin Succession (Source - Bamberry, 1992)

SUBGROUP	FORMATION	MEMBER	OBSOLETE NOMENCLATURE
Sydney Subgroup	Bulli Coal		Nattai Seam
	Eckersley Formation	Balgownie Coal Member Lawrence Sandstone Member Cape Horn Coal Member Hargrave Coal Member Woronora Coal Member Novice Sandstone Member	Gillan Creek Seam
	Wongawilli Coal		Bend Creek Seam
	Kembla Sandstone		Colemans Creek Sandstone
	Allans Creek Formation	American Creek Coal Member	Bimlow Seam
	Appin Formation	Darkes Forest Sandstone Member	
		Bargo Claystone Member	Lacys Creek Sandstone
	Tongarra Coal		Brimstone Seam
	Wilton Formation	Woonona Coal Member	Kooloo Seam Higgins Creek Conglomerate
Cumberland Subgroup	Erins Vale Formation	Kulnura Marine Tongue	
	Pheasants Nest Formation	Figtree Coal Member Unanderra Coal Member Berkeley Latite Member Minumurra Latite Member Calderwood Latite Member Five Islands Latite Member	Tonalli Seam

Figure 2.3: Stratigraphy of the Illawarra Coal Measures, Southern Coalfield (Source - SCCG, 1971), Including Obselete Nomenclature for Comparison

The palaeoenvironmental setting for the entire Sydney Sub-group has been suggested by Bamberry *et al* (1989) to be deltaic and, more specifically, of the Deltaic System C type. Throughout this Sub-group there are sequences of prodeltaic, delta front, distributary mouth bar and interdistributary bay deposits. The sandstones of the upper Eckersley Formation, which immediately underlies the Bulli Seam, are interpreted by Bamberry *et al* (1989) to represent laterally coalesced meander belts, evidenced by a succession of vertically-stacked fining upwards sequences. They found that there is little evidence of contemporaneous development of this seam with the fluvial sequence and conclude therefore that it has been formed following the abandonment of the fluvial setting. Williams and Moore (1983) similarly found that the Bulli seam and the partings within the seam are laterally extensive, suggesting that the depositional environment during coal formation was a broad, shallow swamp or lacustrine.

2.2 Coal Beneficiation

An important facet of modern coal mining is coal beneficiation. Coal preparation embraces all the handling and the treatment of the coal from the time it reaches the mine outlet until it is finally despatched to the market. Australian coals tend to be young in geological age and higher in ash content by world standards[1], and to conform to the consumers' low-ash quality standards, preparation of the coal before marketing is essential.

These tighter specifications have led to a continually rising proportion of coal mined in the world being washed. For example, in Australia, the raw coal washed in New South Wales has increased from 67.2% of total production to 74.1% over the past ten years (Joint Coal Board, 1990). Beneficiation has the additional benefit that the coal deliveries are of a consistent quality.

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[1] Indicative analyses of North American, British and Australian coals are 5-15%, 2-15% and 5-23% respectively (Ward, 1984).

The output of a colliery consists of organic coal and inorganic mineral matter. The mineral matter has its origin in the rock strata overlying or underlying the coal seam, or from layers of shale (generally) occurring in the coal seam or from fine particles of mineral matter occurring more or less intimately with the organic material.

Coal washing for the market place generally includes a composite process of crushing, screening, washing and dewatering in some form. Figure 2.4 shows the flow chart of the West Cliff washery. The actual washing itself consists of separating the particles of coal and refuse which occur in all particle size ranges from a few microns to hundreds of millimetres.

Generally, separation is made by exploiting differences in specific gravity and wetting characteristics of the coal and refuse particles. The raw coal entering the washery is reduced in size to below 127 mm, by a rotary crusher, and then passed over a trash screen to remove foreign objects, for example pit props and metal bars. The coal is then separated into sizes above and below 12.7 mm preparatory to washing.

The coarse material (12.7 to 127 mm in size) is treated in a Baum jig, with provision for the retreatment of the middling product. The intermediate size, from 12.7 down to 0.5 mm, is treated in single-stage, magnetite-based, heavy-medium cyclones. Both the coal product and the waste material from the cyclones are washed to recover the magnetite.

Material less than 0.5 mm in size is processed in a two-stage froth flotation plant, using Davcra and Warman cells, before being de-watered by multileaf vacuum filters. Washed coal and reject material are stored in reinforced concrete bins before being despatched or stockpiled. The reject from the froth flotation separation is known as tailings. The tailings must be treated for final disposal and to clarify the water so that it can be returned to the plant's water circuit and re-used for washing.

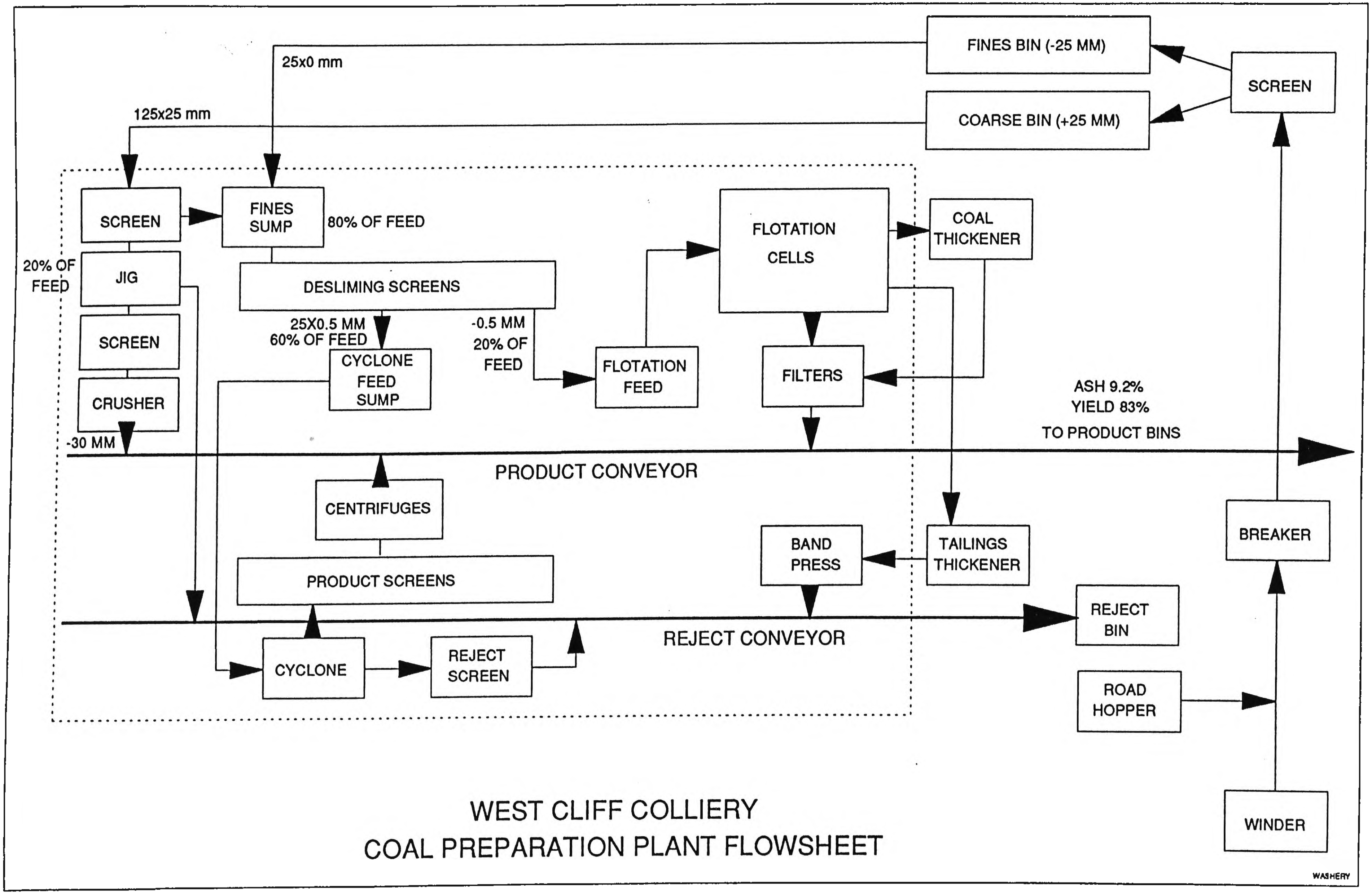

Figure 2.4: West Cliff Colliery Coal Preparation Plant Flowsheet

A major problem in the washing circuit is attributed to the presence of ultrafine mineral matter known as 'slimes'. Slimes are formed when a shale is placed in contact with water because the clay components soften, swell, and tend to disperse causing the shale to disintegrate. The extent to which this occurs is largely dependent on the microstructure and ionic characteristics of the clays present (Ward, 1980).

The presence of these minerals very strongly affects the plant process as fine clay is difficult to remove by settling, and even more so by filtration. As most coal washeries attempt to operate with complete water recycle, it is essential to remove the slimes because they will build up rapidly and seriously affect the washing process.

The process of separating the clay suspension from the water is carried out by a combination of thickeners and a scavenging flotation circuit. Solids from this circuit consist of both fine coal, which goes to the vacuum filtration unit then onto product storage, and slimes, which are de-watered and usually mixed with the coarser tailings for disposal.

West Cliff washery has an additional step in its processing of slimes - a band-press filter (see Figure 2.5) which further reduces the moisture content of the slurry to about 40% by weight. The use of this filter results in cake moisture contents that are low enough so that the slimes can be transported by conveyors. The slimes are then either combined with the coarser refuse for disposal or dumped separately.

Originally, super-fines reject, in the form of a slurry concentrate, was removed from the West cliff washery by road tankers, but disposal costs by this method were very high and use of this method was abandoned.

Figure 2.5: Band Press Filter, Used for De-watering of Slimes, in Operation

2.3 Tailings Disposal

Sound engineering and environmental practice requires that refuse created by coal beneficiation is contained rather than being released into the environment. As there is little scope for the underground disposal or 'stowage' of coarse washery refuse in modern underground mines alternative methods of disposal must be used (Ward, 1980). Where coal is mined by surface methods, the refuse can be readily returned to the pit as part of the land regeneration process.

In underground mining, where disposal of the waste material underground is not possible, then surface emplacement must be used to contain coal preparation wastes. In this disposal method, the site has to be stable, with as low a slope angle as possible. Natural valley drainage has to be diverted around the emplacement area during its formation, while adequate ponds have to be incorporated to prevent water contaminated with suspended solids from entering otherwise clean river systems. Figure 2.6 illustrates some systems adopted for coal refuse emplacement, including both downhill and uphill sequences of operation. West Cliff Colliery uses the uphill (b) emplacement technique, as shown in Figure 2.7. The individual layers are compacted to approximately one metre in thickness. A cross-section through a sequence of layers is shown in Figure 2.8. These layers are usually composed of combined coarse, mid-range and fine wastes. However, the slimes are occasionally dumped separately, as shown in Figure 2.9.

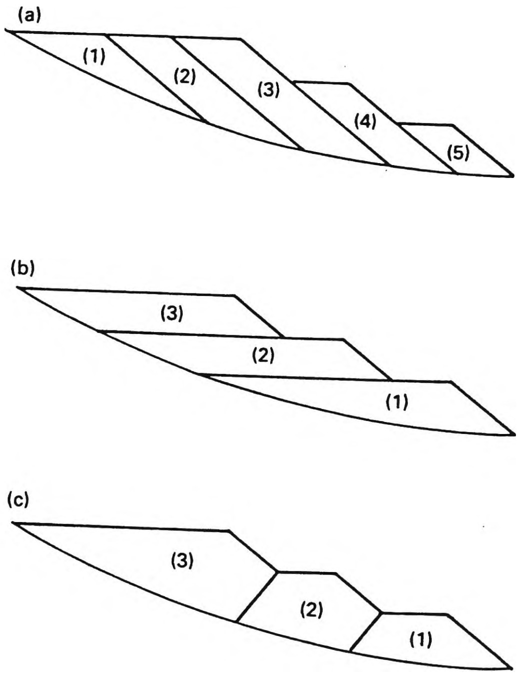

Figure 2.6: **Schematic of Systems Adopted for Coal Refuse Emplacement, Including Both Downhill (a) and Uphill (b and c) Sequences of Operation (Source - Ward, 1984)**

Figure 2.7: Uphill Technique of Stockpile Construction Using Horizontal Layers

Figure 2.8: Cross-section Through Layered Sequence of Reject Material

Figure 2.9: Slimes Dumped Separately in Impoundment

Drainage from the rejects stockpiles flows into a settling pond adjacent to the stockpile area. Overflow from this pond runs into Brennan's Creek, a tributary of the George's river. The George's River ultimately flows into Botany Bay, south of Sydney.

Tailings from coal preparation plants may also be disposed by suspension in wash water slurries, generally pumped from the washing plant into impoundments where the sediment is allowed to settle. The clarified water is then decanted or pumped from the ponds and recycled. The use of dams and ponds, however, creates environmental problems with regards to visual impact and rehabilitation.

Other methods of disposal have been proposed as alternatives to current emplacement methods. These include fluidised bed combustion, alumina production, brick manufacture, road base and structural fill, and offshore disposal. Of these alternatives, fluidised bed combustion (FBC) has been investigated most fully, although the problem of disposing of at least most of the original waste still exists after combustion (Department of Mineral Resources, 1984). The waste from FBC's is much finer than the feed and this presents its own disposal problems.

A significant environmental advantage of FBC was highlighted in a commission of inquiry into the Investigation of Proposed Sites and Methods of Disposal for Coal Washery and Industrial Waste Within the Wollongong Plain Sub-region. The report noted that the leachability of the combusted material is generally reduced compared to the original feed. This, of course, has implications for the release of heavy metals from the waste material.

Despite the investigative work carried out to date on the alternatives for coal waste disposal, none of the above methods is available as a technologically, economically and environmentally proven method at the present time. In the early 1980's a number of mines in Britain introduced the addition of cement to the slurry concentrates from the washeries to form stable disposal material (English, 1981), thereby reducing the migration of heavy metals through acid mine drainage.

West Cliff is in the fortunate position of emplacing refuse without any significant accompanying problems, compared with A.I & S at Port Kembla, approximately 30 kilometres southeast of West Cliff Colliery, where the availability of such emplacement sites is limited because of the intense competition by other land uses.

CHAPTER 3

PREVIOUS WORK

This chapter summarises the previous research that has been carried out on the environmental impact of coal washery tailings, and of reject material in general. In particular:

- tailings mineralogy,
- trace elements,
- use of leaching tests to characterise the magnitude of heavy metal releases from the tailings, and
- the use of thermodynamic, reaction path modelling to model releases from coal washery tailings.

3.1 Tailings Mineralogy

The mineralogical makeup of tailings is drawn from both the in-seam 'dirt' bands and the generally shaly rock that forms the roof and floor of the Bulli seam. The in-seam bands are commonly shaly and are generally similar in composition to that of the roof and floor material. The original source of the partings in the coal is generally thought to be clay and silt-sized inland water sediments washed in over the coal forming swamps by occasional floods or changes in the river deltas within and surrounding the swamps (Williams and Moore, 1983). A coal forming environment requires a very slow moving water system. These layers of mud, later compacted and lithified into shale, vary slightly in composition depending on the original source of the river sediments.

Considering the many possible sources of such sediments, it is interesting to note that the composition does not vary greatly from that of a typical shale

(Williams and Moore, 1983). The reason for this is the natural particle size classification which occurs in any river system. Only very fine particles can be transported into coal forming swamps due to the decreasing velocity of the rivers and streams as they widen out releasing the suspended sediment load as the topography became increasingly flat. Under these conditions, the last particles in the river water to drop out of suspension are the clay sized particles. It is for this reason that the common rock types that form within coal seams are claystone, shale and siltstone. Thicker partings within coal seams are generally due to tectonic movements causing uplift of the surrounding area, or sinking of the swamp relative to the upstream area, and a subsequent influx of sediment (Williams and Moore, 1983).

The clays and associated minerals which comprise shales assume a stratified structure in which the clay acts as a binding material. The dominant clays in shale are kaolinite, illite and, more rarely, montmorillinite. All three are hydrous aluminium silicates, together with other ions such as calcium, magnesium, potassium, iron and sodium (Ward, 1980).

Probably the most common of the clay minerals are those of the kaolinite group and they are formed (often accompanied by quartz, iron oxides, iron sulphides, carbonates and by other clay minerals) principally by the hydrothermal alteration or weathering of feldspars, feldspathoids and other silicates (Libicki, 1983).

The mineralogy of tailings generated from Australian coals are similar to those from other areas of the world except that there are generally much higher levels of sulphide compounds in overseas coals. The lower levels of sulphide minerals in coal washery wastes in Australian mines means that the importance of environmental problems caused by the oxidation of sulphides, and the accompanying acid mine drainage from coal mines and refuse dumps, is less severe than that experienced in the United States and Britain.

Ward (1980) described the mineralogy of New South Wales coals as consisting typically of clay, quartz, sulphide and carbonate minerals. This includes minerals which are either intimately incorporated in the coal itself (inherent mineral matter), and those minerals associated with the intra-seam dirt bands/partings, and the material that comprises the floor and roof of the seam (extraneous mineral matter). Ward (1980) also examined the mineralogical characteristics of colliery waste materials from 28 of the operating 36 coal washeries in New South Wales. Using X-ray diffractometry he identified peaks for calcite, dolomite, expandable clays, feldspar, gypsum, halite, illite, kaolinite, pyrite, quartz, siderite and thernadite.

3.2 Mineral Dissolution

The kinetics of mineral dissolution in water is dependent on a number of factors, including the types of minerals present, the surface area to solution volume ratio, and the temperature and partial pressure of CO_2 (Amrhein *et al*, 1985). The kinetics of dissolution of carbonates, for example, in most environments, are considered to be intermediate, i.e. more rapid than for the clay minerals, but slower than for the typical evaporite minerals (Chilingar *et al*, 1967).

In a solid/aqueous system, when the solution concentration of a species is equal to its solubility limit then the forward (dissolution) and reverse (precipitation) reactions rates are the same and the solution concentration will not change with time. On the other hand, if an element has not reached its solubility limit then the dissolution of the solid phase will continue, albeit under some conditions at a very slow rate, until the solubility limit is reached. Under these conditions, the solution concentration of the element will continue to increase with contacting time.

Most previous work on mineral solubility has focussed on calcite. Garrels and Christ (1965) described the solubility of calcite, as a representative of the carbonate minerals, under five different sets of conditions to show that many variables have to be specified to fix the solubility of a carbonate mineral. One of the set of conditions chosen was the reaction of calcite in pure water with the system open to CO_2; i.e. in contact with a reservoir of fixed partial pressure of CO_2. They considered this system to be of great geological importance, as it represents lakes, streams and other dilute natural waters in intimate contact with the atmosphere, in which the pH of the system is controlled entirely by the carbonate equilibria. This system compares closely with those conditions that exist in a tailings dam or disposal area.

Jenne (1979) refers to experiments which also investigated the CO_2 dependence of calcite dissolution. The experiments showed that the rate of dissolution was directly proportional to surface area and the stirring rate, but independent of CO_2 gas velocity being bubbled through the solutions. Therefore, the reaction rate was independent of transfer of CO_2 from the gas to the liquid phase.

These results suggest that transport of dissolved species from the surface of the solid was the controlling mechanism of dissolution which agrees with the work of Reeder (1983). He found that in highly undersaturated solutions, the rate of calcite dissolution is controlled by transport processes between the mineral surface and the bulk solution. Sjoberg and Rickard (1983) found that a stationary diffusive layer is created over much of the reactive surface of fine calcite (<100um).

Sjoberg and Rickard also suggested that where movement occurs during reaction, such as in a shake leach test, convection also plays a role. The effect of experimental conditions on the dissolution of calcite suggests that extrapolation of solubilities from one set of conditions to another may not be valid.

3.3 Major Elements Associated with Mineral Matter In Coal

Major constituents of coals are considered to be elements that are present in quantities usually above about 0.1% weight (Swaine, 1985). For the purposes of this current work, this concentration will also be used to distinguish between the major and trace constituents in the tailings.

Major elements that have been identified in tailings from the processing of Australian coals include magnesium, calcium, aluminium, iron and silicon. These elements are generally associated with carbonate minerals, clays, quartz and sulphides (Ward, 1980).

3.4 Trace Elements Associated with Mineral Matter In Coal

Trace elements may be associated with the mineral matter in coal seams as discrete minerals, as replacement cations, or associated with clays, either as replacement cations or adsorbed (Swaine, 1985).

Depending on the reference examined, for example Purves (1977), Ward (1980), Heaton *et al* (1982), the suite of trace elements which are considered to be of most environmental importance differs. However, the elements which regularly appear in the literature as potential environmental hazards are those highlighted in Figure 3.4.1.

The origin of trace elements in coal and the associated mineral matter have been covered by many workers and has been summarised well by Swaine (1989). It is likely that the trace elements in coal originated from one or more of the following processes:

- concentration of the elements in pre-coal vegetation by physiological and physicochemical processes,

- deposition into coal-forming peat swamps after leaching from rocks and ore bodies,
- concurrent deposition with the coal,
- deposition at a later stage in the form of cleats and other mineralisation zones.

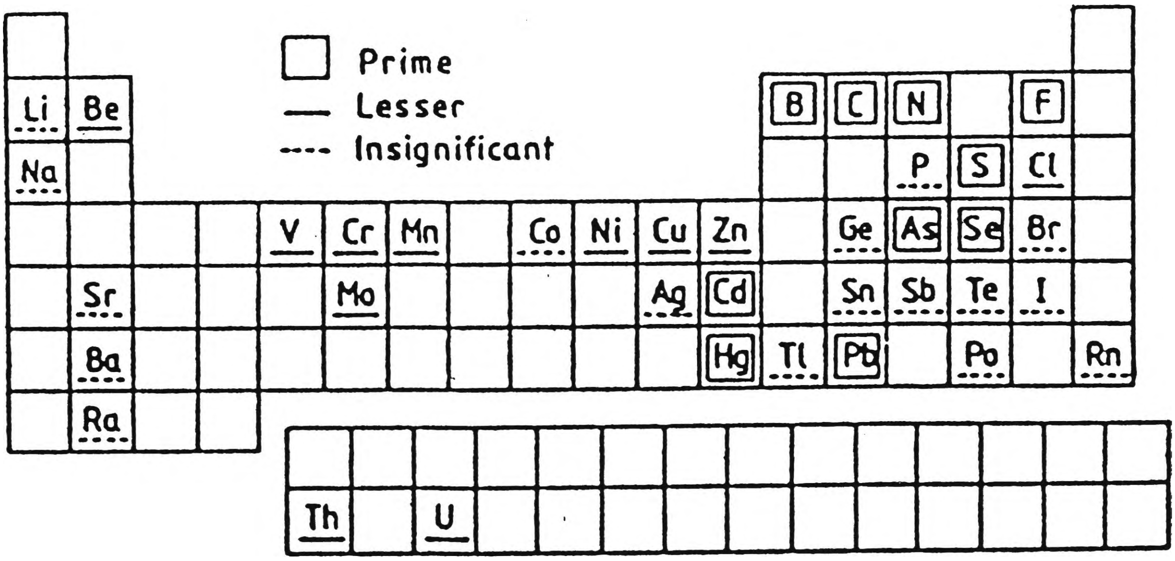

Figure 3.4.1: Trace Elements of Relative Environmental Significance (Source - Swaine, 1985)

A comparison of the trace element contents between Australian and overseas coals was made by Swaine (1985). Table 3.4.1 lists those same elements, and their concentrations, that have been studied in this work. The Table shows that for most elements Australian coals have a lower trace element concentration than for those of the U.S. This historically has given Australian steaming coal exporters a marketing advantage over exporters from most other parts of the world.

Other studies carried out on trace elements associated with bituminous coal seams include those of Dale *et al* (1986). They studied the trace element partitioning during fluidised bed combustion carried out at the Glenlee fluidised bed pilot plant in the Burragarong Valley in the Illawarra region.

Plant feed included high ash steaming coal and washery rejects (including tailings) taken directly from the nearby Glenlee washery. The Glenlee coal preparation plant, like West Cliff, washes Bulli seam coal. Their study investigated the use of both feed types but in their paper they presented results to a trial carried out using high ash steaming coal only. Analytical data for the trial are given in Table 3.4.2.

TABLE 3.4.1: Trace Element Concentrations (in ppm) Associated with Bituminous Coals Worldwide (Source - Swaine, 1985)

Element	Australia	U.S.	South Africa	U.K.	Poland	West Germany
As	<0.1-55	<1-170	0.9-8.2	2-73	0-40	1.5-50
Cd	0.05-0.20	<0.004-9	ND	<0.3-3.4	0-4	<1.3-10
Cr	<1.5-30	2-84	12-63	3-45	0.6-12	4-80
Cu	2.5-40	3-160	4.2-16	12-50	8-150	10-60
Hg	0.026-0.40	0.01-1.8	ND	<0.2-0.7	ND	<0.7-1.4
Mn	2.5-900	1-1400	0-180	11-250	ND	ND
Pb	1.5-60	<1-62	1.9-25	8-63	4-150	20-270
Th	<0.2-8	<3-26	4.0-21	0.7-6.7	ND	ND
U	0.4-5	<0.1-15	3.0-7.3	0.5-2.3	0-1	<1-1.3
Zn	12-73	1-1600	3.2-16	30-200	5-300	17-210

ND - Not Determined

Swaine (1984) refers to an extensive study on some US bituminous coals, carried out by Finkelman (1980), to determine the likely mode of occurrence of the trace elements they contained. Table 3.4.3 shows the occurrence of some of the trace elements he investigated. The elements listed are the trace elements investigated in this work.

TABLE 3.4.2: Analytical Data for High Ash Steaming Coal Feed to Glenlee Fluidised Bed Combustor (Source - Dale, Patterson and Duffy, 1986)

Element	Concentration (mg kg^{-1})
Arsenic	3.2
Cadmium	0.5
Chromium	Not Determined
Copper	15
Lead	15
Manganese	190
Mercury	0.2
Thorium	7
Uranium	1.9
Zinc	14

TABLE 3.4.3: The Inorganic Occurrence of Some Trace Elements Associated with Bituminous Coals, Mainly from the US (Source - Swaine, 1984)

Element	Occurrence
Arsenic	In solid solution in pyrite
Cadmium	In sphalerite
Chromium	In clays
Copper	As chalcopyrite
Lead	As galena
Manganese	In siderite
Mercury	In solid solution in pyrite
Thorium	In rare earth phosphate minerals
Uranium	In zircon
Zinc	As sphalerite

Swaine (1985) believed that these results were in general agreement with Australian coals investigated. Additionally, he found that manganese was also associated with calcite and that arsenic may occur as arsenopyrite.

Deer, Howie and Zussman (1977) reported the following associations between particular minerals and heavy metals:

- Calcite - Mg, Mn, Fe^{2+}, Sr, Ba, Co and Zn.
- Siderite - Mn, Mg, Ca, Zn and Co.
- Magnesite - Fe^{2+}, Ca, Mn, Ni, Co and Zn.

The amounts occurring, they suggest, depend on physicochemical and/or biochemical influences.

Manganese is often found in association with coal seams. It was suggested by Swaine (1986) that manganese is commonly found associated with Australian coals in carbonate minerals. Swaine refers to other studies that found in the absence of carbonates, clays are another possible association. Warne (1986) listed a number of possible inorganic sources for manganese, including rhodochrosite ($MnCO_3$) and siderite, the latter being the most common. Isomorphous substitution between rhodochrosite and siderite readily occurs.

In United States coals, manganese has been found to be associated with sulphide minerals e.g. sphalerite. Only minor proportions have been found to be similarly linked in Australian coals. Swaine (1986) pointed out that the manganese content of Australian coals was higher than that for the United States, and suggested that this was due to the presence of greater amounts of siderite in Australian coals than in North American coals.

The ability of the tailings to filter, attenuate, adsorb, and retain or neutralise contaminates such as heavy metals in the reject material can be traced to the nature and manner of interaction of the various constituents of the rejects heap, and in particular to the bonding forces, cation-exchange capacity, surface functional groups, specific surface areas, and surface activity of the particles contained in the waste piles (Yong, 1988) These properties of the waste material will change as a result of interaction with specific contaminates. Yong (1988) found that heavy metals in waste dumps occur predominantly in a sorbed state. He believed that co-precipitation with iron oxyhydroxides and incorporation in silicate lattices appear to be primary sorption mechanisms of heavy metals on clays.

In addition to the properties of the solid phase, groundwater chemistry, particularly pH, can affect retardation of heavy metals in the reject dumps. The role of pH was highlighted by Yong (1988), who found that at high solution pH (~8.5), heavy metal hydroxides and carbonates may form precipitates.

3.5 Leaching

Solubility studies by laboratory extraction or leaching procedures are currently considered the best available approach for assessing the potential environmental impact of leachates from solid wastes (Roy *et al*, 1984).

Although leaching studies have been the fundamental basis of assessment of environmental risk of waste materials for a long period time, a comprehensive investigation in the Netherlands (De Groot *et al*, 1989) set out to establish that the leach tests in the BEOP-31 standard for the leaching of combustion residues (and similar materials), developed five years earlier, were reproducible and reliable. De Groot *et al* believed that this was necessary because of a general lack of agreement between results of the other various test methods. They applied the standard tests to fifty samples from a wide variety of sources.

The term leaching is generally used to describe selective cation removal by ion exchange with H^+ from solution, leaving the network lattice essentially intact (Jostsons *et al,* 1990). The process by which the structure dissolves uniformly is referred to as dissolution rather than leaching.

More appropriately, in reference to this work, the process of weathering describes surface reactions for minerals exposed to atmospheric conditions. In these circumstances, the pH of a thin film or trapped volume of water can, through ion exchange, reach values at which breakdown of lattice occurs. This type of reaction has been invoked for solution attack on borosilicate glasses, through the formation of 'solution cells' at pores and fissures within which high pH levels lead to the base-catalysed hydrolysis of the silicate framework (Jostsons *et al,* 1990). Such a mechanism could be occurring within the silicate framework of the clays, in particular, in the tailing samples investigated in this work.

The choice between a column test and a shake test for the assessment of leaching behaviour depends to a large extent on the situation. If it is of interest to know the initial concentration in the percolate of a dump, only the column test will give the answer. A shake test, on the other hand, is the more obvious way of obtaining information on the total quantity of an element leachable from a residue. Jackson *et al* (1984) found that the batch extraction method offers advantages over the column method because of its greater reproducibility and simpler design, while the column method is more realistic in simulating leaching processes which occur under field conditions. It is one of the aims of this thesis to determine the source term for the tailings under investigation, i.e. to determine the total quantity of an element leachable from the tailings, so the more applicable test is the shake test.

3.6 Geochemical Modelling

The chemical characteristics of any aqueous system are controlled by:

- Physical conditions, especially temperature and pressure
- Concentrations of dissolved species
- Presence of solid phases
- Time

Accordingly, these characteristics form the basis for geochemical modelling of rock/water interactions. The model used in this work is the EQ3/6 program developed by Wolery, 1983, and Wolery and Daveler, 1989.

The EQ3/6 software package consists of two programs - a geochemical aqueous speciation-solubility FORTRAN program (EQ3NR), and a program for making thermodynamic, reaction path, and kinetic path calculations (EQ6). The relationship between the two programs is shown in Figure 3.6.1.

Basically, the speciation-solubility model is a static model of an aqueous solution which estimates the concentrations and activities of all of the important aqueous species in the solution and calculates the relative saturation of various minerals. EQ6, the reaction path model, predicts the path of a reacting system by calculating changes in total concentrations, concentrations of individual aqueous species and their thermodynamic activities, and the appearance and disappearance of reactants and products as a reaction progress or time variable advances (Wolery, 1983).

The output of EQ3NR contains the concentrations and thermodynamic activities of individual species in solution, and this can be incorporated into the EQ6 input file. EQ6 can then calculate models of titration processes, rock/water interactions, interactions of water with substances other than rocks and minerals, effects of heating and cooling, fluid mixing, etc (Wolery, 1983).

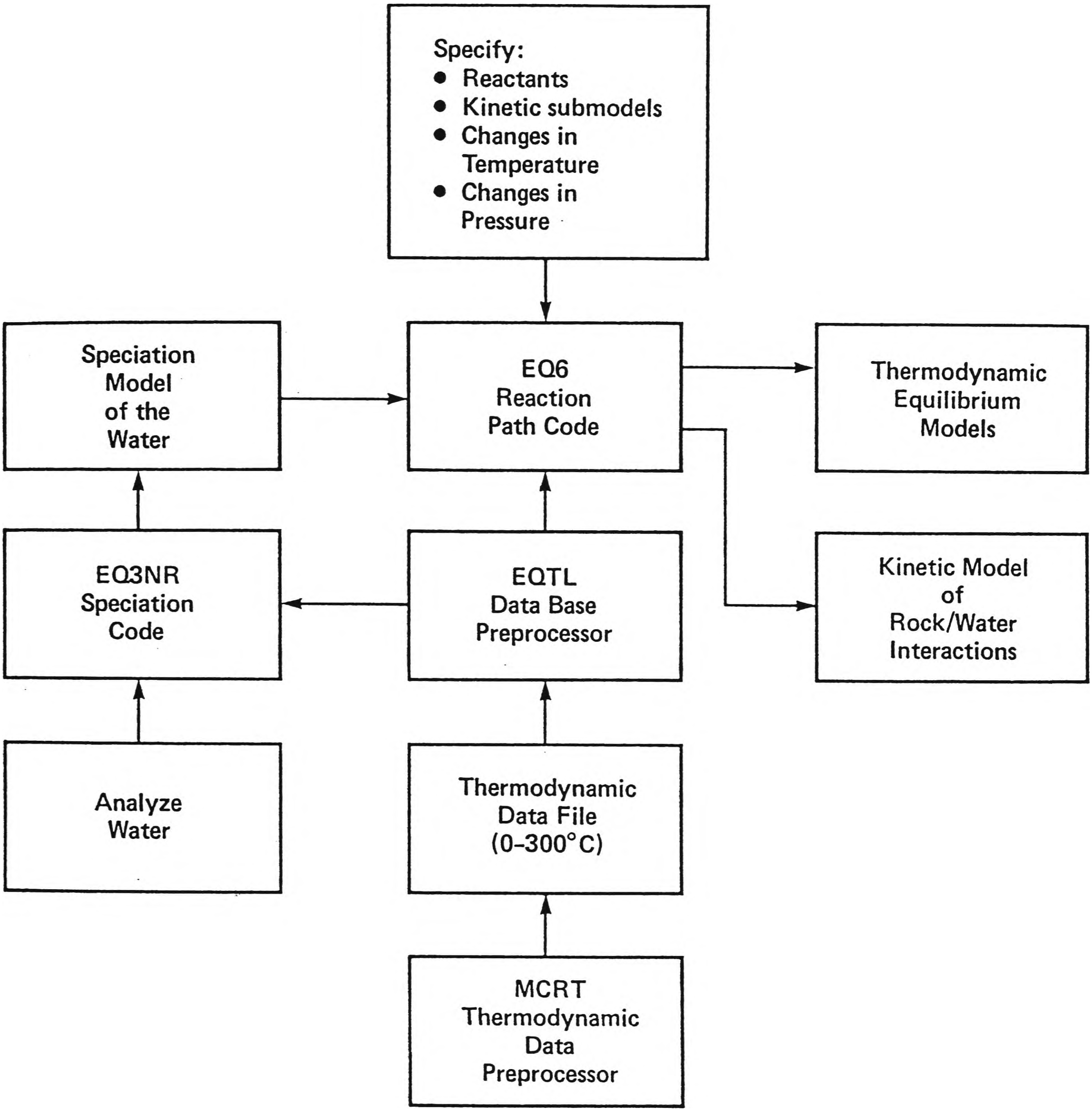

Figure 3.6.1: The Relationship Between the Aqueous Speciation/Solubility (EQ3NR) and Kinetic Path (EQ6) Programs (Source - Wolery, 1983)

CHAPTER 4

EXPERIMENTAL PROGRAM

At present, the determination of all the elements in coal and coal waste is difficult and costly. Nevertheless, the experimental program carried out in this thesis was fairly intensive and a number of analytical techniques were used to characterise the solids and leachates prior to, and after, leaching.

After collection of the tailings from West Cliff Washery they were prepared for testing at the Ansto Lucas Heights Research Laboratories. Characterisation of the tailings was carried out at Ansto using analytical instrumentation in both the Environmental Sciences Program and the Advanced Materials Program areas. Leach testing was performed in the Environmental Sciences block in a laboratory specifically set up for leaching experiments.

4.1 Sampling of Tailings

Sampling of the tailings at West Cliff Washery was carried out by washery personnel, both for safety and industrial relations reasons. The washery staff at West Cliff Colliery are well-trained and competent with product sampling techniques and followed sampling procedures according to the appropriate Australian Standard AS 2646 Part 2 - Sampling of Solid Mineral Fuels from Moving Streams. Although the material collected was not a mineral fuel *per se,* the method employed was adequate to obtain a representative tailings sample.

The tailings were taken from the end of the band press prior to it falling onto the reject belt leading to the reject bin. Increments were taken regularly over a 48 hour period to arrive at a gross sample of approximately 100 litres in volume. The plant was in operation for the entire 48 hour period of sampling so the sample represents a full two day's washery production.

The tailings sample was collected from the plant the day after sampling, minimising the effect of leaching of the tailings from the water associated with the sample. In fact, the delay time in the roof, floor and intraseam material being removed from the coal face, processed in the washery to form tailings, and delivered to the laboratory for leach test preparation, was estimated to be only 72 hours.

4.2 Sample Preparation for Leaching

The Australian Standard AS 2646 Part 6 - Preparation of Samples, was used to prepare sub-samples to ensure that they were representative of the original bulk sample. The procedure gives the drying, grinding and sub-sampling techniques to be used. The individual steps involved in this procedure are given below.

The first step in preparing the sample for testing was drying. Air-drying of the sample was used to ensure that it will pass through the sample division equipment without loss, through sticking, or contamination. The sample was dried until there was no moisture visibly present.

As the sample had a particularly high moisture content, oven drying (at 80°C) was used to achieve drying of the sample as quickly as possible. This was to minimise unmonitored contact with water.

The particle size of the tailings was fine (<118 μm) so it was anticipated that there would be no need to carry out particle size reduction by grinding or crushing. However, after drying of the tailings, the sample remained aggregated and was not suitable for sample division. Consequently, a mortar and pestle was used to gently break up the aggregated material, taking care not to change the particle size distribution in the sample.

Division of the sample was carried out manually by two methods - open riffling and strip-mixing and splitting. The final samples required for leach testing were to weigh as little as 4.5 g so riffling was carried out down to a size of approximately 8 g, after which strip-mixing and splitting was used to arrive at the required sample size. Strip-mixing and splitting was also used to obtain small samples, of only a few grams, for analytical work described later.

Strip-mixing and splitting involves forming the sample into a strip and then dividing it into a number of segments. Sampling is carried out by taking a number of evenly-spaced segments from the strip.

4.3 Chemical Analysis of Leachates

Chemical analysis of the leachates was carried out by Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES), using a Bausch-Lomb Model 3510 spectrometer linked to a Hypec 286 personal computer, and Inductively Coupled Plasma/Mass Spectrometry (ICP/MS), using a VG Plasmaquad II spectrometer linked to a Compaq 386 personal computer. ICP/MS generally has greater precision and higher sensitivity than ICP/AES, a distinct advantage when measuring the extremely low concentrations of trace elements that were present in the leachates. ICP/AES, however, is capable of analysing particular elements without the interference which occurs when analysing those elements by ICP/MS.

Both ICP/AES and ICP/MS use an argon plasma, operating at temperatures of around 10000°C, to ionise the solution being analysed. With ICP/AES, the ions lose their energy when returning to their ground state and in doing so they emit photons with a wavelength characteristic of that particular element. A spectrometer selects each wavelength line and measures the intensity of the line. Because the light intensity is proportional to the concentration of the element in the sample, the composition of the sample can be determined by comparing the light intensity to that measured for known standards.

By comparison, ICP/MS extracts ions from the argon plasma into a two stage interface, through a small orifice in the sampler cone and again through a further orifice in the skimmer cone where the pressure drops to 10^{-6} mbar, thereby minimising the probability of free-ion collisions (*pers comm* Lam, 1991). A system of electrostatic lenses accurately focuses the positively charged ions into a mass filter, which only transmits ions of a selected mass-to-charge ratio. Individual ions are detected by an ion counting electron multiplier. Ion counts are accumulated in a multi-channel analyser (MCA) and, after collecting a large number of scans, the accumulated data is transferred to the computer data system. The data is processed, similar to that of ICP/AES, by comparing the sample counts to those measured for known standards.

4.4 Characterisation of Solid Samples

The tailings were characterised to determine their physical properties and mineralogical and elemental composition using a combination of techniques. Physical properties measured were size distribution and density. The amount of organic matter was also determined, by combustion techniques. Elemental analysis was carried out on those elements considered to be more environmentally hazardous, such as arsenic, cadmium, chromium, copper, mercury, manganese, lead, zinc, thorium and uranium. ICP/MS was used for elemental analysis of these trace elements after dissolution of the samples using a combination of hydrofluoric and boric acids.

Radionuclide analysis techniques were also used to determine the uranium and thorium content of the tailings.

Concentrations of several of the more common elements such as iron, magnesium, calcium and aluminium were also determined to help describe mineral dissolution. These elements are contained in the major mineral components of the tailings - aluminium (kaolinite), iron (siderite), calcium (calcite) and magnesium (magnesium-bearing siderite). These determinations were carried out by ICP/AES.

Silicon, although a major constituent of the tailings, was not measured because there were possible sources of silicon contamination arising from the analysis techniques.

4.4.1 Physical Properties of the Tailings

Particle size analysis

Particle size analysis of the tailings was carried out using a Malvern 3600 LBD Particle Sizer (Class IIIB Helium/Neon Laser). The Malvern 3600 LBD is a complete unit for the measurement, by laser diffraction, of particle size distributions in the range 1 to 1800μm. The laser is a 5mW helium-neon laser. The laser transmitter produces a parallel, monochromatic beam of light which is arranged to illuminate particles suspended in water in a sample cell. The incident light is diffracted by the particle to give a diffraction pattern which is focussed onto a multi-element photo-electric detector. The detector, which produces an analogue signal proportional to the received light intensity, is interfaced directly to a computer. The computer analyses the diffraction pattern to determine the particle size distribution.

To carry out the measurement, the tailings sample was suspended in one litre of deionised water in an agitated and ultrasonically-mixed tank. The resulting slurry is pumped through the sample cell, which is located in the path of the laser beam, and recycled to the ultrasonic tank.

Relative density

Relative density of the tailings was measured using using a pycnometer and deionised water. Relative density of a material is the ratio between the weight of the material and the weight of an equal volume of water. Briefly, the technique requires four weighings to be made - the empty pycnometer (W1); the pycnometer with the tailings added (W2); the pycnometer with tailings and water (W3); and finally the pycnometer with the water alone. The relative density was then calculated using the following relationship, where L is the density of water at ambient temperature and pressure:-

$$\text{Relative Density} = L \times \frac{(W2-W1)}{(W4-W1)-(W3-W2)}$$

Ash and organic material content

Tailings are essentially mineral matter with a relatively small proportion of organic material. The organic content of tailings varies considerably depending on the efficiency of the beneficiation process and the coal type. Australian Standard AS 1038 (Part 3 - 1979) is used to determine the ash content of coal, i.e. coal with a relatively small proportion of mineral matter. However, providing certain precautions are taken, the same standard can be used for the determination of organic material in tailings.

Ash determination is based on the heating of a representative sample of ground material in a muffle furnace, until combustion is complete, and expressing the mass of the residue as a percentage of the mass of the air dried material used. The sample is heated from ambient temperature to 800°C in 30 minutes, then to 815°C in a further 60 to 90 minutes, and maintained at that temperature until constant mass is achieved.

The numerical values for repeatability of an ash determination differ according to the ash content of the material, but for a sample with an ash content of >20% should not exceed 0.25% (Standards Association of Australia, 1979).

According to the standard, for a high ash content sample, such as tailings, combustion to constant mass may take considerably longer than for low ash samples. It is therefore important that the sample is heated for sufficient time to achieve complete combustion of the organic material. At temperatures as high as 800°C, the more volatile components of the tailings such, as lead and cadmium, are released. One of the aims of this work was to determine the amount of release of these elements from the tailings, so it was important to determine, as accurately as possible, the proportions of the elements originally in the tailings.

Chapman (*pers comm,* 1991) suggested combustion at the much lower temperature of 450°C, and over a much longer period of time (approximately 48 hours), to minimise the loss of the more volatile components of the tailings. This would also reduce the loss of carbon dioxide from carbonates, and the oxidation of pyrite. Consequently, this technique was used in this work.

4.4.2 Mineralogy of the Tailings

The mineralogical makeup of each of the tailings samples, before and after leaching tests, was carried out using a combination of X-ray Diffractometry and Scanning Electron Microscopy fitted with EDS. A high temperature technique (Department of the Interior U.S. Geological Survey, 1980), in conjunction with XRD, was also used for more detailed characterisation of clay components in the tailings.

X-ray Diffractometry

The X-ray Diffractometer used was a Siemens D500 equipped with a cobalt k_{α} radiation source and a graphite monochromator, and linked to an IBM portable computer. Samples were scanned through a diffraction angle range of either 5 to 80°, or 10 to 100°. The detection limit is 2% by volume, but this depends on the scattering effects of the minerals and interference patterns.

X-ray diffraction has been used previously in the analysis of the mineral components of coal (Ward, 1980). Coal has no particular crystalline structure and therefore does not contribute to the XRD pattern. This allows analysis of the crystalline components without the necessity to remove the coal fraction.

Clays, by their very nature, are stratified, and many exist as inhomogeneous layers of individual clay types. As water forms an integral part of a clay's composition, heating the material can dispel interlayer water and change the spacing between layers in some clays more readily, at at lower temperatures, than other clays. This characteristic makes it possible, through XRD, to determine the types of clay present in a specimen.

Many of the XRD peaks for kaolinite and illite overlap, so a dehydration experiment was carried out on a tailings specimen to assist in discriminating between the peaks. Kaolinite loses its interlayer water at a lower temperature than illite (Deer, Howie and Zussman, 1977), leading to changes in the crystallographic structure. The sample was heated at 550°C for 30 minutes and then analysed by XRD. After heating at 550°C for 30 minutes the constitutional OH content of kaolinite is lost (Deer, Howie and Zussman, 1977), with a subsequent destruction of its crystallography, and therefore undetectable peak intensity. Illite, on the other hand, the only other clay of notable proportions in the tailings, shows no discernible change in its crystallography after heating at 500°C. This is because illite generally contains no interlayer water and remains unaffected unless heated to temperatures greater than 550°C.

Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was used to assess the microstructure of the unleached tailings and each of the leached samples. The Scanning Electron Microscope used was a JEOL JXA 840 fitted with an energy-dispersive X-ray spectrometer (EDS) and a Tracor Northern X-ray analysis system. EDS quickly and easily determines the elements present in specimens, from which the mineralogy may be implied. It can be used to identify/speciate minerals present as minor components, generally below the detection limits of XRD. Spectra collected using this system could be quantified using Tracor Northern's commercial software package.

Powdered tailings specimens were coated with carbon to prevent surface charging and placed into brass holders for examination by SEM. SEM and electron probe X-ray energy dispersive spectroscopy were carried out at 15kV.

Special attention was given to dissolution features in the minerals which may help explain the observed composition of the leachates generated in this study. After dissolution tests the surface morphology of each of the leached specimens was examined by SEM to determine if leaching had caused any changes in the microstructure of the individual minerals. The tailing samples were viewed under magnification of up to 10,000 times. The SEM is capable of much higher magnification but this was not required to study the surface morphology of the tailings.

The EDS detection limit for unpolished, uneven surfaces, as examined in this work, is approximately 0.05%. For polished specimens this limit can be as low as 0.01% (*pers comm* Day, 1991).

4.4.3 Chemical Analysis of Tailings

For chemical analysis to be able to be carried out on the tailings the solid samples must be dissolved. Dissolution of the tailings was carried out using a procedure outlined in the Bureau Energie Onderzoek Projecten's (BEOP) standard for the leaching of combustion residues and similar materials (Van der Sloot *et al*, 1984). After digestion of the solid, elemental analysis of the material was carried out using ICP/AES and ICP/MS. These instruments together can determine most of the elements in the periodic table with high precision and sensitivity.

Analysis of the starting material requires complete dissolution. The BEOP-31 standard recommends that 750mg of the material is treated for two days with 20ml 20% hydrofluoric acid (HF). Then 80ml 5% boric acid (H_3BO_3) is added to dissolve a possible precipitate of calcium fluoride. The standard states that if the weight of the residue is more than 5% of that of the original sample, the residue has to be worked up and analysed separately. The figures so obtained are included in the total concentration. Otherwise the solution is filtered through a 0.45 µm Millipore filter and the filtrate used for analysis.

A tailings sample was combusted at 450°C to remove the organic material, after which the solid was digested according to the standard. The amount of residue remaining after digestion was 0.7%, so no further working up of the sample was necessary.

The filtrate was diluted to reduce the solids loading and acid concentration of the solution to within the limits acceptable to the ICP/AES and the ICP/MS, and to prevent blockages of the narrow apertures in the instrument during solution uptake. The ICP/AES has a tolerance of 1% solids loading, and the ICP/MS has a tolerance of 0.1%, The maximum acid concentration allowable for both spectrometers is 1%. Higher concentrations of acid can lead to dissolution of the glass components of the instruments. Samples for ICP/AES were diluted by a factor of four, and those for ICP/MS were diluted by a factor of seven and a half.

A digestion trial was carried out on uncombusted tailings to determine if the organic fraction of the tailings could be digested as well as the inorganic component. However the organic component was essentially unattacked by the acids and more than the specified 5% by weight of residue remained.

ICP/MS and ICP/AES were particularly useful for analysis because of the low concentrations of the trace elements in the leachates. ICP/AES was used for determining the levels of those elements in higher concentrations, namely calcium and magnesium, and for the analysis of elements that are difficult to analyse by ICP/MS, viz. aluminium and iron. Iron cannot be reliably analysed on the ICP/MS due to interference patterns from other elements, and there appears to be high variability in aluminium analyses using the Mass Spectrometer. This may be due to contamination caused by the use of an aluminium based cleaning paste used to clean parts of the instrument which come in intimate contact with the solutions aspirated into the plasma (*pers comm* Lam, 1991). For most elements, ICP/MS is more sensitive than the ICP/AES and was able to determine extremely low concentrations of trace elements in the leachates.

Table 4.4.3 gives the technique used for each element and its detection limit.

4.4.4 Gamma-Spectrometry

Uranium and thorium determinations were carried out on the tailings using γ-spectrometry as well as ICP/MS. Radionuclides occur as a result of the decay of naturally occurring uranium and thorium. The decay chains for uranium-238 and thorium-232 are shown in Appendix A. The gamma activities of the tailings were measured using a lithium-drifted germanium (GeLi) detector, supplied by EGG Ortec, linked to an IBM-XT based multichannel analyser. A 39g sample of the tailings was packed into a re-entrant container, commonly known as a Marinelli beaker. The detector has detection efficiences of 4.9% for the Marinelli geometry.

TABLE 4.4.3: Detection Limits of Elements Analysed by ICP/AES and ICP/MS (Source - Elan ICP Elemental Analysis System)

Element	Technique	Detection Limit (ng ml^{-1})
Aluminium	ICP/AES	75
Arsenic	ICP/MS	0.4
Cadmium	ICP/MS	0.07
Calcium	ICP/AES	0.1
Chromium	ICP/MS	0.02
Copper	ICP/MS	0.03
Iron	ICP/AES	10
Lead	ICP/MS	0.05
Magnesium	ICP/AES	1
Manganese	ICP/MS	0.04
Mercury	ICP/MS	0.1
Thorium	ICP/MS	0.02
Uranium	ICP/MS	0.02
Zinc	ICP/MS	0.08

Table 4.4.4 lists the most useful γ-peaks used in these analyses. Care must always be taken that the monitoring peak is in equilibrium with the parent nuclide. Processing of samples can affect secular equilibrium because of the different chemical behaviour of the radionuclides in each processing stage. Secular equilibrium will however begin to be re-established after processing. The rate of approach to secular equilibrium is determined by the half-life of the **daughter** (or daughters) and not the parent. A useful 'rule of thumb' is that secular equilibrium is approached within five half-lives of the longest-lived daughter. Included in Table 4.4.4 is an indication of how long it takes for the monitoring peaks to be in secular equilibrium with the radionuclide of interest.

TABLE 4.4.4: Gamma Peaks Used for Radionuclide Analysis

Peak (keV)	Radionuclide Detected	Half-life	Monitors*	In Equilibrium After
63.3	Thorium-234	24.1 d	Uranium-238	121 d
338.4	Actinium-228	6.13 h	Thorium-228*	31 h
583.2	Thallium-208	3.07m	Thorium-228*	18 d

* For short-lived radionuclides the long-lived parent is listed

Radionuclide activities are measured by comparing the sample to a standard counted in the same geometry. Concentrations of the radionuclides in the solid are calculated from the measured activity as follows:

$$C = \frac{A}{F} \times 10^6$$

where C = concentration in the solid (ppm)

A = Activity (Bq g^{-1})

F = conversion factor Bq g^{-1} to g g^{-1}

4.5 Leach Testing

Throughout this thesis, experiments wherein the coal tailings have been exposed to solutions (at different pH and for various periods of time) have generally been referred to as leach tests. Occasionally they have been referred to as dissolution tests. Wherever 'leach' is used in the context of macroscopic solution-based results, it is not meant to be inferring reaction mechanisms.

Leach testing was carried out in general accordance to the BEOP - 31 standard for leach testing procedures for coal ash and similar materials (Van der Sloot *et al,* 1984). The standard method is applicable to fine wastes from coal preparation plants as the mineralogical nature of the fines is generally very similar to that of the mineral constituents of the associated coal seam. The test results permit the assessment of short-term (< 5 years), medium-term (5-50 years) and long-term (> 50 years) environmental impact by varying the liquid to solid ratio (L/S)[1] used in the tests. The L/S ratio represents a relative time scale in practice.

To gauge roughly the relativity between the L/S ratio and these time periods in the case of a tailings dump, Van der Sloot *et al* (1984) proposed that in a hypothetical situation in which tailings are dumped on land (height of dump 5m), and the rate of percolation is one metre per year, it could be assumed that an L/S ratio of 1 is reached after approximately five years. On this basis, medium-term is represented by an L/S of 1 to 10, and the longer-term by an L/S greater than 10.

Of course, the specific relationship between the L/S ratio and actual time in a particular dump is dependent on a number of factors including the porosity of the material and the hydrogeology of the dump site. Establishing these factors for the West Cliff Washery waste emplacement is beyond the scope of this thesis. Generally, however, in the case of a dump, it will take a long time to reach an L/S ratio higher than about 3 (Van der Sloot *et al*, 1984).

Although the relativity between L/S and actual time for the West Cliff emplacement cannot accurately be specified, the results of this thesis can be used to predict the likely consequences of emplacing West Cliff tailings, and tailings of similar composition, under conditions where L/S ratios, such as those measured in these studies, exist. Leaching behaviour over a wide range of L/S ratios have been measured in this work, and these correspond to a variety of hydrogeological conditions that could exist in a tailings disposal area. Additionally, as the tests were used to determine the leaching behaviour of the tailings under standard conditions, so that they can be used

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[1] The L/S ratio is the ratio of the volume of liquid used, in millilitres, to the weight of solid leached, in grams.

for possible decisions about precautions to be taken when dumping the material.

The BEOP-31 standard includes a leaching test in which the leaching agent is percolated through a column filled with the material under investigation, or a series (cascade) of shaking tests at a given L/S ratio. The column test is used to determine the leaching behaviour at low L/S ratios, whereas the cascade tests simulate conditions at medium to high L/S ratios. Studies by Van der Sloot *et al* (1984) on the leachability of precipitator ash from a coal-fired power stations showed fair agreement between the percentages of various elements present in the first bed volume of a column test (L/S ~ 0.5) and the leaching percentages obtained by extrapolation of shake test results at different L/S ratios to an L/S ratio of 0.5. However, large differences do occur at extremely low percentages leached out where the limit of detection and analytical imprecision play a role of some importance.

For reasons outlined in Section 3.4* (Chapter 3), a cascade of shake tests was used in the current experimental studies. In the cascade test the long-term behaviour of tailings undergoing leaching is simulated in five steps. However, this work has also investigated the maximum leachability from the tailings of all the elements studied and leaching tests were carried out over much longer periods of time than suggested in the BEOP standard. It was intended to carry out leaching until such times that the levels of the elements leached out were insignificant, i.e. less than a factor of five greater than the blank (background) concentrations. However, even after 200 days of leaching the levels of some of the elements were still measurable.

For the purposes of this work the shake test, carried out a L/S ratio of 5/1, was used. However, instead of a single shake test, the test was carried out 25 times for each tailings sample. According to Jackson *et al* (1984), a single extraction of waste would provide only an indication of intensity of leaching and would not provide insight into the capacity of the waste to sustain a given concentration of analyte in the leachate. Intensity and capacity factors are important for assessing the half-life of leachable analytes of wastes once interned in a waste disposal facility and submitted to leaching.

The standard shake test chosen for this investigative work suggested that the leach test be carried out at a L/S ratio of five to one. To determine the effect of the L/S ratio on the leachability of the tailings, and to assess whether saturation of the leachate had occurred, a number of specimens were leached at the required pH 4, but at different L/S ratios.

The L/S ratios chosen for the comparison were 1:1, 2.5:1, 4:1 and 5:1. This phase of the work is referred to as the Preliminary Leach Tests.

After the results of these tests were analysed it was decided to add another step to the experimental program, a leach test with a L/S ratio of 10/1. Another two samples were leached at L/S ratios of 5:1 and 10:1 but with a starting pH of 9. The rationale for this particular phase of experimentation will be discussed in the experimental results.

The shake tests were carried out in the following manner:-

- The required amount of tailings were weighed directly into a 50mL centrifuge tube.
- Doubly deionised water (45 mL), acidified with high-purity nitric acid to pH 4, was added to the tailings. Approximately 20mL of the acidified water was kept as a blank.
- The tailings and water were shaken on a shaker table at between 150 and 200 cycles per minute for 24 hours, with the centrifuge tube sealed to prevent leakage.
- After shaking the contents were centrifuged and the leachate decanted and filtered through a 0.45μm filter by suction to remove any particulates.

- The leachates were measured for pH, Eh and conductivity after filtration.
- High-purity nitric acid, 1% by volume, was added to stabilise the leachates. The blank was similarly acidified and prepared for analysis along with the leachate.
- Fresh solution was added to the solid residue and this was leached for another 24 hours.
- The leachate was replaced with fresh solution every 24 hours up to ten days, thereafter the leachate replacement was not as frequent. The frequency of leachate replacement was reduced as the elemental concentration in the leachates with time, particularly the trace elements, was so low that a longer leach period was required to achieve concentrations measurable by ICP techniques.

Conductivity, pH and Eh determinations were made on all leachates, as well as elemental analysis for the major components of aluminium, calcium, iron and magnesium, and the trace elements of arsenic, cadmium, copper, chromium, mercury, manganese, lead, zinc, uranium and thorium.

The quantity of each element leached from the tailings, Q (g m^{-2}), was calculated from the equation:

$$Q = \frac{CV}{A}$$

where C = the concentration in the leachate (g L^{-1}),

V = the volume of leachate (L),

A = the surface area of the tailings (m^2).

Leaching was characterised by the leach rate, R, which is simply:

$$R = \frac{Q}{t}$$

where t = leaching time (days).

Presenting the leach data in terms of real time, as given above, allows the determination of the maximum leachability of the tailings under the prevailing conditions. However, the BEOP standard uses the liquid/solid ratio (L/S) as a relative time scale.

The assumed precision for the tests are given by the BEOP-31 standard as:

- Approximately 10% for major components and for trace elements present in relatively high concentrations,
- About 30% for trace elements of which relatively low concentrations are present,
- For the estimation of long-term leaching effects (L/S > 10), a standard deviation of plus or minus 50% for percentages leached out lower than 10% is considered acceptable.

4.6 Tailings Oxidation

In a full-scale, real, reject dump situation there will be times when the reject material will be exposed to the air; often for extended, dry periods. It is during these times that oxidation of the material can proceed relatively rapidly (*pers comm* Cook, 1990).

This work investigated the possible effect of oxidation on the leaching behaviour of the tailings by placing a tailings sample in an oven for 31 days at 90°C to accelerate oxidation, followed by leaching under standard conditions for 71 days.

4.7 Geochemical Modelling

Coal washery wastes will ultimately be exposed to leaching by groundwater when landfilled and buried. The chemistry of the groundwater could be significantly different from that of typical rainwater or plant processing waters, so one way to extrapolate the results from laboratory studies to the field conditions is to model the effect of groundwater on the leaching behaviour of the tailings. As a first step in this process, if the model used reasonably represents the leaching behaviour attained in the laboratory, the model can be used to predict the likely leaching behaviour of those same tailings under different hydrogeological and atmospheric conditions.

In this work, concentrations of species incorporating the major elements contained in the minerals viz. calcium, magnesium, aluminium and iron, and contained in the pH 4 and pH 9 leaching solutions, were computed using EQ3NR (release 3245R124, supported by EQLIB version 3245R153). Simulations of the major minerals, viz. calcite, siderite, kaolinite and magnesite[2], placed in contact with the leaching solutions were then carried out using EQ6 (release 3245R119).

The system simulated was a closed system, at 25°C, using atmospheric fugacities of carbon dioxide and oxygen, as the leaching solutions were assumed to be in equilibrium with the atmosphere.

The output file from the EQ3NR run, which includes the speciation and concentrations determined, was appended to the input file for the EQ6 kinetics model. The kinetics model relies on a number of input parameters to run - the number of moles of the respective minerals in the system; the dissolution rate constants for the minerals; and the surface area of the minerals.

The number of moles of each mineral was calculated from the elemental concentration in the tailings of its main constituent. This assumes, of course, that that particular element is associated entirely with the mineral.

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[2] Magnesite was used in the model as a substitute for the magnesium-bearing siderite as the latter is not an identifiable mineral and, as such, was not in the program's database.

Surface area of the minerals was also calculated according to their proportions in the tailings.

The dissolution rate constants given in Table 4.7 were obtained from previous studies on single-phase dissolution experiments. These constants have been arrived at after much experimentation by previous workers, generally under specified conditions, such as controlled pH and CO_2 partial pressure, and using single phase materials. Use of these rates to model an unbuffered, multi-phase system, such as exists in this current work, therefore poses problems. A multi-phase system has interferences set up by other minerals present in the material, and pH differs throughout leaching. Although the model takes the variation of conditions into account, it does not allow the reaction rate to vary.

TABLE 4.7: Input Data Used in EQ6 to Model Dissolution of Tailings Comprising Calcite, Siderite, Magnesite and Kaolinite

	Dissolution Rate (mol cm^{-2} s^{-1})
Calcite	4×10^{-10}
Siderite	1×10^{-8}
Magnesite	1×10^{-8}
Kaolinite	3×10^{-19}

Once a geochemical code like EQ6 has successfully modelled a system, it is possible to alter certain input parameters to determine how the material being modelled would react under different conditions. For the purposes of this current work, the surface area of the components was changed to determine if there would be any corresponding changes in elemental concentrations in the simulated leachates. The surface areas of the respective minerals used in this phase of the modelling was calculated using the mid-point of the size range (approximately 6.5mm) of coarser reject material from West Cliff washery as the mean diameter.

CHAPTER 5

EXPERIMENTAL RESULTS

5.1 Physical Properties of the Tailings

5.1.1 Particle Size

The particle size distribution of tailings from coal preparation plants are typically less than 0.5 mm in size, and ultrafines (slimes) are less than 100μm. The particle size distribution measured for slimes from the West Cliff washery are given in Table 5.1.1. The majority of the slimes (93.9%) is below 118 μm in size, and the mass median diameter is about 10 μm. The particle size distribution is skewed towards the smaller sizes as shown in Figure 5.1.1.

5.1.2 Relative density

The relative density of the tailings was determined to be 2.151g cm^{-3}, which is typical of the lutites that make up dirt partings and the roof and floor rocks commonly associated with coal seams.

5.1.3 Combustible and Non-combustible Matter

The organic matter content of the tailings determined by the Australian Standard method AS-1038, Part 3 (heating at 815°C), was 35.2 ±0.1% by weight. Analysis was carried out in duplicate. The amount of combustible matter lies within the range typically determined by West Cliff Colliery analyses, 30 to 40% (*pers comm* Cooney, 1991). The colour of the tailings after combustion was pale brown.

TABLE 5.1.1: Particle Size Analysis of Tailings

Size Band (µm)		Cumulative Weight % Below	Weight % in Band	Cumulative Weight % Above
Upper	Lower			
118.4	54.9	93.9	6.1	0.0
54.9	33.7	81.9	12.0	6.1
33.7	23.7	76.9	5.0	18.1
23.7	17.7	68.6	8.3	23.1
17.7	13.6	61.7	6.9	31.4
13.6	10.5	52.2	9.5	38.3
10.5	8.2	43.1	9.1	47.8
8.2	6.4	34.5	8.6	56.9
6.4	5.0	26.4	8.1	65.5
5.0	3.9	19.3	7.2	73.6
3.9	3.0	10.3	9.0	80.7
3.0	2.4	4.8	5.5	89.7
2.4	1.9	2.8	2.0	95.2
1.9	1.5	1.9	0.9	97.2
1.5	1.2	1.4	0.5	98.1

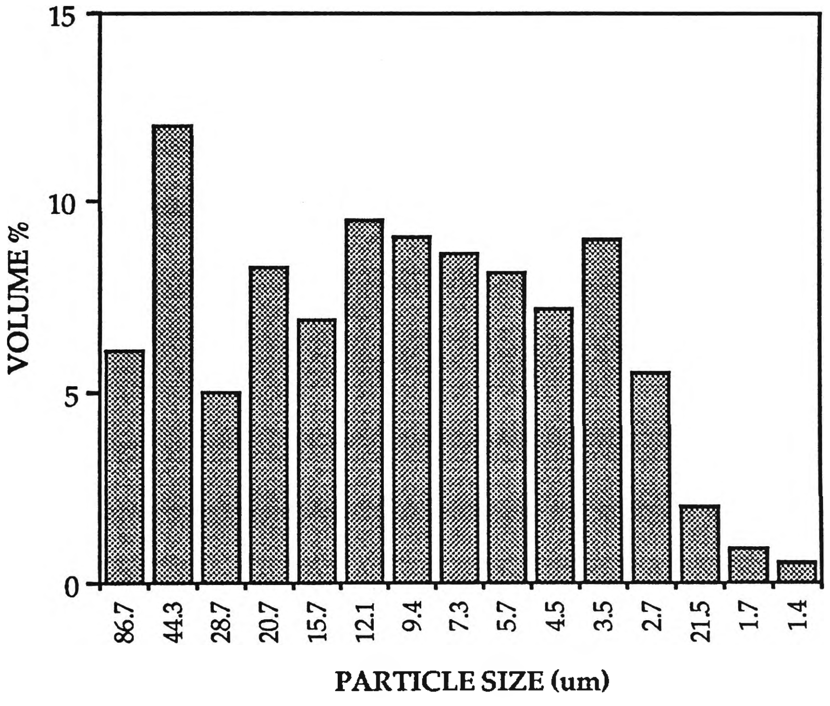

Figure 5.1.1: Particle Size Distribution of West Cliff Slimes

The proportion of combustible matter determined by heating at 450°C, also carried out in duplicate, was 32.8 ± 0.1% by weight. The colour of the residue was a pale brown-grey. The difference in weight loss for the tests carried out at 815°C and 450°C is probably accounted for by the greater loss of water of crystallisation which occurs at the higher temperature.

The sample heated at 450°C was used for elemental solids analysis, and was almost completely digested by hydrofluoric and boric acids during preparation for analysis; only 0.7 ± 0.03% by weight remained undigested.

5.2 Mineralogy

SEM and XRD techniques were used to determine the mineralogy of the tailings. The combination of these techniques allows the description of the mineralogy on microscopic and macroscopic scales.

5.2.1 X-Ray Diffractometry (XRD)

The X-ray diffraction profile of the tailings prepared for leaching is shown in Appendix B, Figure B-1.

Typically, quartz, kaolinite, siderite, and calcite are distinct components, with illite and magnetite being likely constituents. The diffraction peaks for illite and magnetite are not definite, but appear to be a reasonable fit to the data. There are several diffraction peaks assumed to be illite that could also represent mixed-layer clays. The crystallography of these clays is similar (*pers comm*, Glassley, 1991), making exact identification difficult.

Distinction between the identified kaolinite and illite XRD peaks was made possible through a dehydration experiment, outlined in the previous chapter. The diffraction profile for the dehydrated sample is shown in Appendix B, Figure B-2, superimposed onto the profile for the uncombusted sample for comparison. The peaks unaffected by the heating process are assumed to belong to illite, confirming that the peaks identified initially as belonging to illite and kaolinite have been correctly identified.

X-ray diffraction profiles of the specimens after leaching are similar to that for the unleached specimen (see Figures B-3 to B-6, Appendix B). The minerals present are quartz, kaolinite, siderite and calcite, with probably illite, multi-layered clays and magnetite present as minor constituents. This indicates that there has been no large scale mineralogical changes occurring in the tailings during leaching.

5.2.2 Scanning Electron Microscopy (SEM)

Energy-Dispersive X-ray Spectrometry (EDS) generally confirmed XRD analysis of the mineralogy of the tailings prior to leaching. The primary minerals were specifically selected for detailed investigation by SEM as they were considered the most significant contributors to the composition of the leachates.

EDS profiles taken of the un-leached and leached samples show that there were no significant compositional changes of the minerals in the tailings as a result of leaching. The primary constituent minerals were kaolinite, calcite, siderite and quartz, confirming XRD analysis, and a magnesium-bearing siderite not found by XRD[1]. Minor amounts of illite were present. Typical EDS profiles of the minerals are given in Figures C-1 to C-6, Appendix C.

EDS also showed that calcium and manganese were associated with many of the siderite grains examined (see Figure C-7, Appendix C), although not always together as shown in Figure C-7. Manganese was always present in

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[1] The magnesium-bearing siderite is present in similar proportions to the more pure form of siderite. As magnesium readily substitutes for iron in siderite (Deer, Howie and Zussman, 1977), it is likely that this magnesium-bearing siderite has a crystallographic similarity with siderite, and therefore an identical XRD pattern.

the magnesium-bearing siderite. Occasionally, manganese was also associated with calcite grains. Brown and Swaine (1964) found that manganese commonly replaces some iron in siderite in Australian coals, and less frequently calcium in calcite.

As established by XRD, kaolinite is the most abundant clay mineral in the tailings. Although kaolinite is by far the most common of the clay minerals, in coal and associated rocks it rarely occurs entirely on its own (Ward, 1980). Usually there co-exists other clays, particularly mixed layered clays. Illite is present in much smaller quantities, and it is likely that mixed layered clays are present. Many EDS profiles of clay particles showed minor proportions of iron, calcium and potassium (see Figure C-8, Appendix C). This is probably due either to ionic substitution by these elements for aluminium in the lattice structure of kaolinite or may indicate the presence of mixed layered clays.

Analysis by SEM showed morphological changes of some of the minerals after leaching. The most noticeable feature of the leached specimens was the prevalence of dissolution features, viz. pitting and attack along twin planes and grain boundaries, on the mineral surfaces. Some of these features were present prior to leaching but generally they were less pronounced than those in the leached samples.

Figure 5.2.2.1 shows the surface features of a kaolinite grain prior to leaching. Figure 5.2.2.2 is the same particle at higher magnification. There is some pitting on the surface of this grain that is probably a result of natural weathering and alteration.

Figure 5.2.2.3 shows the surface of a kaolinite grain after leaching for 212 days. There is noticeably more dissolution pitting on the leached particle than on the unleached grain. This was typical of most of the kaolinite grains examined.

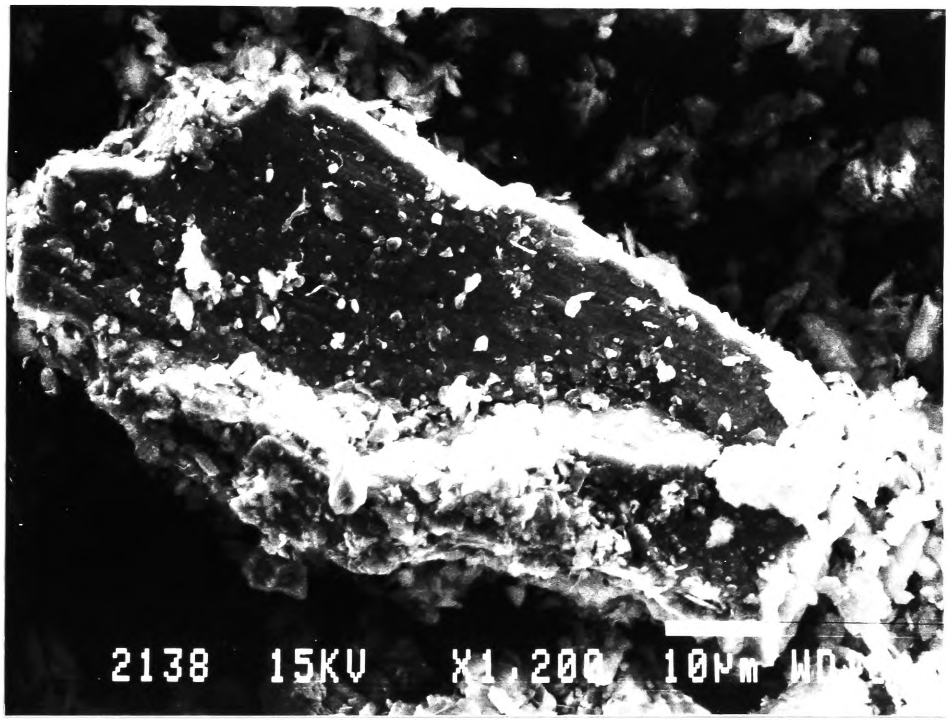

Figure 5.2.2.1: Typical Kaolinite Grain Prior to Leaching - Some Dissolution Features Evident

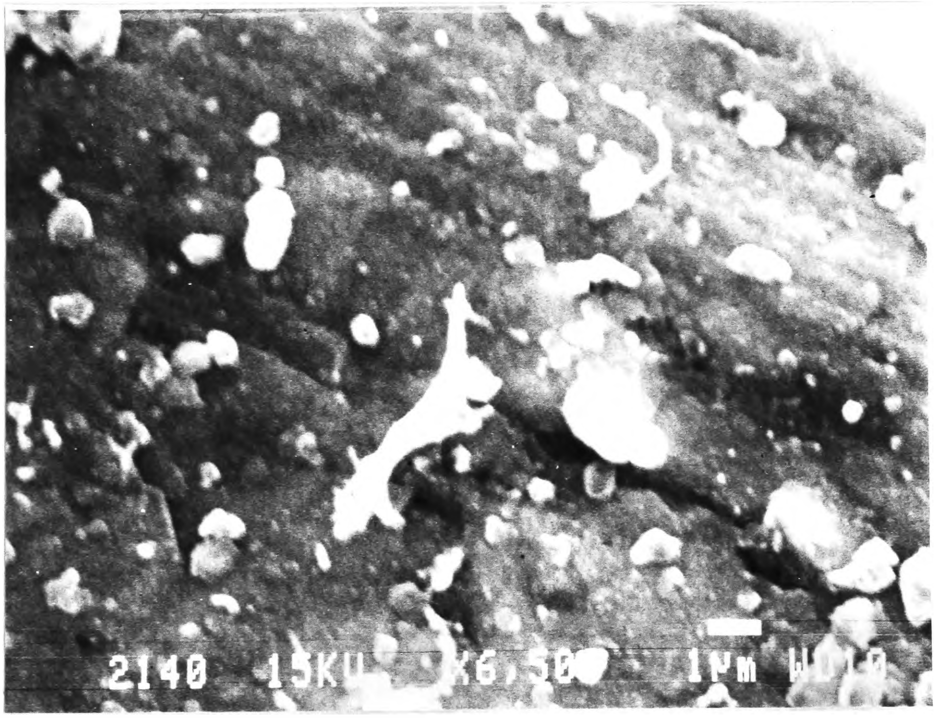

Figure 5.2.2.2: Typical Kaolinite Grain Prior to Leaching at Higher Magnification

In several kaolinite grains there was also evidence of new crystal growth (see Figure 5.2.2.4). The crystals were platy and very small. Similar crystals had not been observed in the un-leached sample, but it is not clear whether this was as a result of the population examined or caused by accelerated leaching.

Figures 5.2.2.5 and 5.2.2.6 show the morphology of a magnesium-bearing siderite grain, at different magnifications, prior to leaching. This particular grain shows little evidence of surface dissolution which was typical of most of the magnesium-bearing siderite grains examined.

After leaching, the surface of the magnesium-rich grains was pitted (see Figures 5.2.2.7 and 5.2.2.8). The surface of these grains had a mottled appearance suggesting uneven dissolution across the mineral surface.

Figures 5.2.2.9 and 5.2.2.10 show the surface of a typical siderite grain before and after leaching. Surface attack has occurred in a similar manner to that of the magnesium-bearing siderite. Generally, however, it was found that the magnitude of surface attack increased as the proportion of impurities in the siderite increased.

Siderite occurred in the tailings most commonly as euhedral grains, which differs with the findings of Kemezys and Taylor (1964) that siderite associated with coal seams in Australia often occurred as nodules.

Quartz grains in the tailings were very small, generally less than 50 μm in size, considerably smaller than the other mineral constituents of the tailings and, by contrast to the carbonate minerals, they were quite rounded. Quartz was usually present as grains in a clay matrix, usually kaolinite, and it was only after thorough examination that it was possible to locate discrete quartz grains to determine the extent, if any, of any surface dissolution that may have occurred.

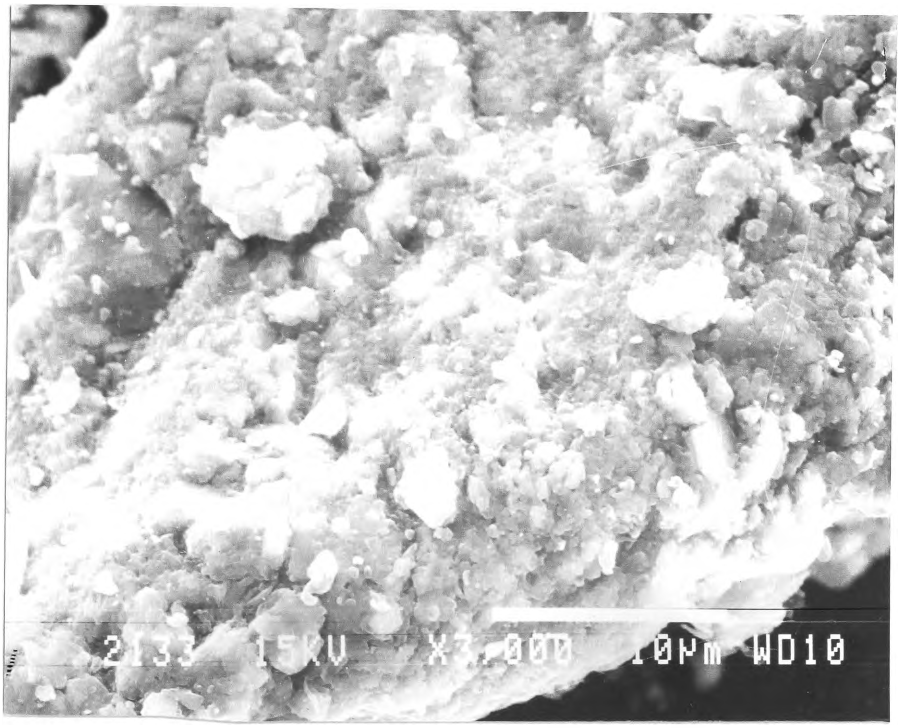

Figure 5.2.2.3: Typical Kaolinite Grain After Leaching for 266 Days Showing Dissolution Pits

Figure 5.2.2.4: New Crystal Growth on Surface of Kaolinite Grain After Leaching for 266 Days

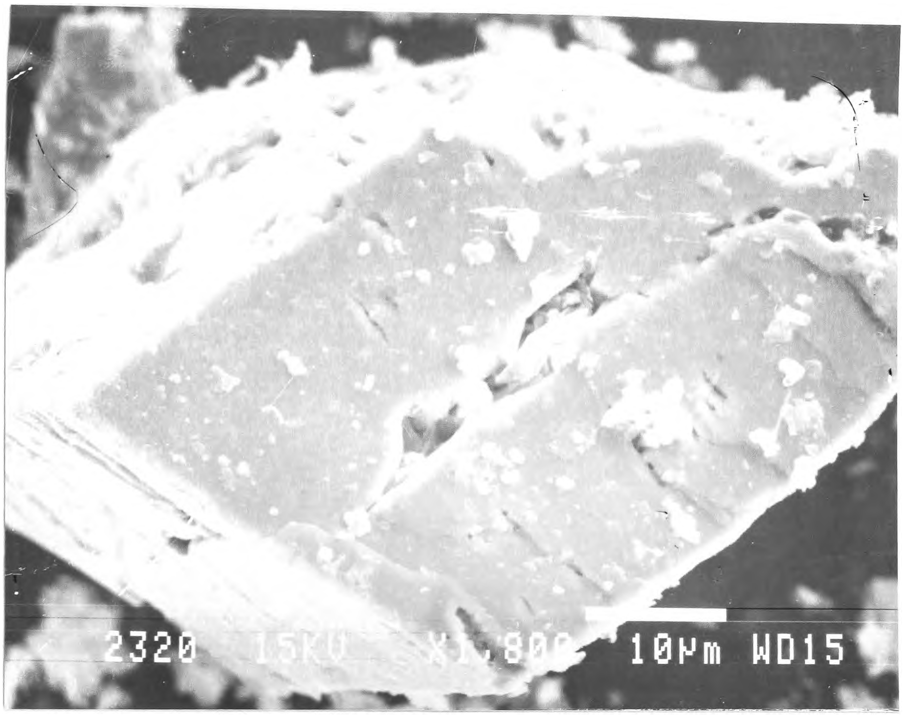

Figure 5.2.2.5: Typical Morphology of Magnesium-bearing Siderite Prior to Leaching

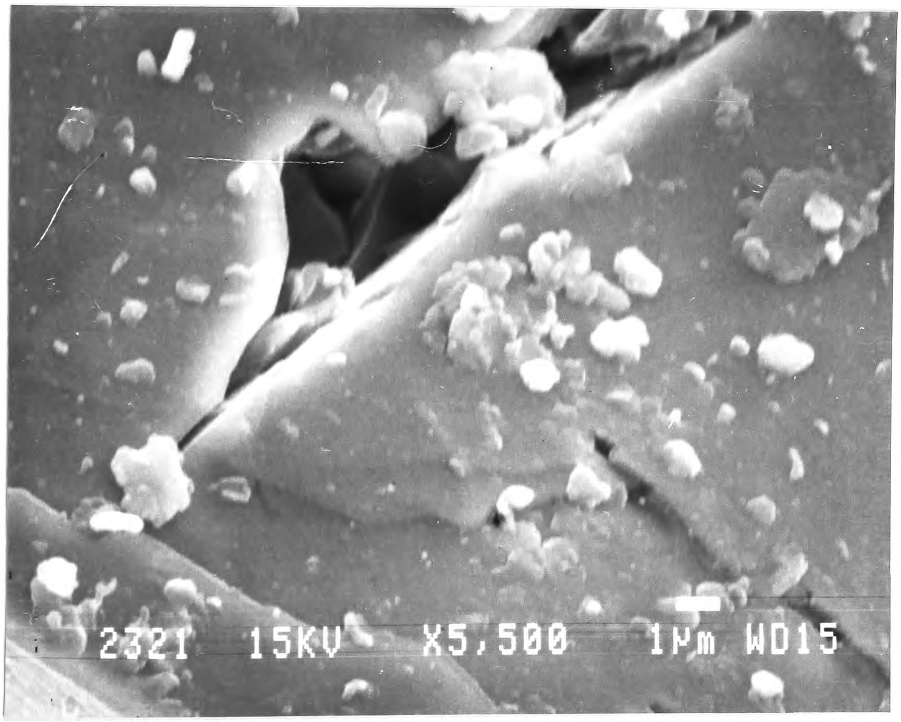

Figure 5.2.2.6: Higher Magnification Micrograph of the Morphology of Magnesium-bearing Siderite Prior to Leaching

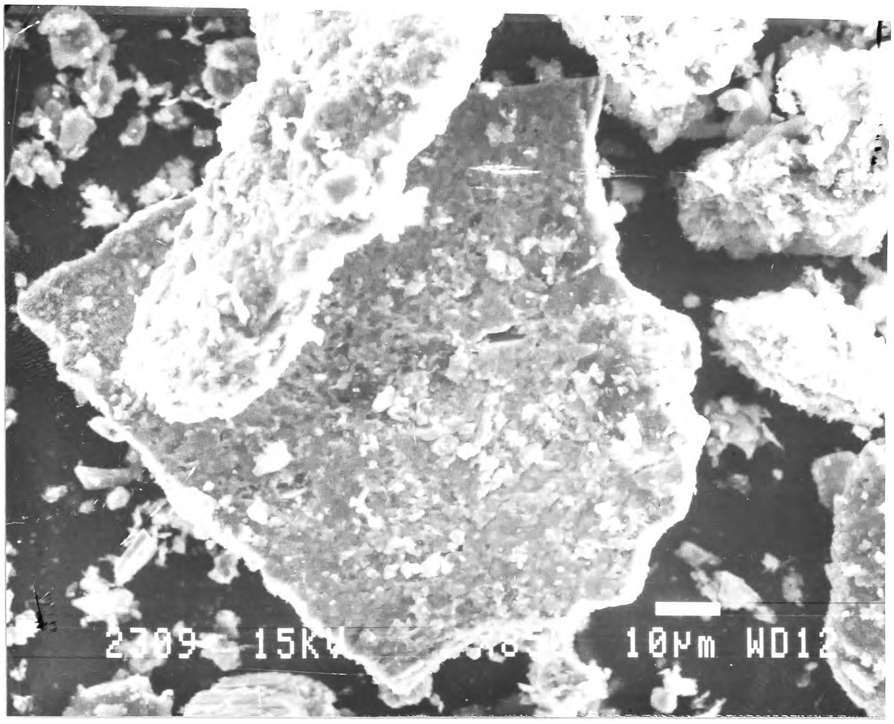

Figure 5.2.2.7: Typical Morphology of Magnesium-bearing Siderite After Leaching for 266 Days

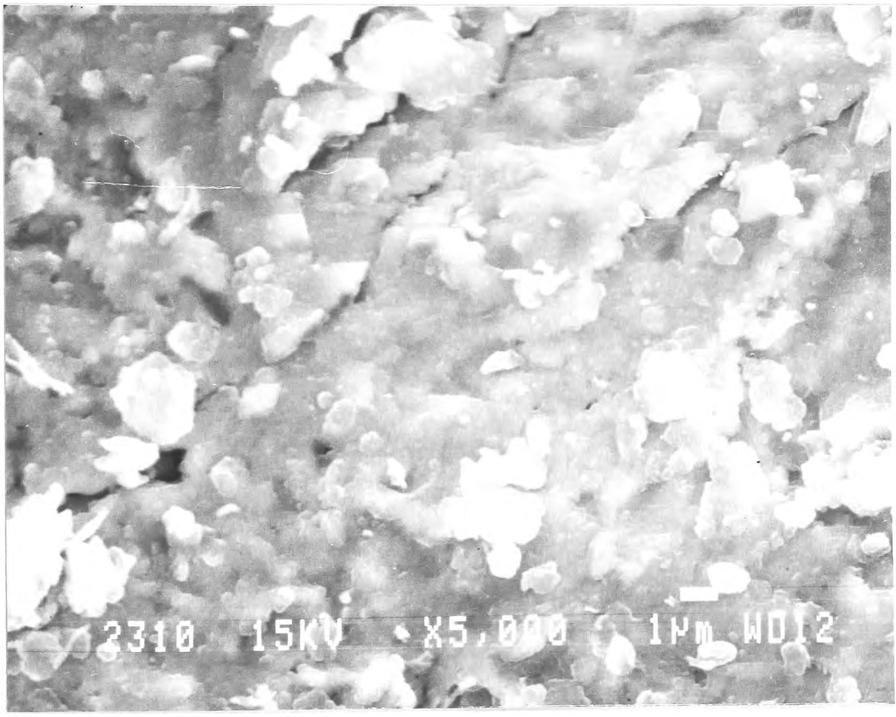

Figure 5.2.2.8: Higher Magnification Micrograph of the Morphology of Magnesium-bearing Siderite After Leaching for 266 Days

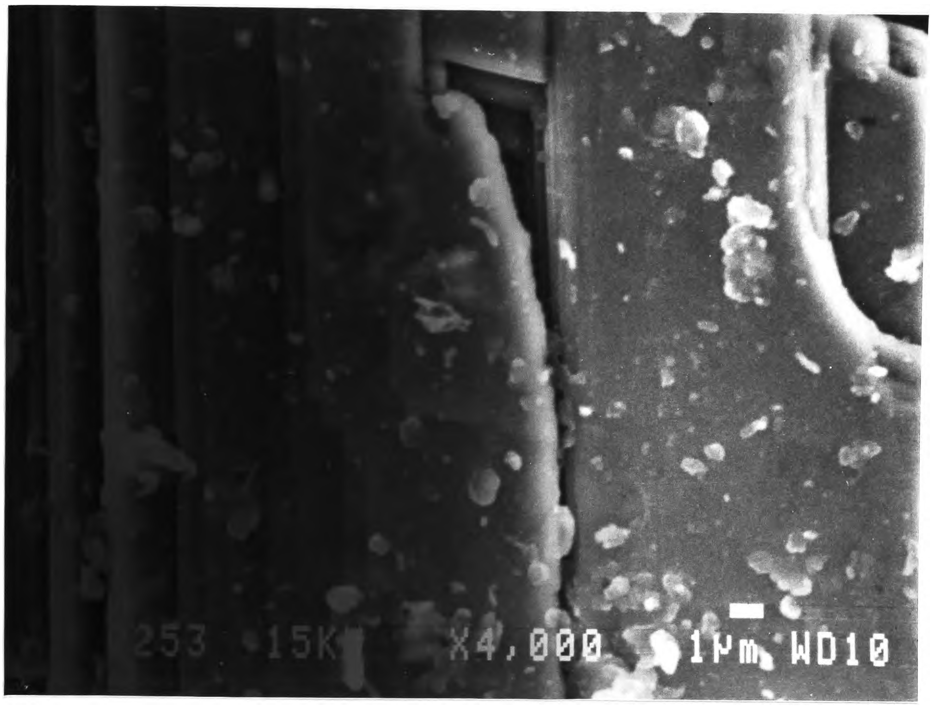

Figure 5.2.2.9: Typical Siderite Grain Prior to Leaching

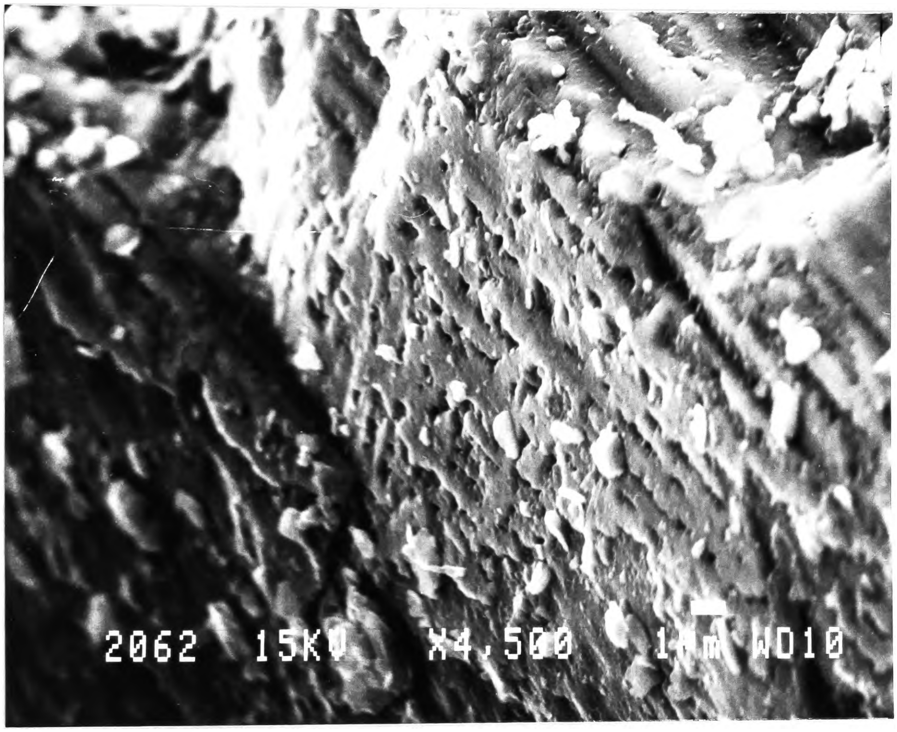

Figure 5.2.2.10: Typical Siderite Grain After Leaching for 234 Days

The fineness of the quartz is typical of that found in Australian coals and intra-seam sediments studied by Kemezys and Taylor (1964). They found that grains measured were frequently about 50 to 100 µm in size, and were often associated with clays.

Figures 5.2.2.11 and 5.2.2.12 compare typical quartz grains before and after leaching. There is some surface pitting on the leached quartz grain.

Calcite is one of the most soluble minerals present in the tailings. Figures 5.2.2.13 and 5.2.2.14 show a calcite grain prior to leaching, exhibiting few dissolution features. Its appearance is typical of most of the calcite grains in the unleached specimen.

Calcite grains were also relatively common in the leached samples. After leaching, however, dissolution features on the surfaces of the calcite grains were more evident. Figure 5.2.2.15 shows dissolution preferentially occurring along the grain boundaries and along twinning planes, areas where dissolution commonly takes place in calcite (*pers comm* Glassley, 1991).

Trace amounts of a titanium-rich mineral (probably rutile), a zirconium-bearing mineral (possibly zircon), and a sodium-bearing phase (possibly albite), were also observed in the tailings. Several grains of gorcexite were found in one of the specimens. These minerals are probably the remnants of a sandstone extracted during the mining of coal at West Cliff Colliery and eventually reporting to the tailings stream in the washery.

Other than new crystal growth on the surface of some of the kaolinite grains, described previously, formation of secondary mineral phases in the tailings, after leaching, was not obvious.

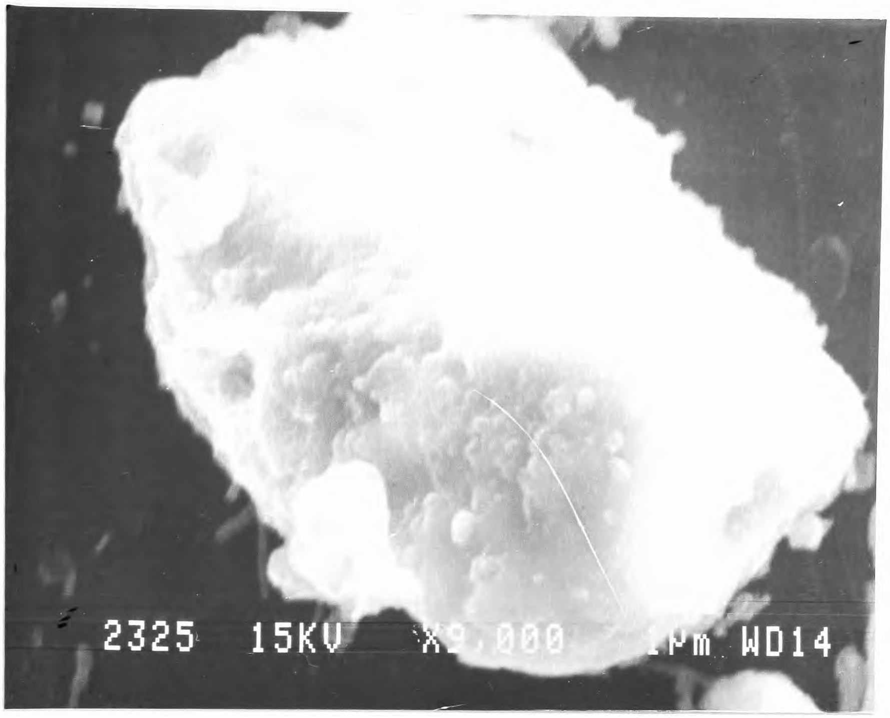

Figure 5.2.2.11: Typical Quartz Grain Prior to Leaching

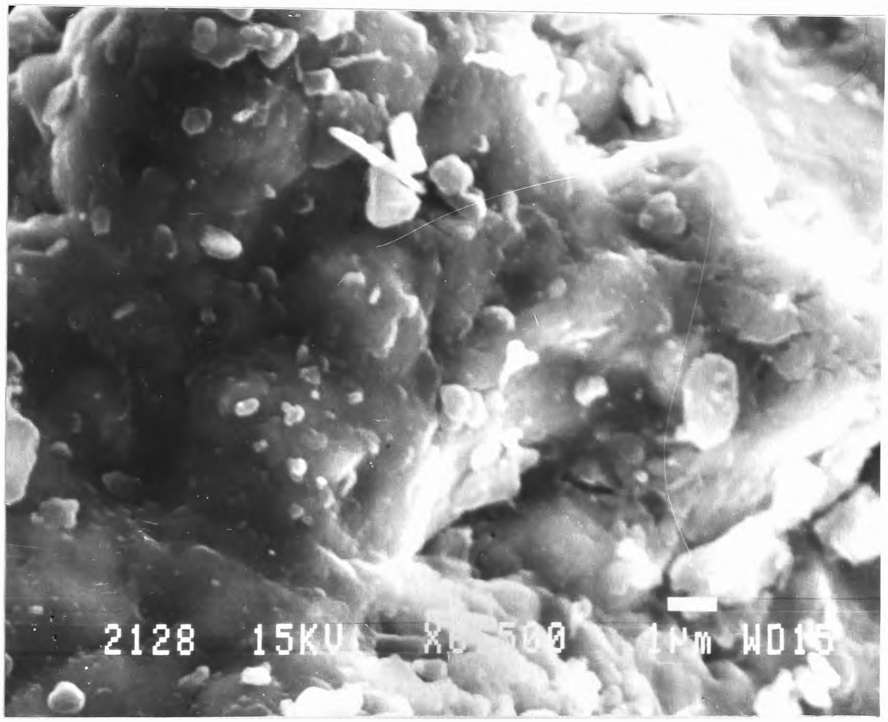

Figure 5.2.2.12: Typical Quartz Grain After Leaching for 266 Days

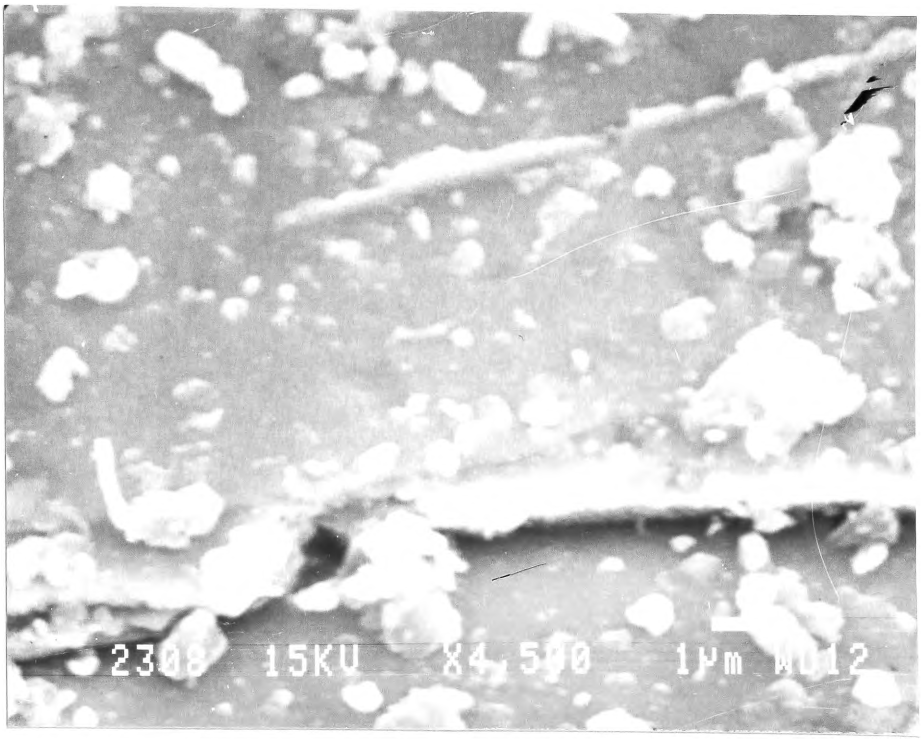

Figure 5.2.2.13: Typical Calcite Grain Prior to Leaching

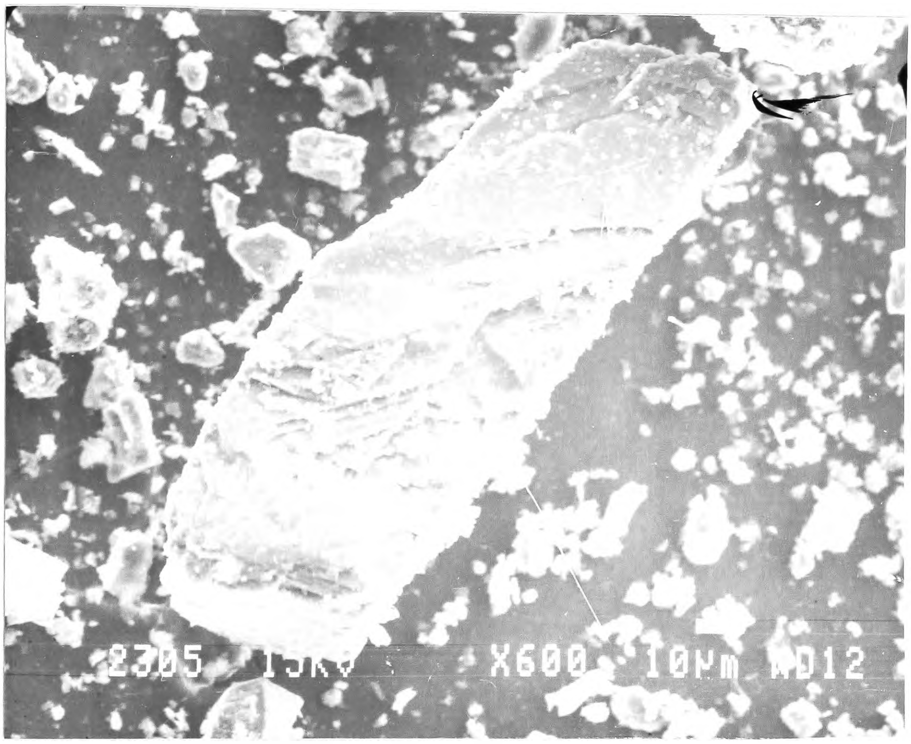

Figure 5.2.2.14: Higher Magnification Micrograph of Typical Calcite Grain Prior to Leaching

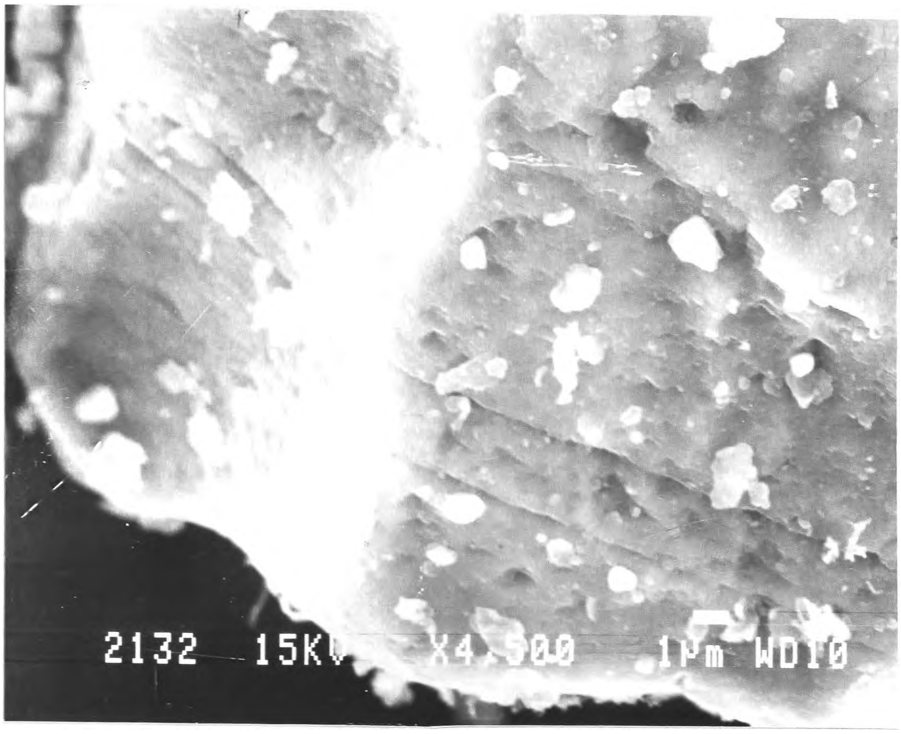

Figure 5.2.2.15: Typical Calcite Grain After Leaching for 266 Days

5.3 Elemental Composition of the Tailings

The elemental composition of the tailings is given in Table 5.3.1. Of the elements that were analysed for, those in greatest abundance were aluminium, iron, calcium and magnesium. These elements are indicative of the major minerals identified by XRD and SEM in the tailings.

Manganese was the most abundant trace element (0.058%). This was expected as manganese was the only trace element regularly detected during SEM analysis, being commonly associated with the magnesium-bearing siderite. The mercury concentration measured in the tailings is not considered to be reliable, as mercury is a volatile element and an unknown amount of the element would have volatilised during combustion of the tailings carried out at 450°C prior to dissolution.

TABLE 5.3.1: Elemental Concentration of Tailings

Element	Concentration (ppm)
Aluminium	117 500
Arsenic	6
Calcium	26 100
Cadmium	2
Chromium	52
Copper	25
Iron	80 400
Mercury	1
Magnesium	7 200
Manganese	583
Lead	29
Thorium	22
Uranium	5
Zinc	52

Determination of the uranium and thorium contents by γ-spectroscopy compared well with the levels determined by ICP/MS (see Table 5.3.2). The uranium results determined by both methods were similar, whilst those for thorium differed by only a factor of two.

TABLE 5.3.2: Comparison of Uranium, Thorium and Total Uranium & Thorium Concentrations in the Tailings Carried Out By ICP/MS and γ-Spectroscopy

U Concentration (ppm)		Th Concentration (ppm)		Total U and Th Concentration (ppm)	
ICP/MS	Gamma–Spectroscopy	ICP/MS	Gamma–Spectroscopy	ICP/MS	Gamma–Spectroscopy
5	7	22	12	27	19

5.4 Leach Test Results

Leaching tests were carried out in two stages; firstly, to check the test procedures with the West Cliff tailings and, secondly, to obtain the release results. The first stage has been referred to as the preliminary leach test and the second as the major phase of leach testing. Detailed leach data for all tests are provided in Appendix E.

5.4.1 Preliminary Leach Tests

The data from the preliminary leaching tests, including leachate concentrations, pH, Eh, conductivity and calculated leach rates, are given in Appendix E, Tables E-1 to E-12. The results, including Figures showing the variation of leach rates with time, are covered in more detail in Appendix D.

Preliminary leach tests were carried out at L/S ratios of 1:1, 2.5:1, 4:1 and 5:1. The results to these tests highlighted several difficulties in studying the leaching behaviour of the tailings. Most of the difficulties were attributed to their high clay content.

The leachates from each L/S ratio test were discoloured. This discolouration became more noticeable at lower L/S ratios and appeared to be due to the formation of suspended material. Generally, the amount of suspended material increased on standing. It appeared that only a small proportion of the suspended material was present as particulates, as only a small percentage of the residue was retained on a 0.45 μm filter. The majority of the suspended material was assumed to be colloids.

The leachates from the tests where colloids formed were allowed to stand for several days to allow the colloids to precipitate, and then the liquor was decanted for analysis.

To determine the nature of the floc in the leachates one of the solutions was filtered through a 1000 Nominal Molecular Weight (NMW) filter to separate any colloidal-sized material from solution. The material was viewed under the SEM and an EDS profile taken. Figure 5.4.1.1 shows the morphology of the colloidal material, and Figure 5.4.1.2 the EDS profile. The EDS profile is characteristic of kaolinite.

The floc presents a problem because, as it forms on standing, then a variable level of elements may sorb onto this material and not be analysed.

Three steps were taken to determine the cause of the colloid formation. Firstly, the leachates were acidified with 2.5% nitric acid instead of the usual 1% to try to prevent colloid formation. The addition of more acid, however, did not appear to hinder the formation of colloids.

Secondly, it was thought that the residue may have formed due to a reaction with the nitric acid added for chemical stabilisation. To test this, two leachates, one from the 5:1 L/S ratio leach trial, and another from the 2.5:1 trial, had no acid added and were left to stand. However, the brown coloured suspension formed in both leachates.

Thirdly, to determine if the colloids were forming due to saturation effects several leachates from the 5:1 L/S ratio leach trial were diluted immediately after pH, Eh and conductivity measurements were taken. The 5:1 leachates were selected as this ratio represented the most dilute of the leach solutions, and therefore they had the lowest elemental concentrations, and were the least likely to become saturated. They were diluted by a factor of two. No colloids formed, even after long periods of standing.

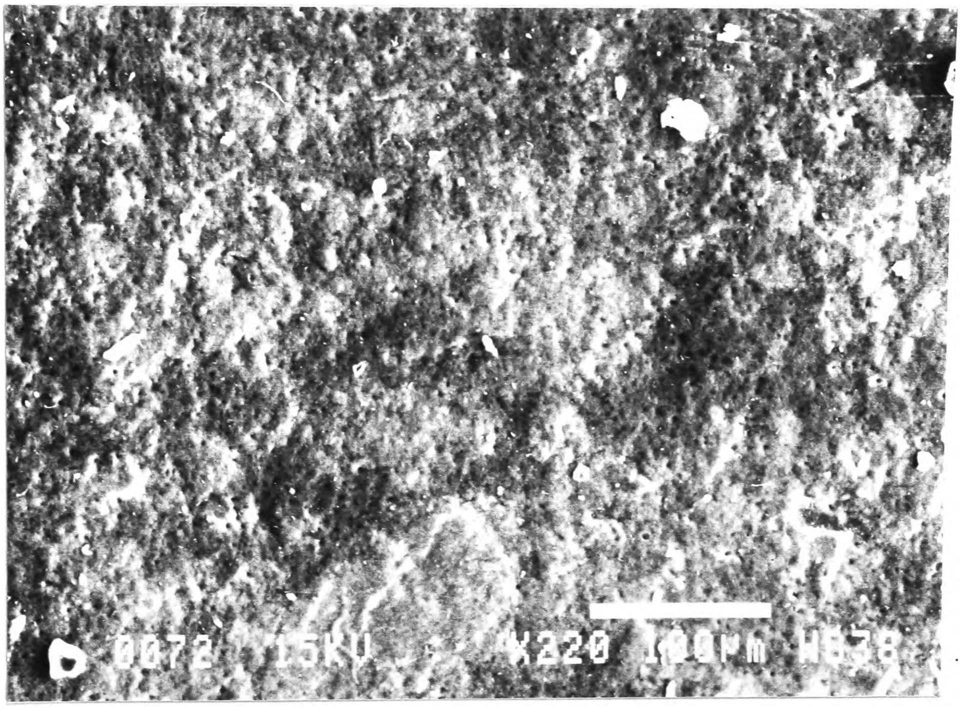

Figure 5.4.1.1: SEM Image of Colloidal Material Remaining on 1000 NMW Filter

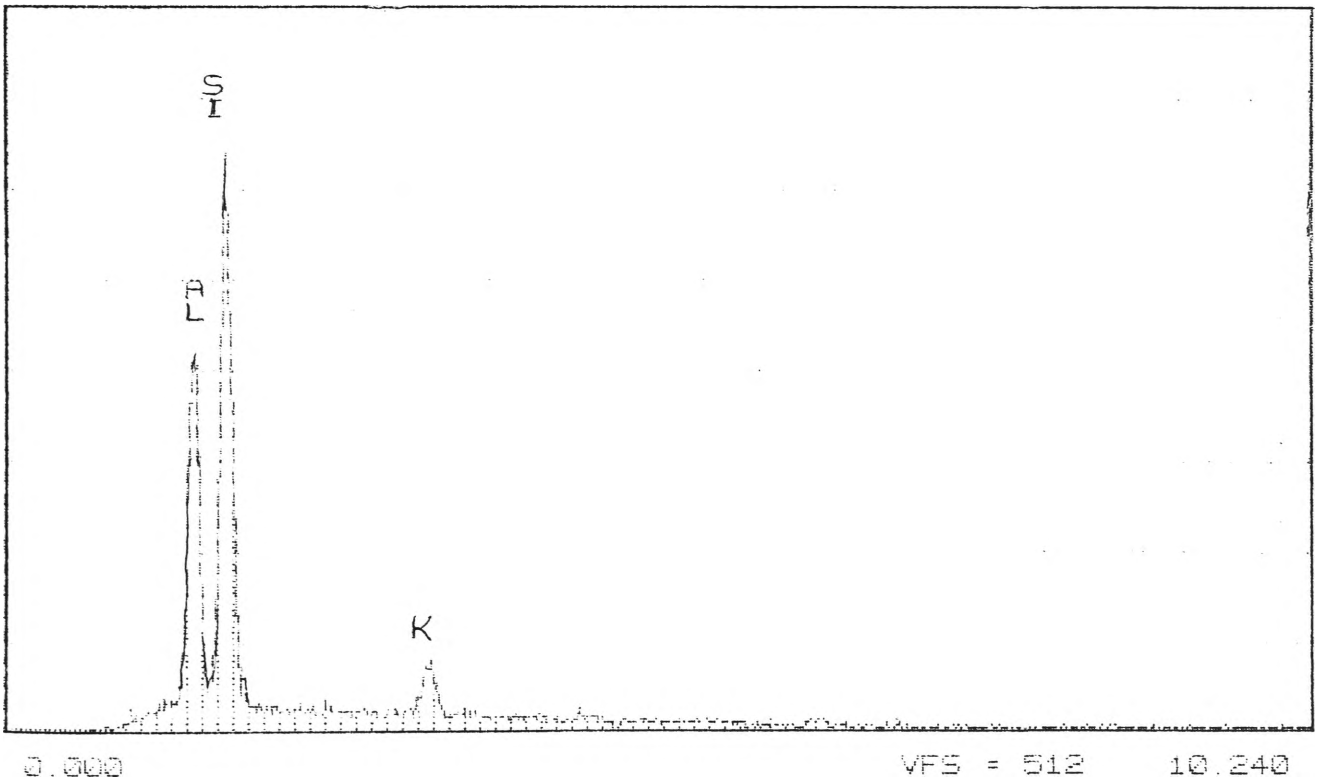

Figure 5.4.1.1: EDS Profile of Colloidal Material Remaining on 1000 NMW Filter

Consequently, the second phase of leach tests was undertaken using a L/S ratio of 5:1, and dilution of the leachates, by a factor of two, was carried out initially. As described in the previous chapter on experimental procedures, a series of leach tests were also carried out using a L/S ratio of 10:1. Under these conditions there was no need to dilute the leachates.

The analytical results for the preliminary work show can be summarised as follows:

- The leach rates of the trace elements analysed were generally lower for the lower L/S ratios. This suggests that, at these ratios, where colloidal formation is most pronounced, the trace elements are being sorbed onto the colloids, taking them out of solution. It may also indicate that high solution concentrations of other elements hindered the release of these elements.

- At 5:1 L/S ratio, acidification of the leachates does not appear to affect the levels of the trace elements in solution.

- At 4:1 L/S ratio, acidification of the leachates has an effect on copper only, where the leach rates for the acidified leachates are at least an order of magnitude greater than those for the non-acidified samples.

5.4.2 Major Phase of Leach Testing

In this section results were obtained during the second, major phase of leach tests are given. This study investigated the effect of leach time, solution pH and L/S ratio on the releases from the tailings.

The preliminary leach test work identified that there was a significant rise in pH of the leachates after 24 hours of leaching (from pH 4 initially to about pH 9 after 24 hours). In a field situation where the tailings may be dumped and remain wet (or moist) for a long period of time, then it could be expected that the tailings would be leached with water with a much higher pH than, say, rainwater[2]. For this reason, the subsequent, and major, phase of leach testing was carried out using starting solutions of pH 9 as well as pH 4. In the case of the tests carried out at pH 9, the first contacting was carried out at pH 5, to simulate the pH of rainwater which typically falls in the vicinity of West Cliff Colliery[3].

5.4.2.1 Redox Potential, pH and Conductivity Measurements

The pH, Eh and conductivity results for the leach tests are given in Tables E13 to E16, Appendix E. Changes in pH and Eh of the leachates with time for each test are shown in Figures 5.4.2.1.1 to 5.4.2.1.4.

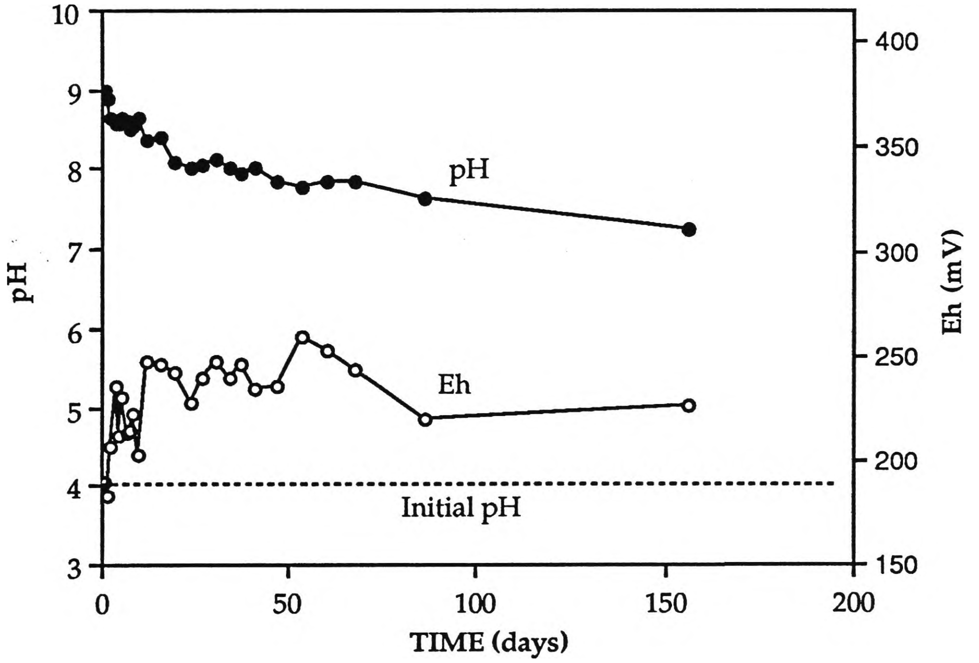

Figure 5.4.2.1.1: Change in pH and Eh With Time - L/S Ratio 5:1 at Ambient Temperature

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[2] The tailings are emplaced in an uncovered impoundment and are therefore subject to leaching by rain.

[3] Rainwater was collected over a three-day period during October, 1990, and pH measured and averaged at 5.0.

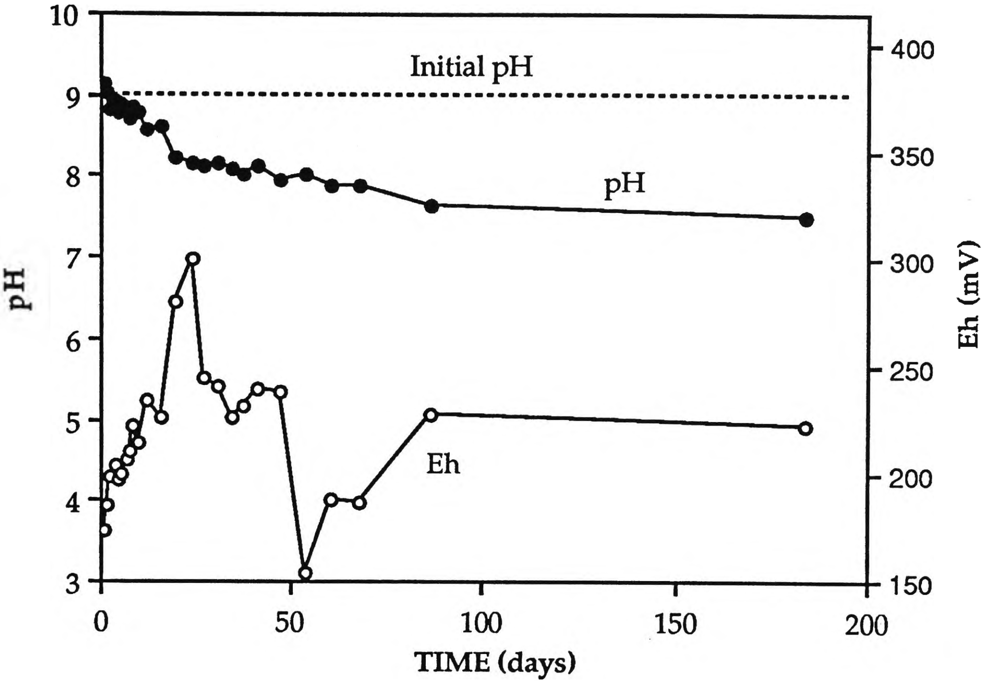

Figure 5.4.2.1.2: **Change in pH and Eh With Time - L/S Ratio 5:1 at Ambient Temperature**

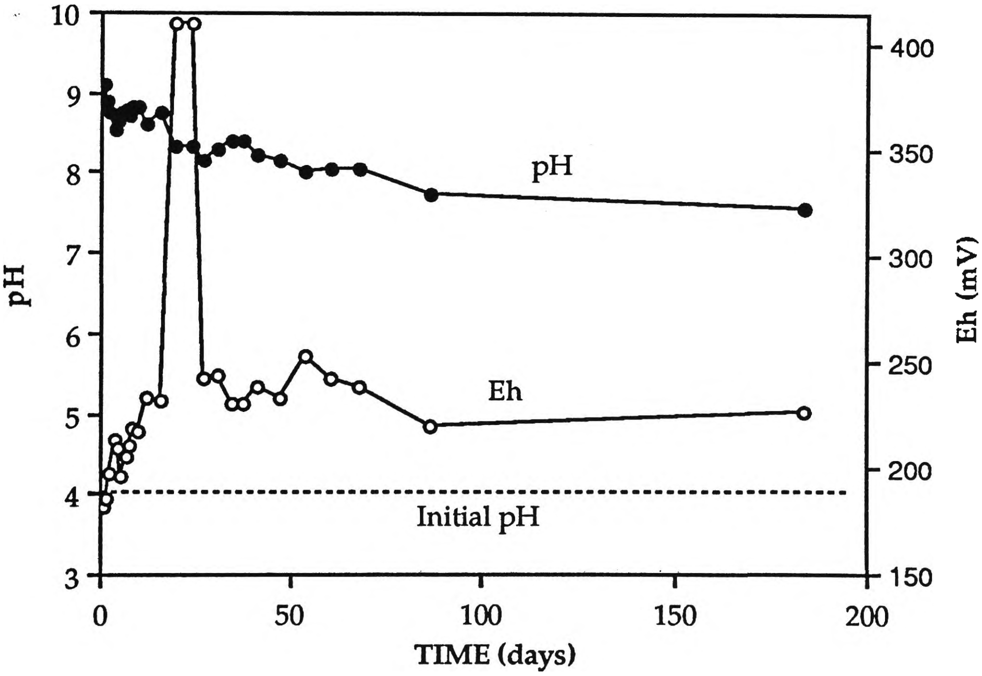

Figure 5.4.2.1.3: **Change in pH and Eh With Time - L/S Ratio 10:1 at Ambient Temperature**

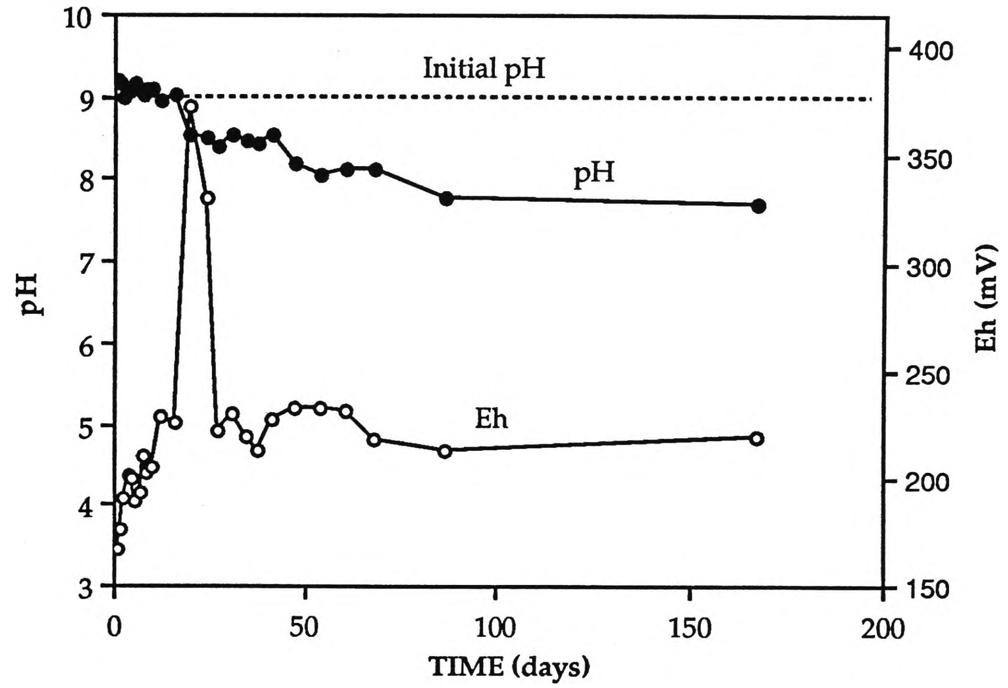

Figure 5.4.2.1.4: **Change in pH and Eh With Time - L/S Ratio 10:1 at Ambient Temperature**

The Figures show that pH generally decreases with time for each leach test. The values are similar under each set of leach conditions and are essentially independent of initial pH.

With the exception of the test carried out at L/S 5;1 and initial pH 4, all of the Eh patterns are similar.

5.4.2.2 Leach Rates

Five tailings specimens were leached, denoted as Leaches 1 to 5. Table 5.4.2.2.1 gives the leach conditions and period of leaching for each sample. Leach 5 entailed heating the tailings sample in air at 90°C for 31 days, to accelerate oxidation, and then leaching under the given conditions. Results for Leach 5 are presented in Section 5.4.3.

Table 5.4.2.2.1: Leach Test Conditions with Leachate Replacement

Leach Test	Initial pH	Liquid : Solid Ratio (mL:g)	Total Leach Time (Days)
Leach 1	4	5	212
Leach 2	9	5	266
Leach 3	4	10	266
Leach 4	9	10	234
Leach 5	4	10	79

Leachates from Leach 1 and Leach 2, up to 32 days of leaching, were diluted by a factor of two. However, after 32 days of leaching, elemental concentrations in the leachates were considered sufficiently low that colloid formation was probably not occurring and dilution was discontinued. In fact, the concentrations of some of the elements were approaching detection limits, and it was therefore preferable not to dilute the leachates.

The results of the five leach tests, including duration of each leach period, are given in Appendix E. As cumulative leaching time increased, the duration of each leach period was extended, as the elemental concentrations of many of the trace elements in leachates from short leaching periods were approaching detection limits. By extending the leach time concentrations could be increased to detectable levels.

The last leach period, for each sample, was between 111 and 165 days. The second last leach period was 30 days for each case.

Discussion of the elemental analyses is considered in two sections - as major components of the minerals in the tailings, viz. aluminium, calcium, iron and magnesium, and trace elements released, viz. arsenic, cadmium, chromium, copper, mercury, manganese, lead, thorium, uranium and zinc.

All of the data have been graphed and lines of best fit have been drawn where appropriate. Detection limits for each of the elements, under each of the leaching conditions, have been converted to a leach rate, based on conditions for the final leach period, and are represented on the Figures by a straight dashed line, except for calcium and magnesium. The detection limits for calcium and magnesium were considerably lower than the measured values and it was not possible to represent them on the figures. Their detection limits are given immediately prior to the Figures.

Aluminium

Aluminium is associated chiefly with the clay minerals in the tailings, and in particular is considered to be representative of kaolinite. Leach rates were calculated for each leach test and the effect of leaching time on aluminium leach rates are shown in Figures 5.4.2.2.1 to 5.4.2.2.4. The Figures show that the leach rates decrease throughout the 250 day leach period. There is a significant decrease in the leach rate after about 8 to 11 days.

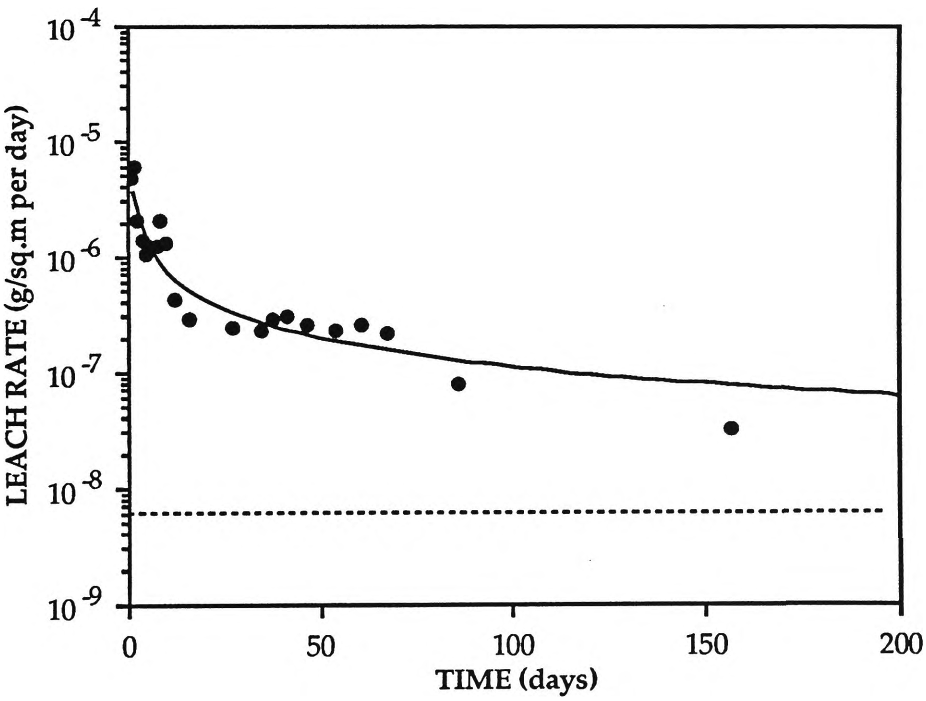

Figure 5.4.2.2.1: **Leach Rate of Al from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature**

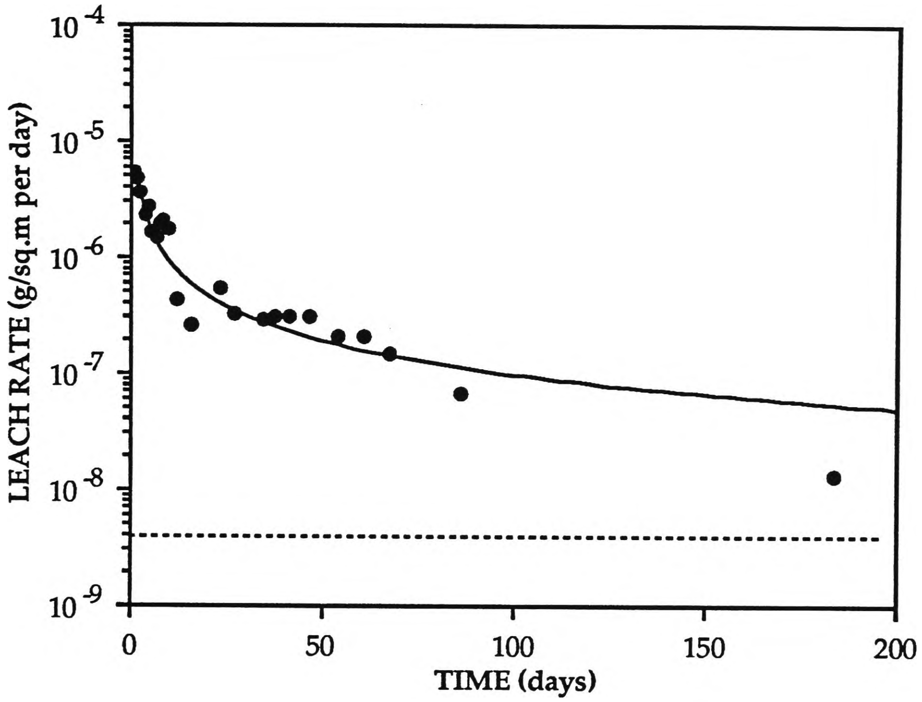

Figure 5.4.2.2.2: Leach Rate of Al from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

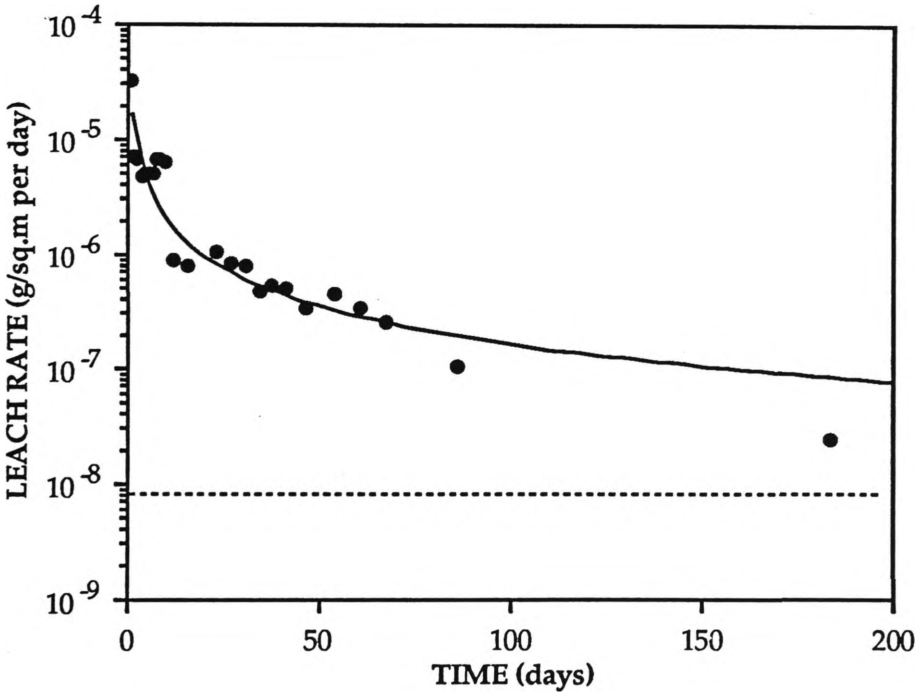

Figure 5.4.2.2.3: Leach Rate of Al from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

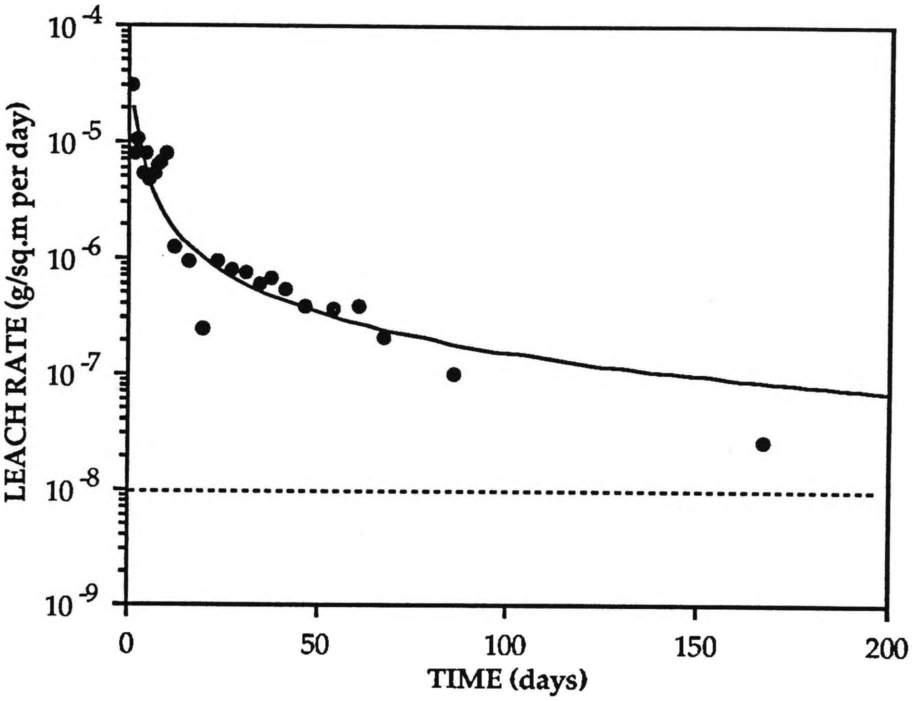

Figure 5.4.2.2.4: **Leach Rate of Al from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature**

Initially the leach rates in tests carried out at L/S of 10:1, are higher than the leach tests at L/S of 5:1, but the difference at longer times is similar to the experimental scatter and all samples appear, at longer times, to have a similar leach rate, ~ 2 to 3 x 10^{-8} g m^{-2} d^{-1}.

Calcium

Calcium is associated primarily with calcite in the tailings. Calcite is highly soluble and this is reflected in the relatively high leach rates for calcium in each of the leach tests. Leach rates of calcium in the four leach tests are shown in Figures 5.4.2.2.5 to 5.4.2.2.8. The detection limits for calcium for each of the tests, calculated using the final leach period, are typically three to four orders of magnitude less than the lowest measured concentrations.

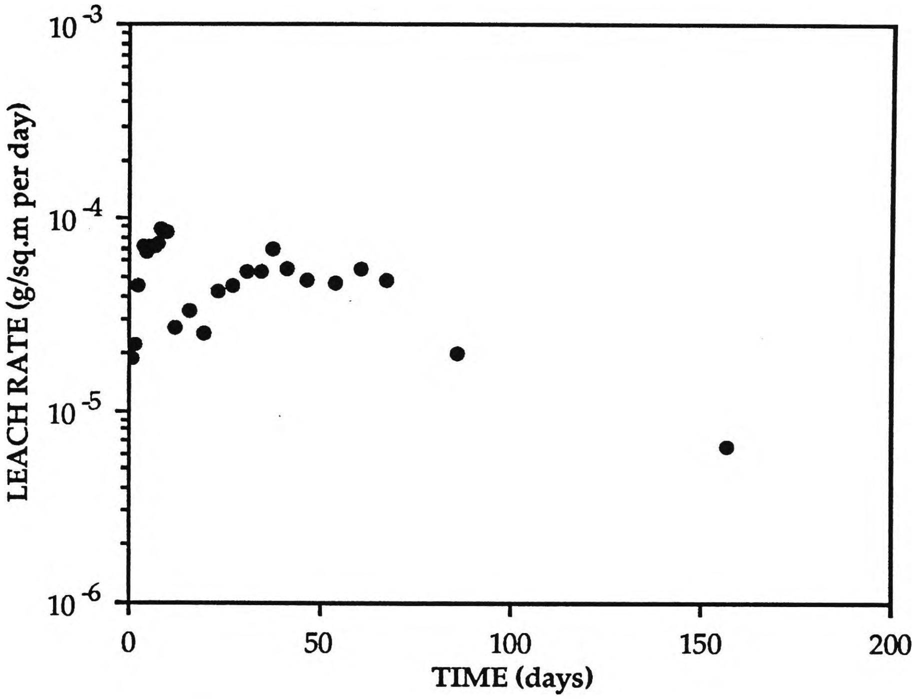

Figure 5.4.2.2.5: Leach Rate of Ca from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

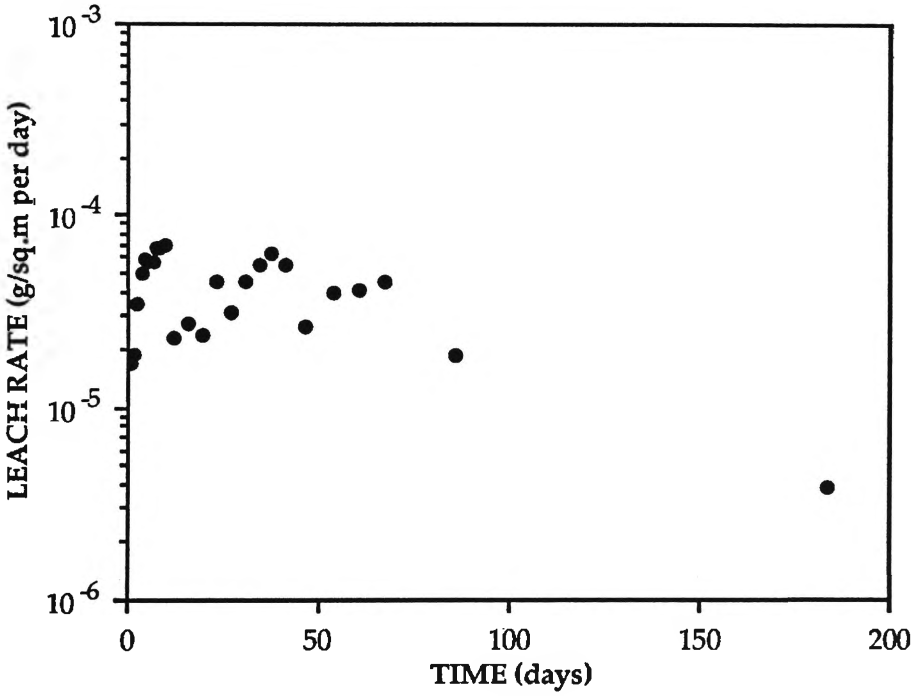

Figure 5.4.2.2.6: Leach Rate of Ca from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

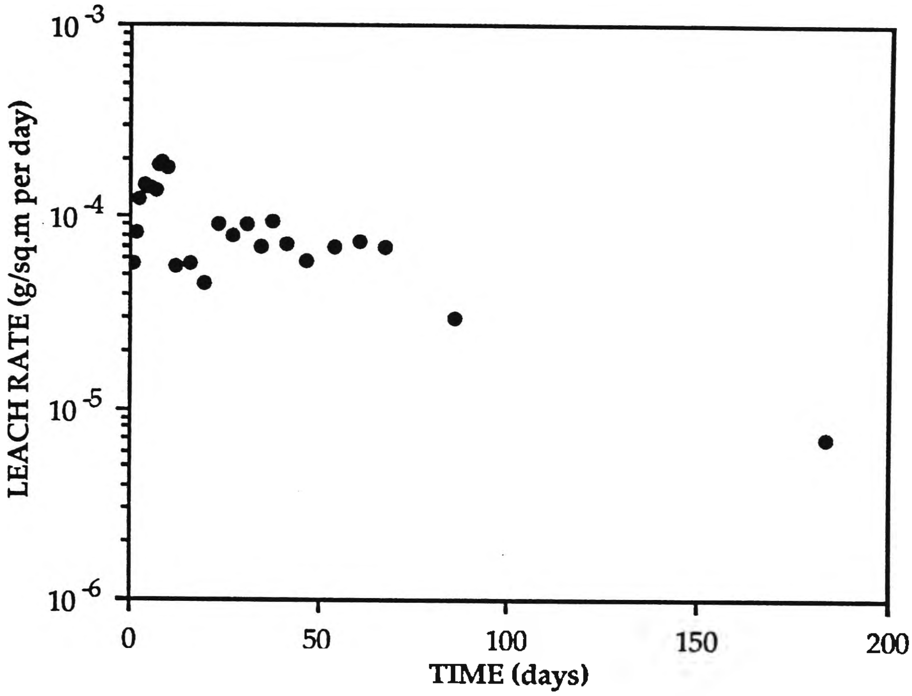

Figure 5.4.2.2.7: Leach Rate of Ca from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

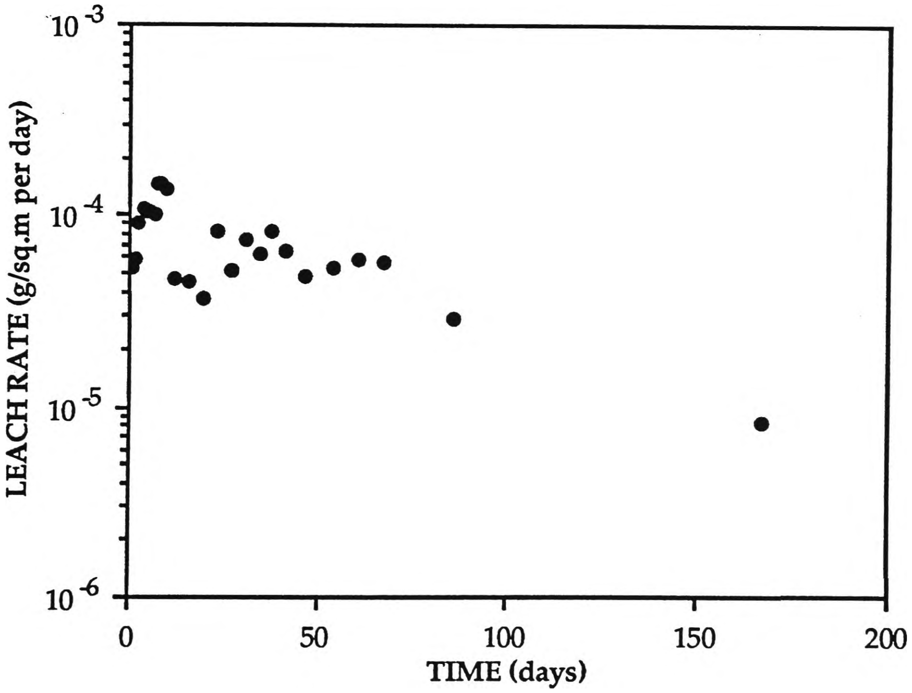

Figure 5.4.2.2.8: Leach Rate of Ca from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

In all leach tests, for the first ten days of leaching, there is a small increase in leach rate. On the eleventh day however, when the leach period is extended from one day to four days, there a decrease in leach rate corresponding to the increase in leach period. This occurs again with subsequent increases in the duration of leaching time, e.g. from 3- and 4-day to 7-day leach periods. In these instances there is an increase in the concentration of calcium in the leachates, but the increase is not proportional to the increase in the leach time, suggesting that the solutions are saturated in calcium.

The leach rate at 10:1 L/S ratio is about a factor of two greater than at 5:1 throughout the tests, confirming that the leachates in both tests are saturated.

After 50 days of leaching the leach rate remains fairly static at about 5 to 6 x 10^{-5} g m^{-2} d^{-1}. The final two leach rates in each case show a significant decrease, reflecting that for longer leach periods the solutions are saturated in calcium.

Iron

Concentration of iron in each of the leachates was low, about two orders of magnitude less than that for calcium, despite a greater abundance, by a factor of about 2.5. The low concentrations of iron in the leachates accounts for the wider scatter of data points, compared to those for calcium, about the leach trend lines drawn in Figures 5.4.2.2.9 to 5.4.2.2.12.

The leach rate of iron from the tailings is similar, and decreases with time, under each of the test conditions. The leach rate approaches 10^{-8} g m^{-2} d^{-1} by the end of leaching.

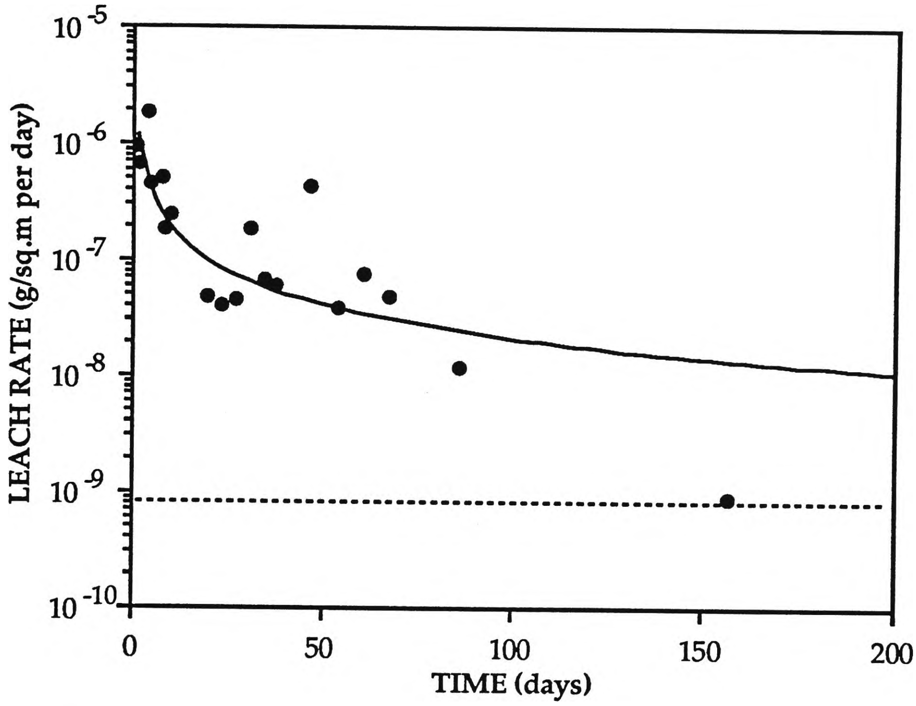

Figure 5.4.2.2.9: Leach Rate of Fe from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

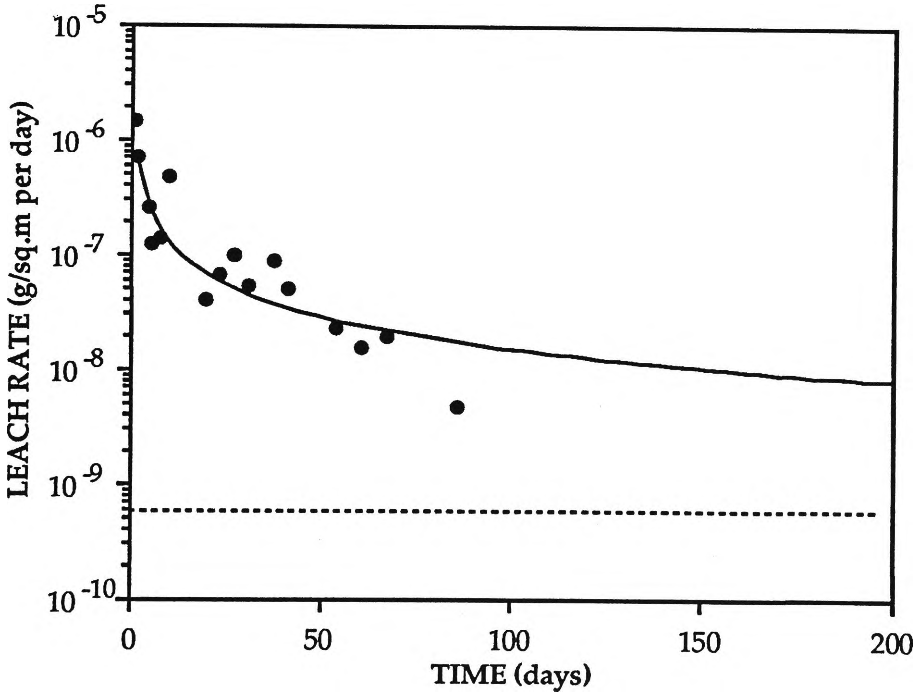

Figure 5.4.2.2.10: Leach Rate of Fe from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

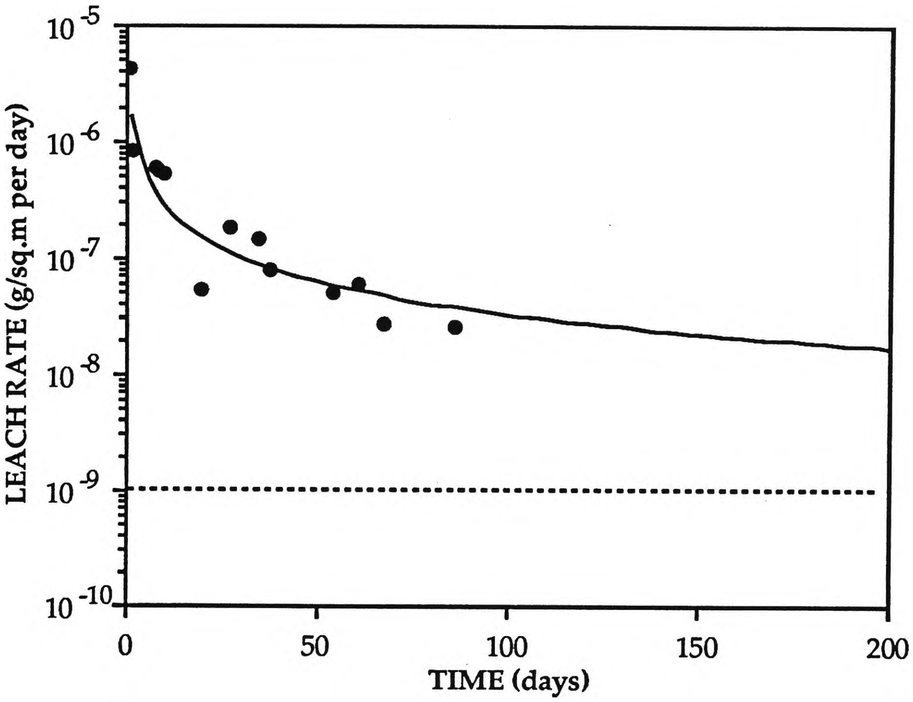

Figure 5.4.2.2.11: **Leach Rate of Fe from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

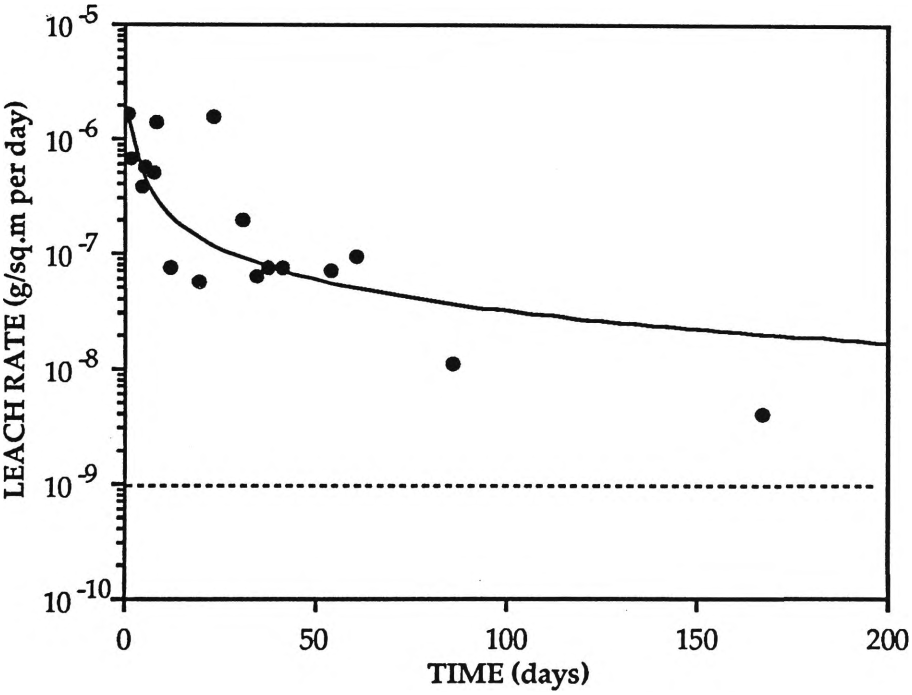

Figure 5.4.2.2.12: **Leach Rate of Fe from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature**

Magnesium

The leaching of magnesium follows a similar trend to that for calcium (see Figures 5.4.2.2.13 to 5.4.2.2.16). In all leach tests, the leach rates increase over the first ten days, after which they remain generally constant, apart from drops which correspond to a lengthening of the leach period, suggesting that the leachates are saturated in magnesium as well as calcium.

The leach rate decreases to approximately 3×10^{-6} g m^{-2} d^{-1} by the end of leaching, in all tests.

The detection limits for magnesium for each of the tests are typically two to three orders of magnitude less than the lowest measured concentrations.

Comparison of Aluminium, Calcium, Iron and Magnesium Leach Rates

A comparison of the four primary elements in the tailings considered in this study (aluminium, calcium, iron and magnesium) is shown in Figures 5.4.2.2.17 to 5.4.2.2.20.

Two types of leaching behaviour are evident; that of calcium and magnesium, which is controlled by saturation of the solution in these elements, and that of aluminium and iron, which are typically of dissolution from sparingly soluble components of the solid.

Leach rates for the four elements decrease in the order:

calcium > magnesium > aluminium > iron

As the leachates are saturated in calcium and magnesium, it is expected that the concentration of these elements in solution is controlling further dissolution of calcite and the magnesium-bearing siderite respectively.

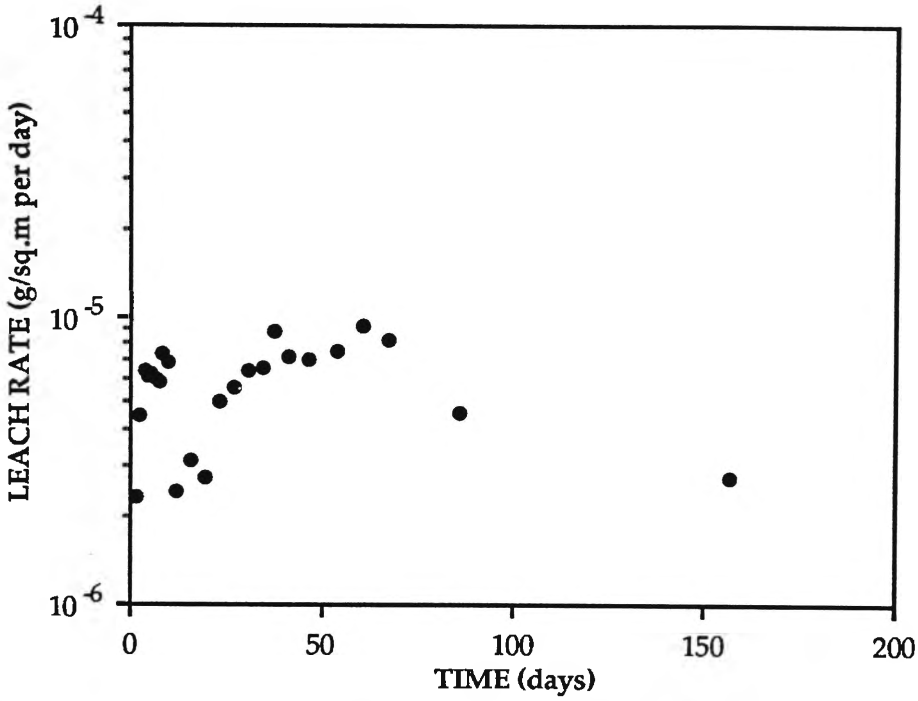

Figure 5.4.2.2.13: Leach Rate of Mg from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

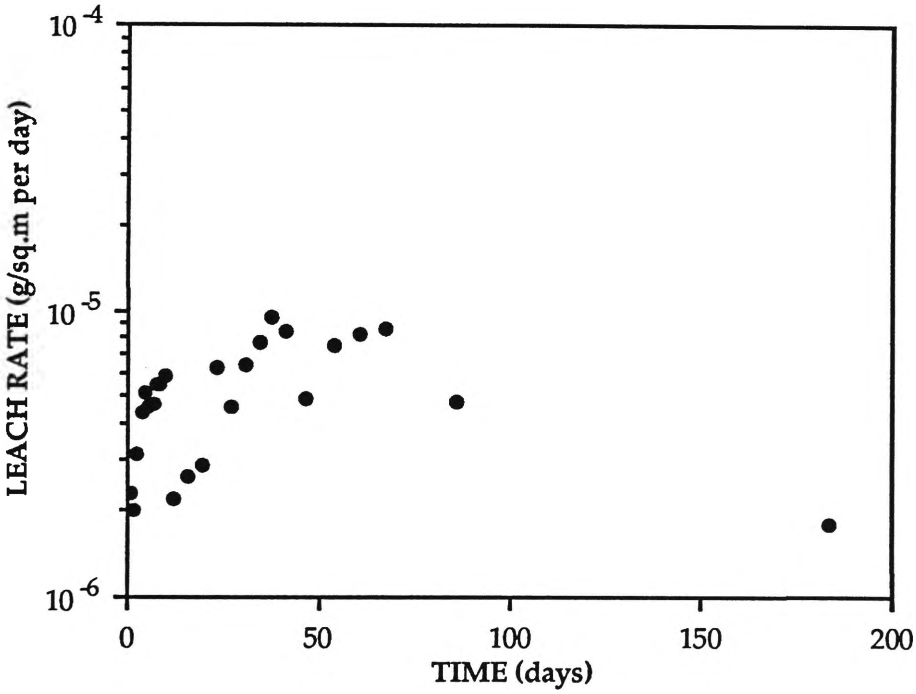

Figure 5.4.2.2.14: Leach Rate of Mg from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

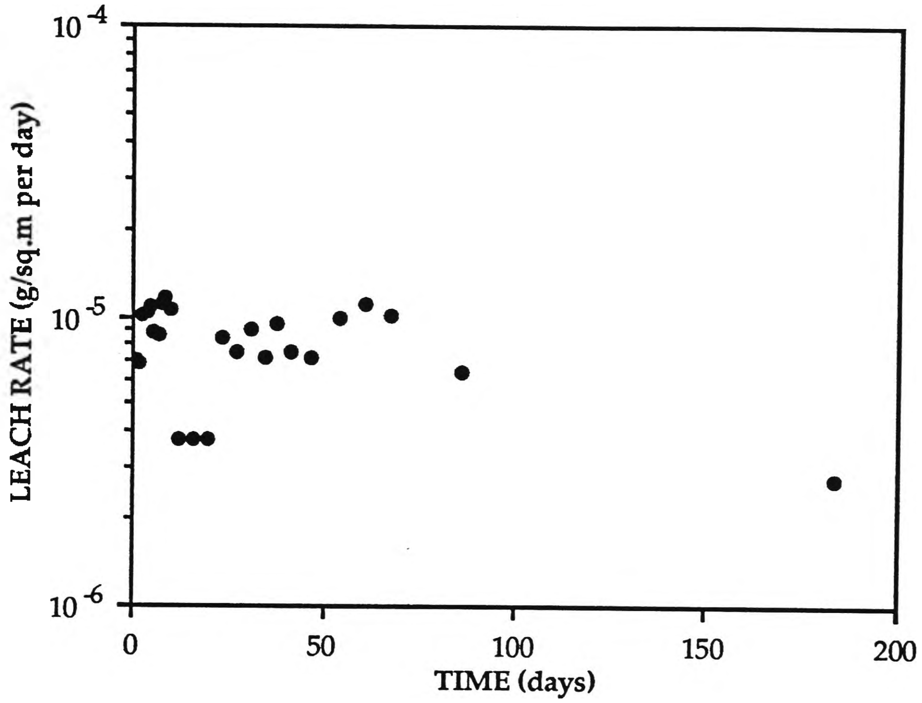

Figure 5.4.2.2.15: **Leach Rate of Mg from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

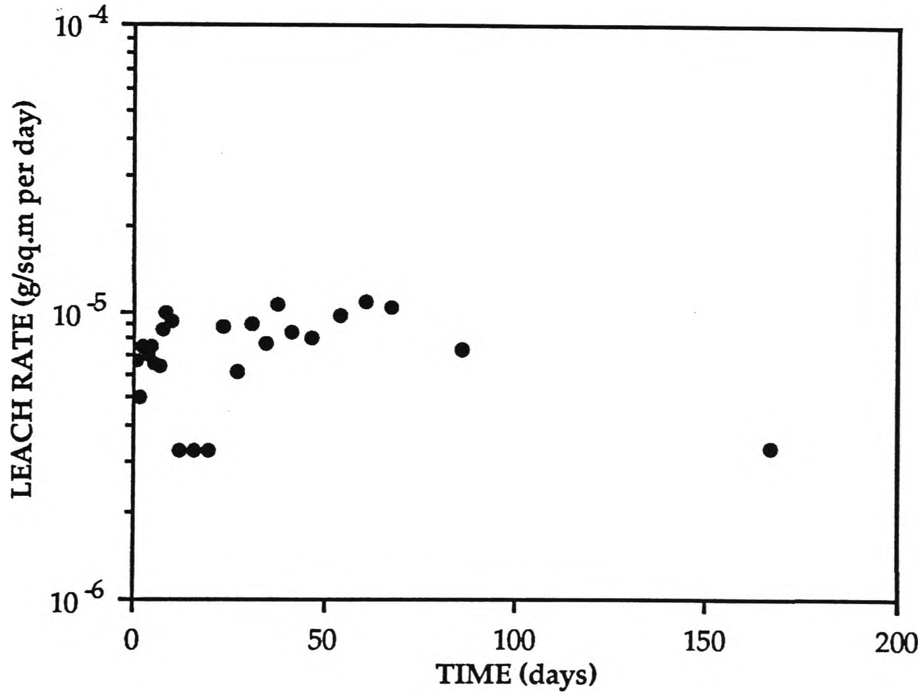

Figure 5.4.2.2.16: **Leach Rate of Mg from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature**

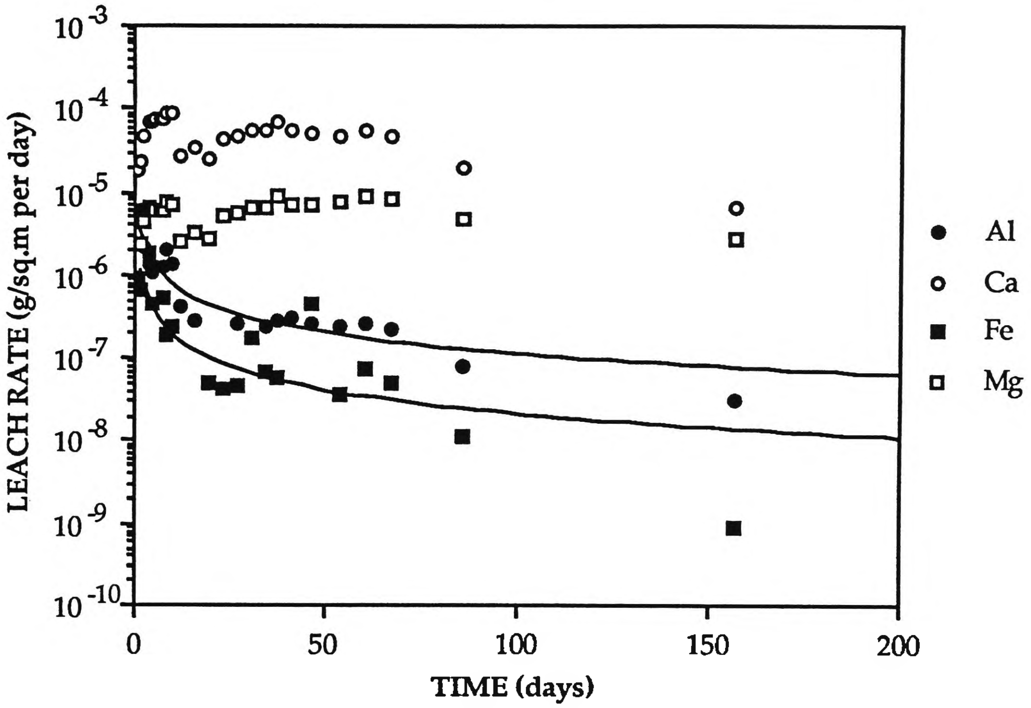

Figure 5.4.2.2.17: Comparison of Leach Rates for Al, Ca, Fe and Mg from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

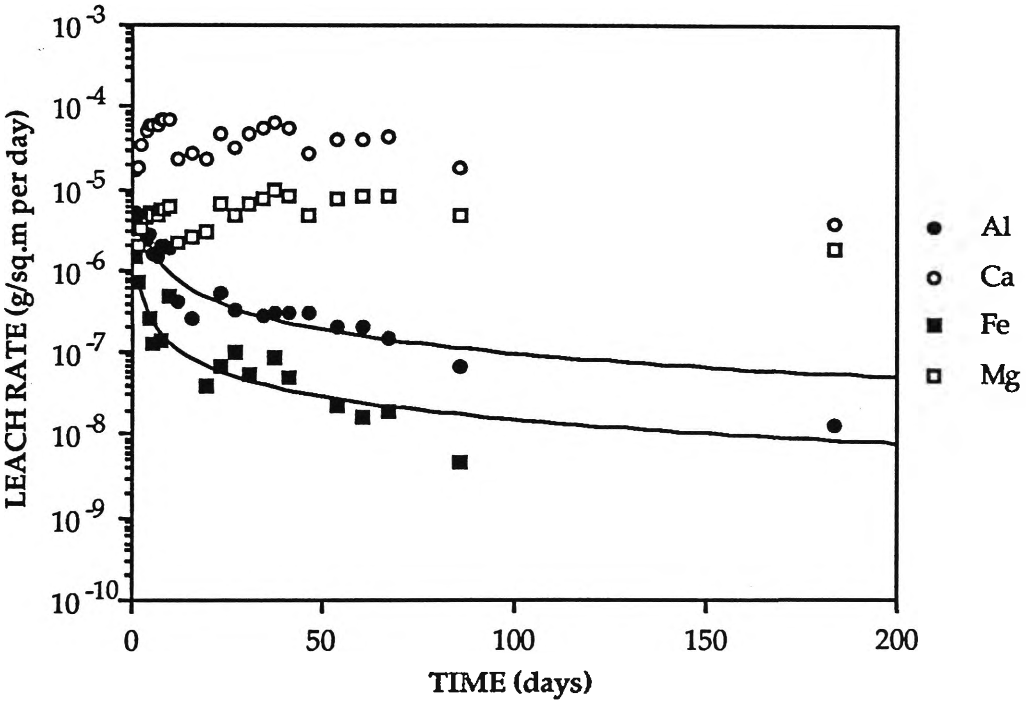

Figure 5.4.2.2.18: Comparison of Leach Rates for Al, Ca, Fe and Mg from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

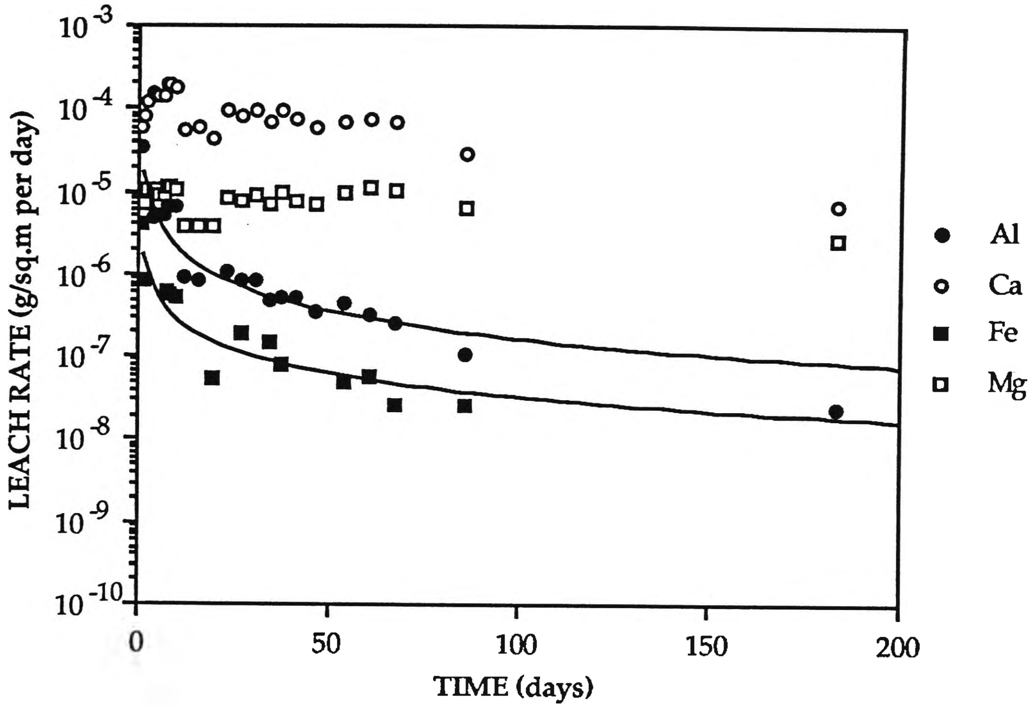

Figure 5.4.2.2.19: **Comparison of Leach Rates for Al, Ca, Fe and Mg from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

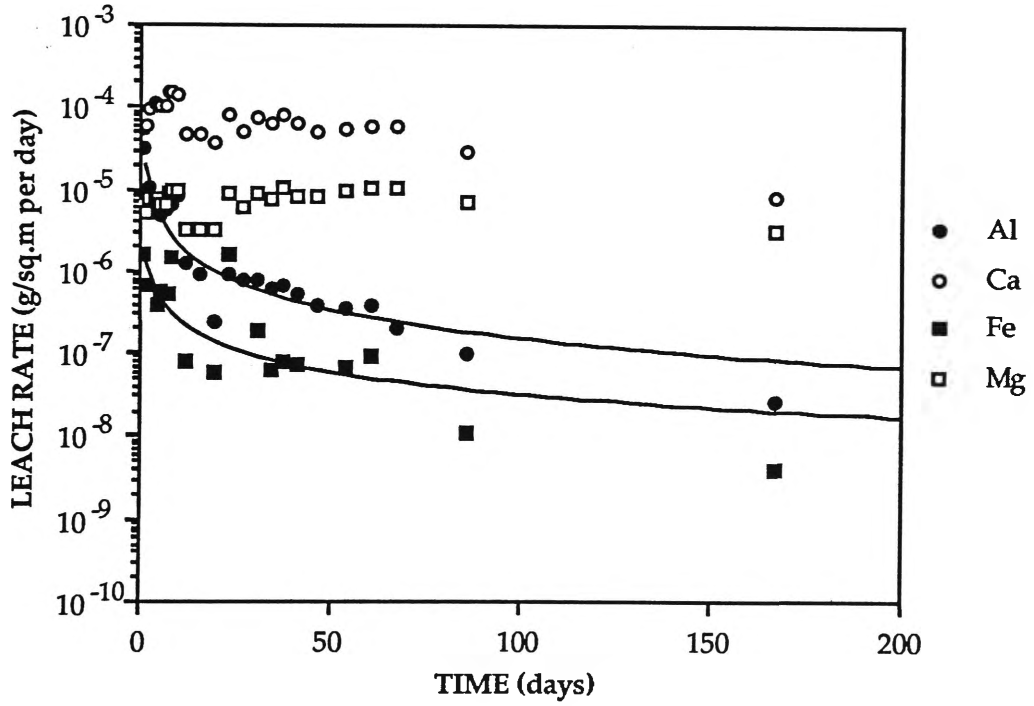

Figure 5.4.2.2.20: **Comparison of Leach Rates for Al, Ca, Fe and Mg from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature**

Iron, on the other hand, shows leaching behaviour that is typical of control by the availability of these ions on the surface of the iron-bearing minerals. The leach rates of iron decrease with time. This behaviour is consistent with the long-term release of this element being controlled by the diffusion of iron into solution, and the counter-diffusion of water into the solid matrix. Similar mechanisms are thought to be controlling the release of aluminium from the clays.

Manganese

Figures 5.4.2.2.21 to 5.4.2.2.24 show that the leach rates of manganese generally decrease over the first ten days, followed by a gradual increase to the end of leaching.

The pH of the initial solution and the L/S have no obvious effect on dissolution.

The leaching behaviour of manganese is similar to that of calcium and magnesium, although saturation of the solutions by manganese does not appear to occur until later leach periods. The effect of saturation is most apparent for the last, and longest, leach period.

Arsenic

The leaching of arsenic from the tailings is similar for each of the leach tests (see Figures 5.4.2.2.25 to 5.4.2.2.28). In all cases the long-term leach rate is approximately 10^{-10} g m^{-2} d^{-1}.

Cadmium

The amount of cadmium leached from the tailings was not significantly different from the background levels.

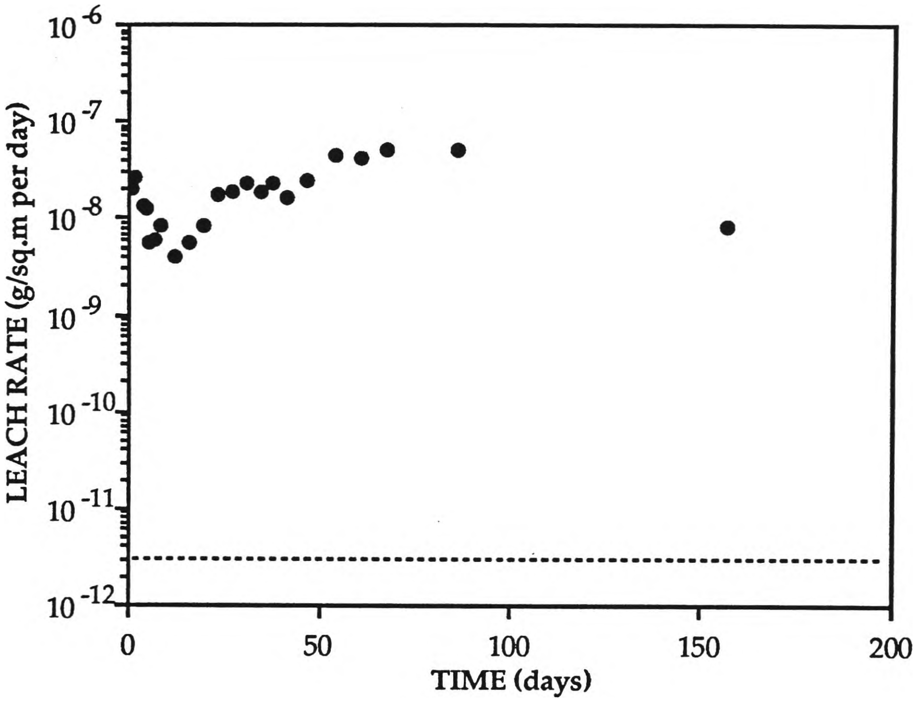

Figure 5.4.2.2.21: **Leach Rate of Mn from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature**

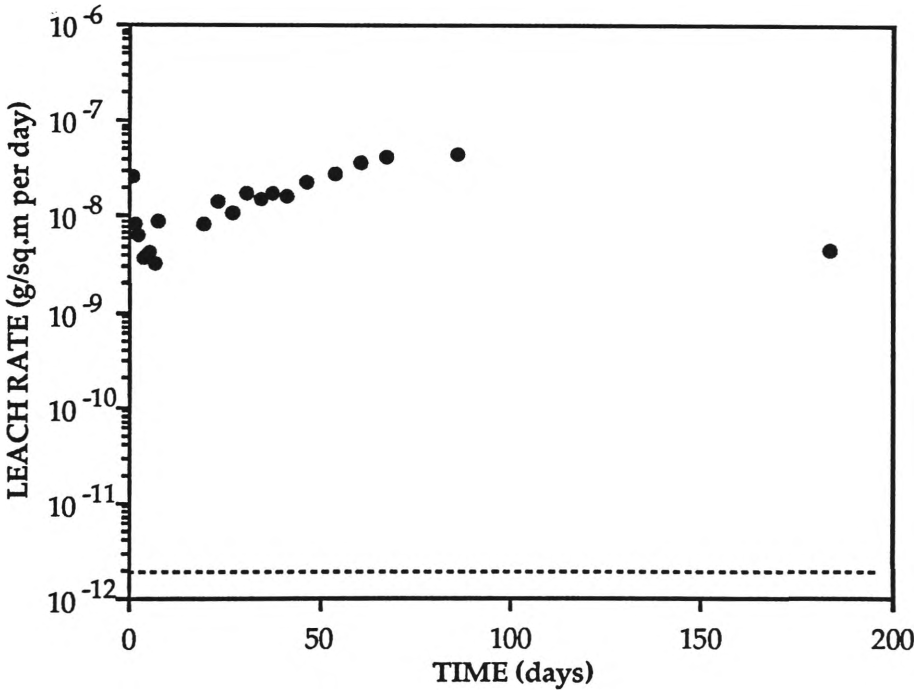

Figure 5.4.2.2.22: **Leach Rate of Mn from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature**

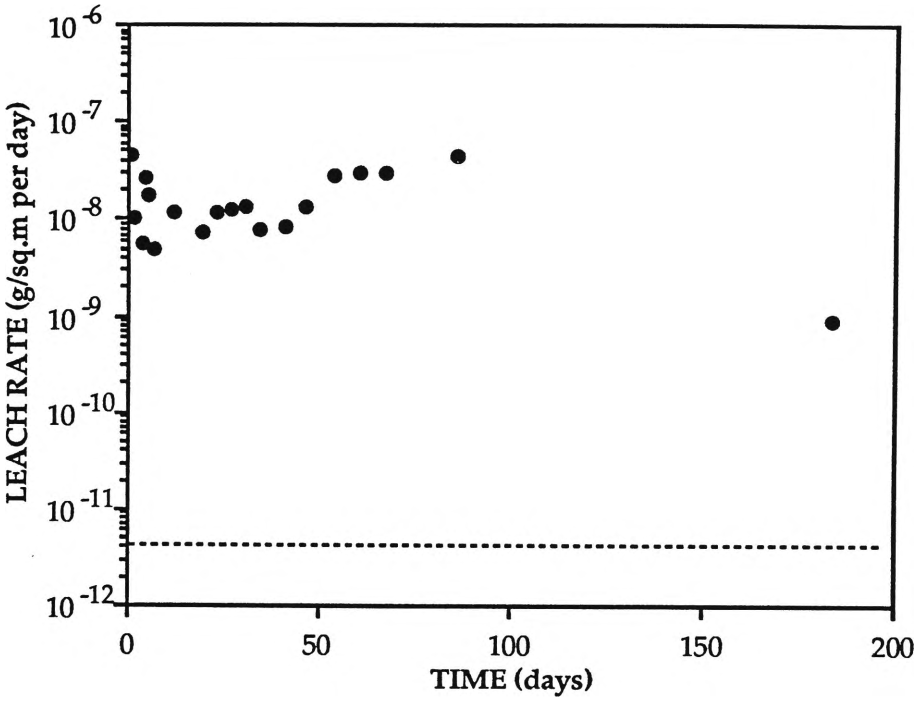

Figure 5.4.2.2.23: Leach Rate of Mn from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

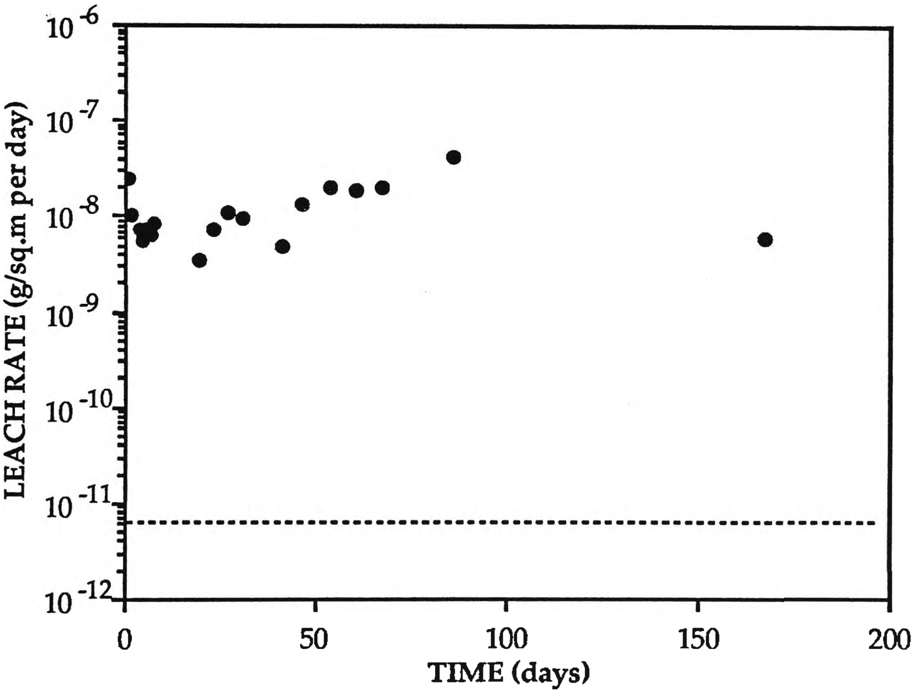

Figure 5.4.2.2.24: Leach Rate of Mn from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

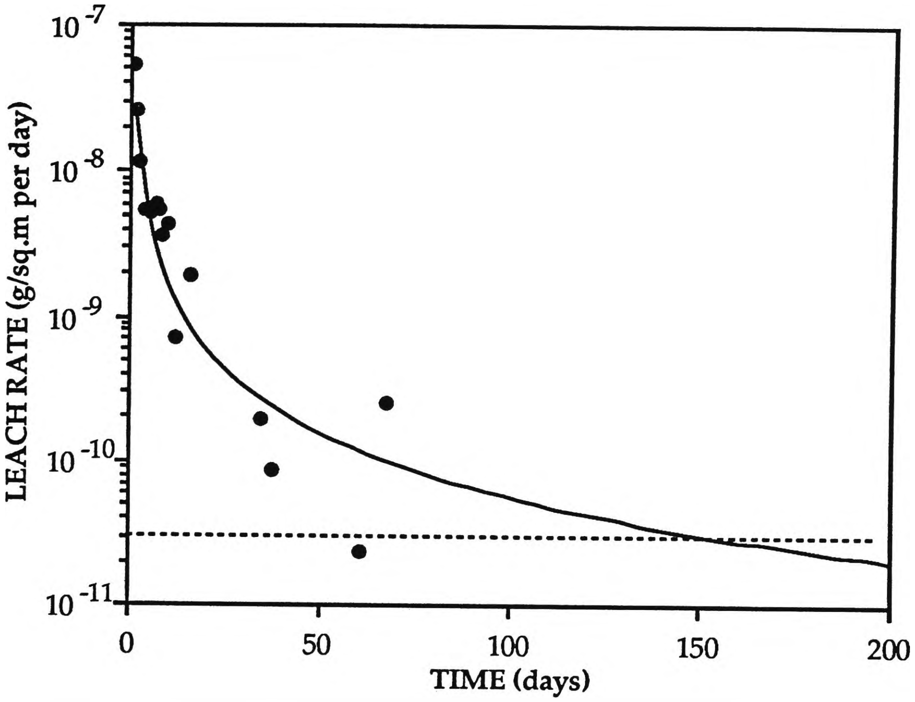

Figure 5.4.2.2.25: **Leach Rate of As from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature**

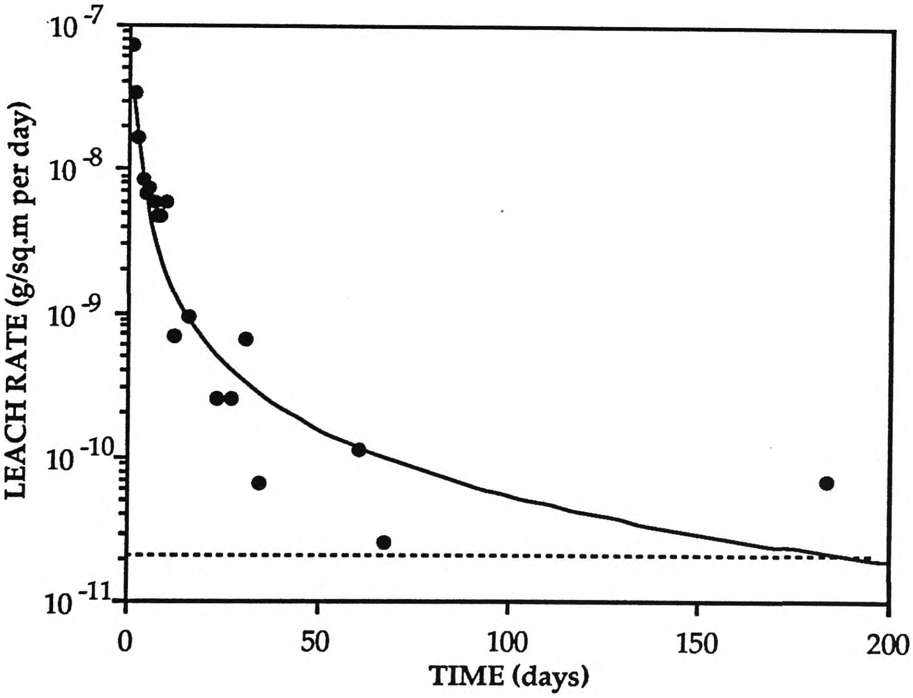

Figure 5.4.2.2.26: **Leach Rate of As from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature**

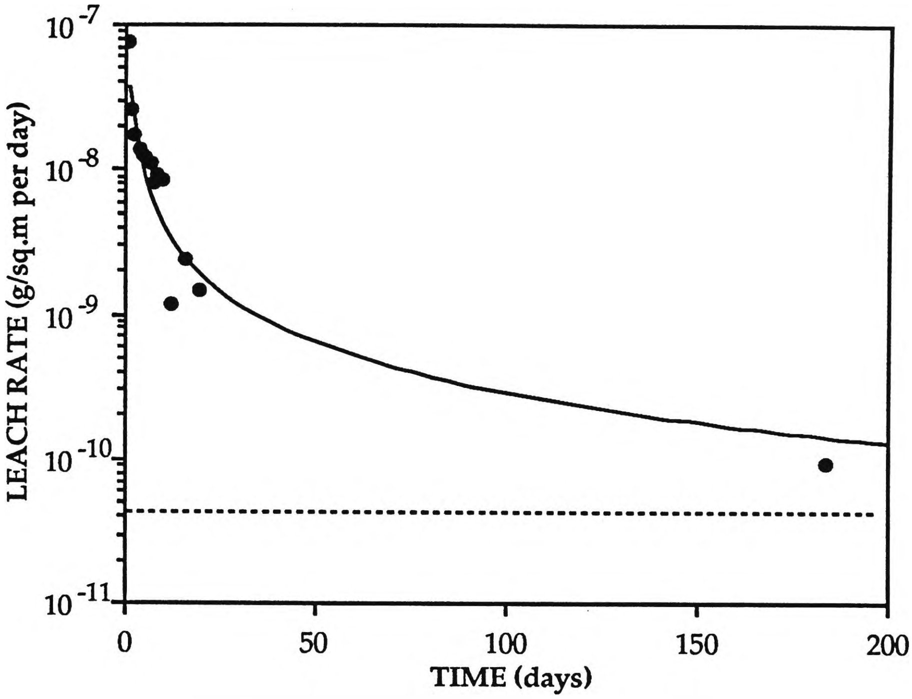

Figure 5.4.2.2.27: Leach Rate of As from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

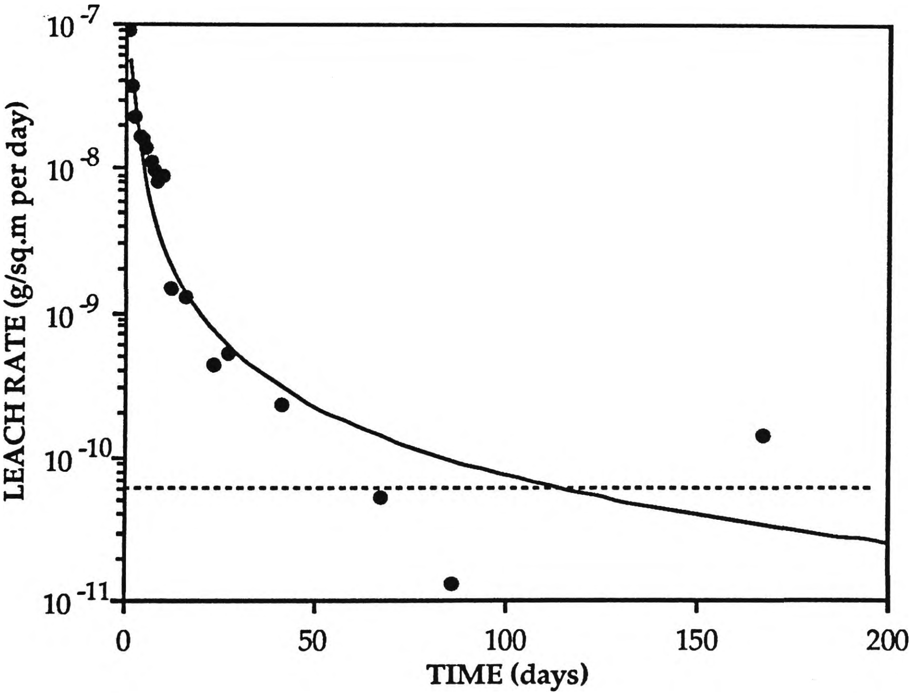

Figure 5.4.2.2.28: Leach Rate of As from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

Chromium

The leach rates for chromium are shown in Figures 5.4.2.2.29 to 5.4.2.2.32. There does not appear to be any significant effect of initial solution pH or L/S.

Copper

A comparison of copper leach rates was only possible for three of the four tests, as only a few leach rates were able to be calculated for the test at 10:1 L/S ratio, initial solution pH 4 test, because of the very low leachate concentrations. The leach rates for copper are similar and are not affected by the initial solution pH or L/S ratio (see Figures 5.4.2.2.33 to 5.4.2.2.36).

Mercury

The concentrations of mercury in the leachates were highly variable. The high variability of the data makes it difficult to establish any effect of leaching conditions. They do highlight, however, the difficulty in consistently measuring the concentration of mercury in solution, particularly at the extremely low levels that existed in the leachates from this work.

Lead

The leach rates of lead are shown in Figures 5.4.2.2.37 to 5.4.2.2.40. For the tests carried out at a L/S ratio of 5:1, leach rates are similar, decreasing with time and are fitted reasonably well by logarithmically derived curves. Data for the tests carried out at 10:1 L/S ratio are scattered and show no apparent trend.

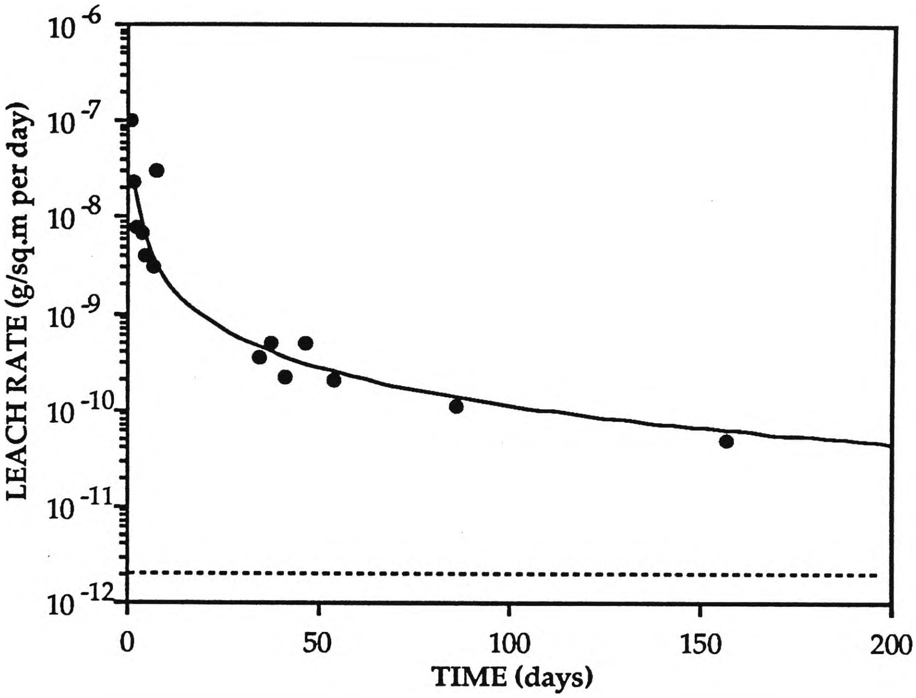

Figure 5.4.2.2.29: Leach Rate of Cr from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

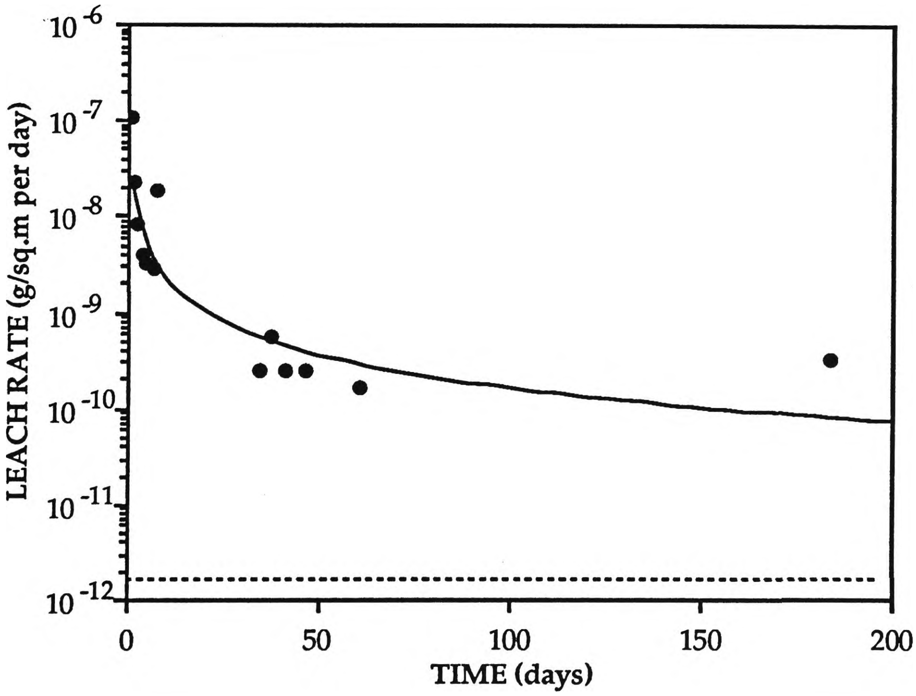

Figure 5.4.2.2.30: Leach Rate of Cr from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

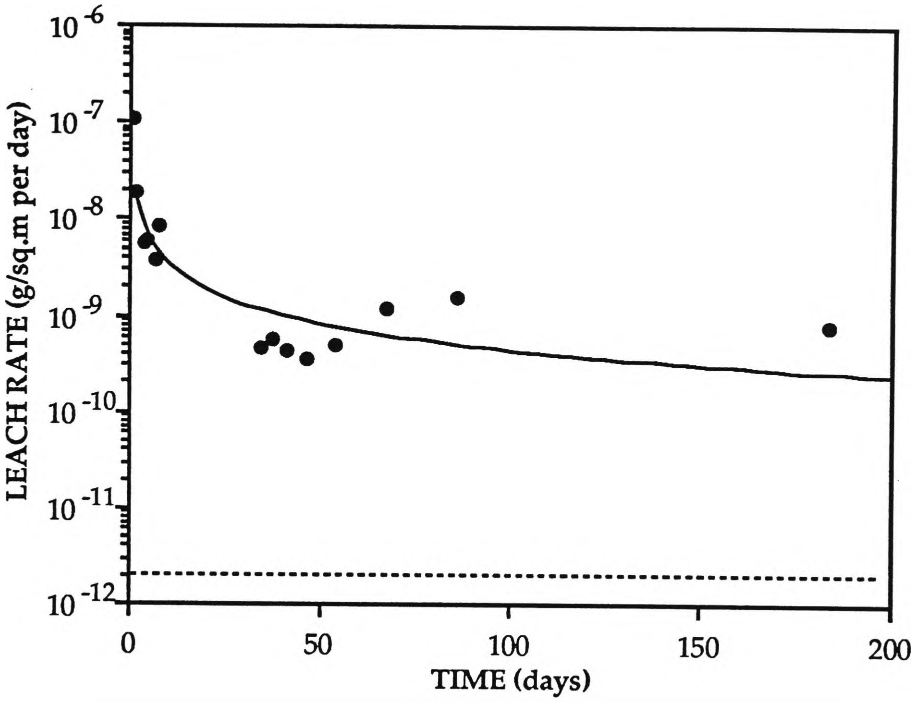

Figure 5.4.2.2.31: **Leach Rate of Cr from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

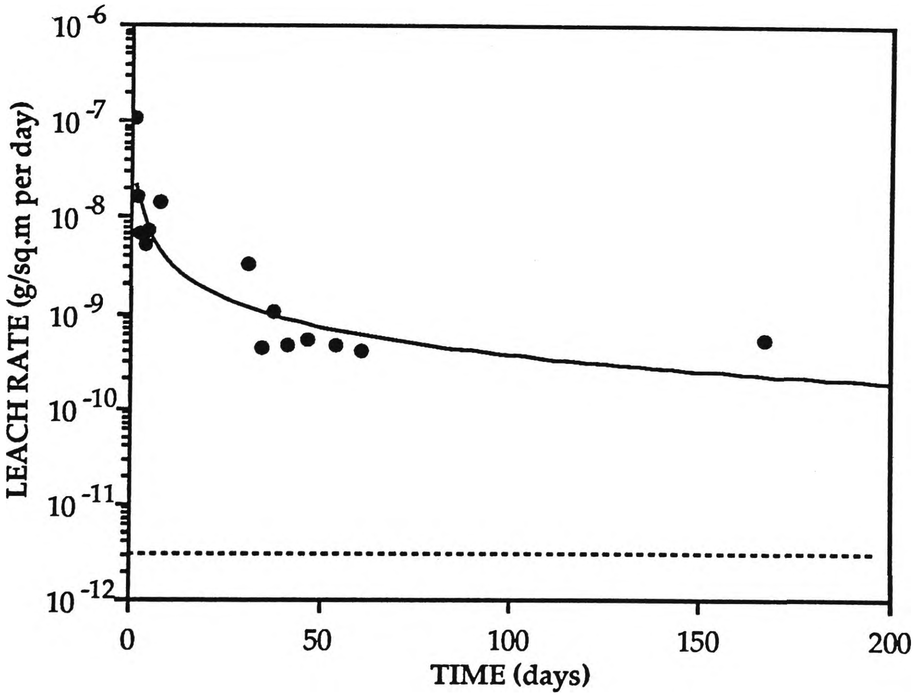

Figure 5.4.2.2.32: **Leach Rate of Cr from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature**

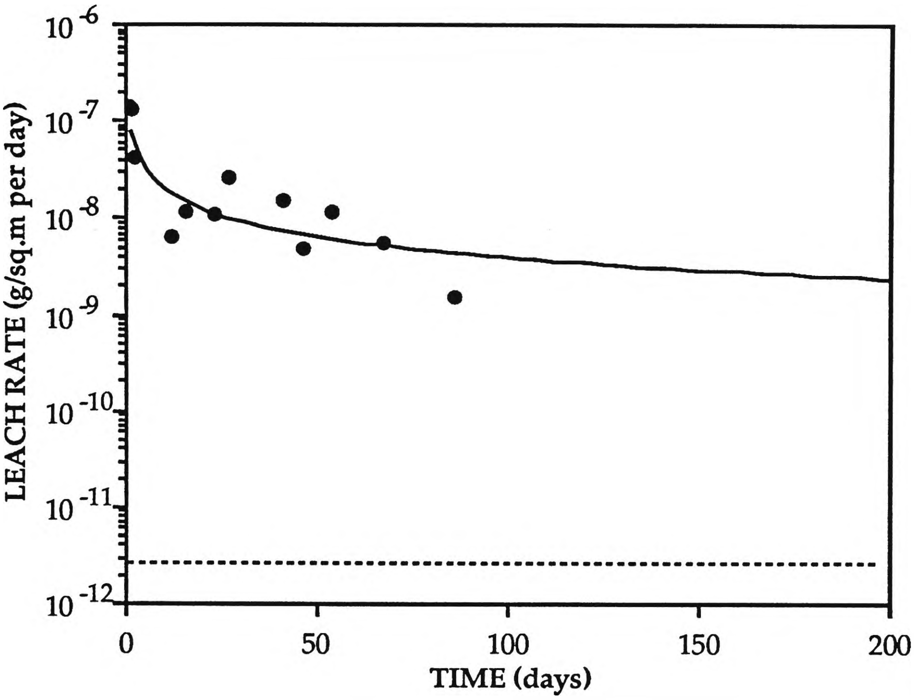

Figure 5.4.2.2.33: Leach Rate of Cu from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

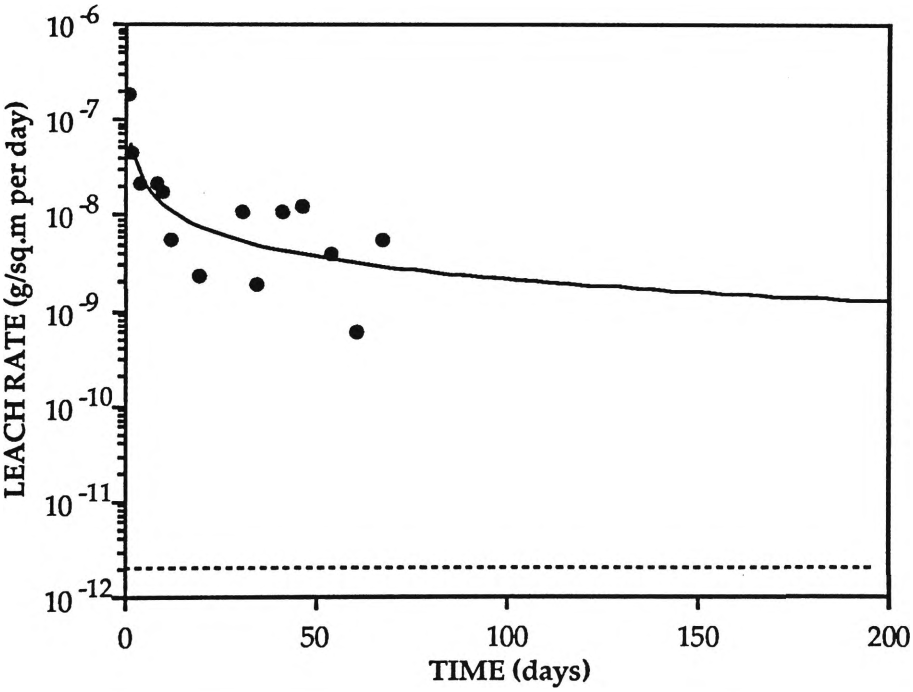

Figure 5.4.2.2.34: Leach Rate of Cu from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

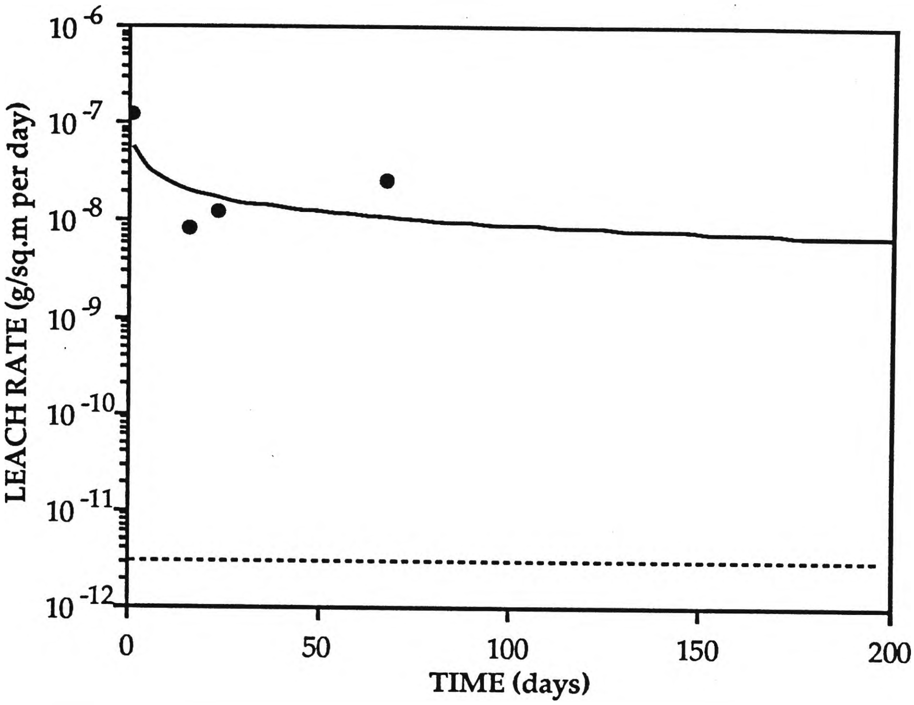

Figure 5.4.2.2.35: Leach Rate of Cu from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

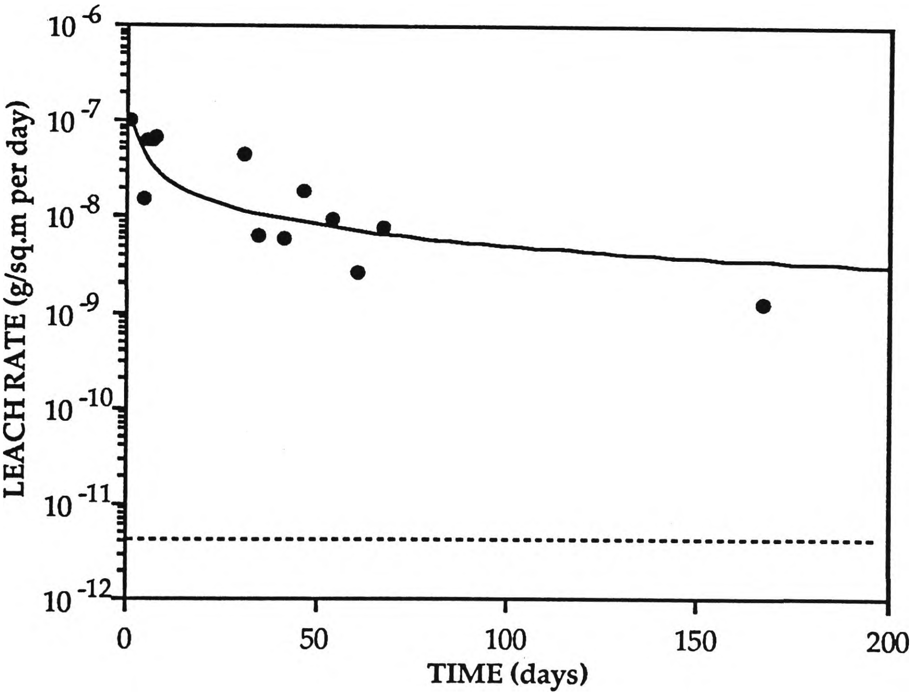

Figure 5.4.2.2.36: Leach Rate of Cu from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

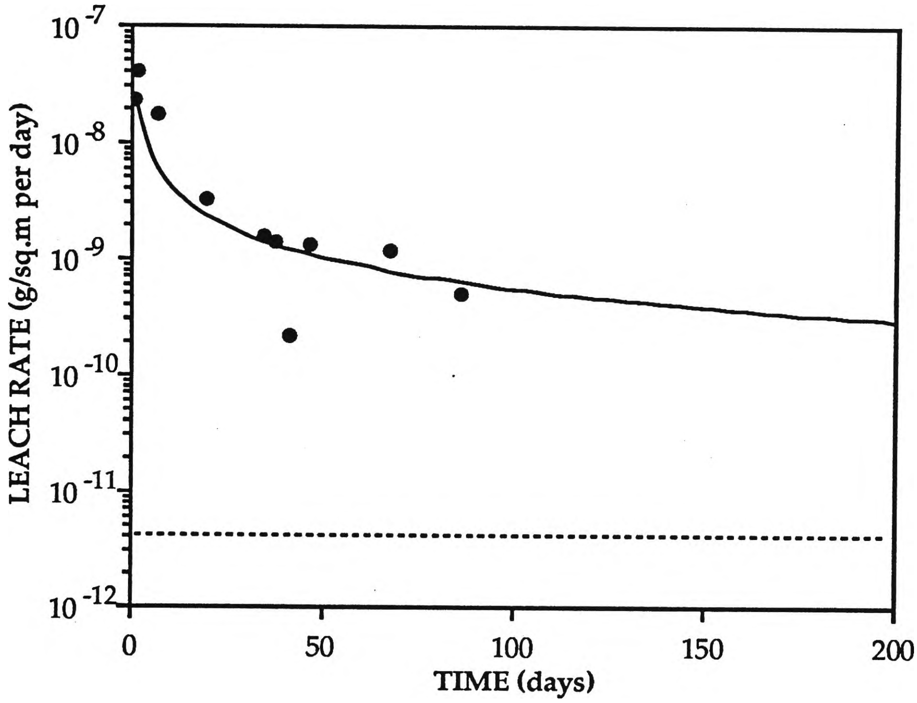

Figure 5.4.2.2.37: Leach Rate of Pb from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

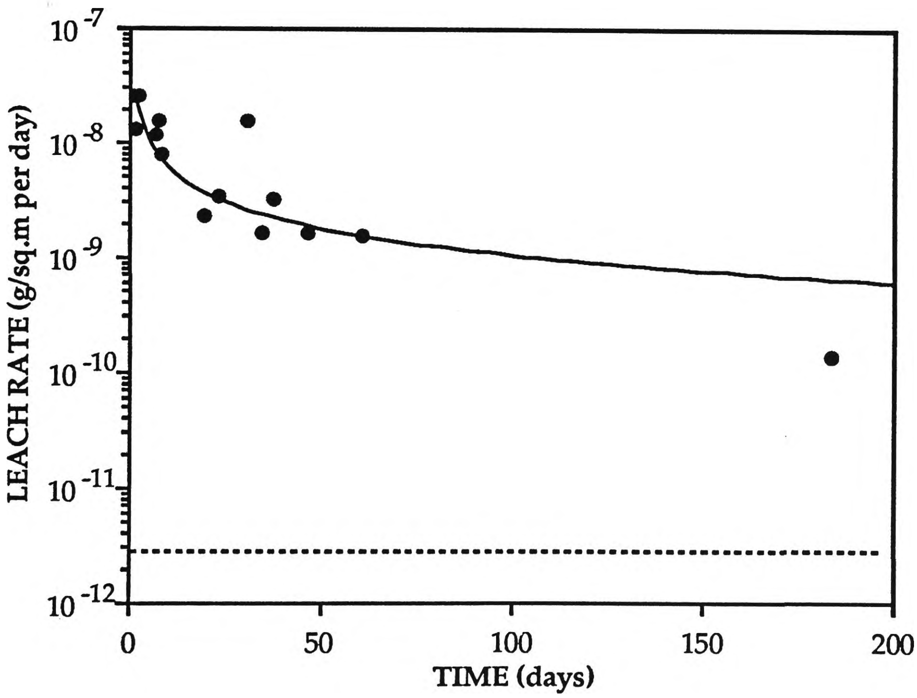

Figure 5.4.2.2.38: Leach Rate of Pb from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

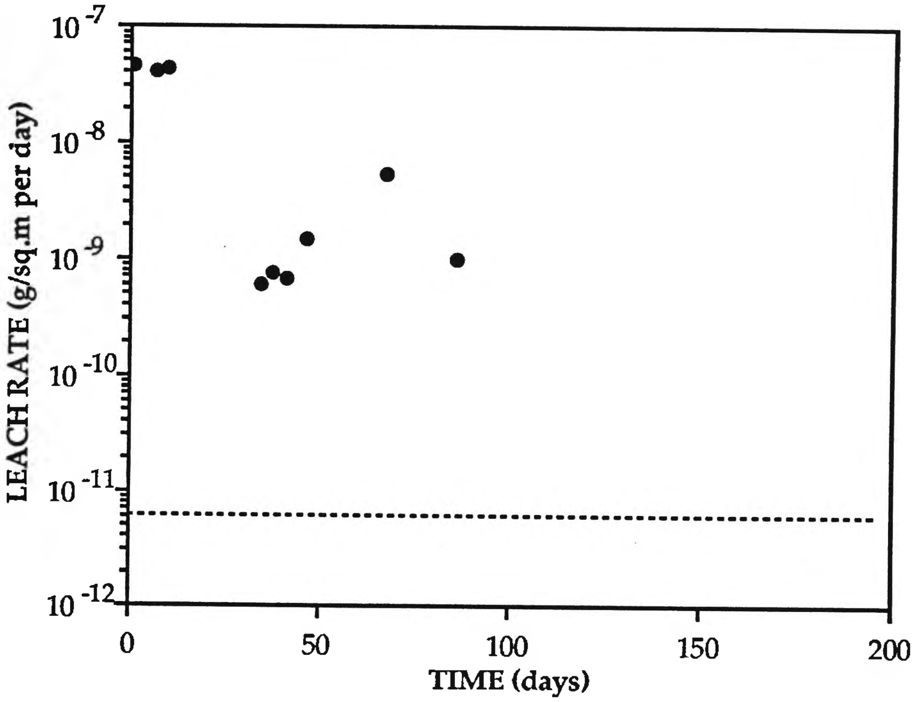

Figure 5.4.2.2.39: Leach Rate of Pb from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

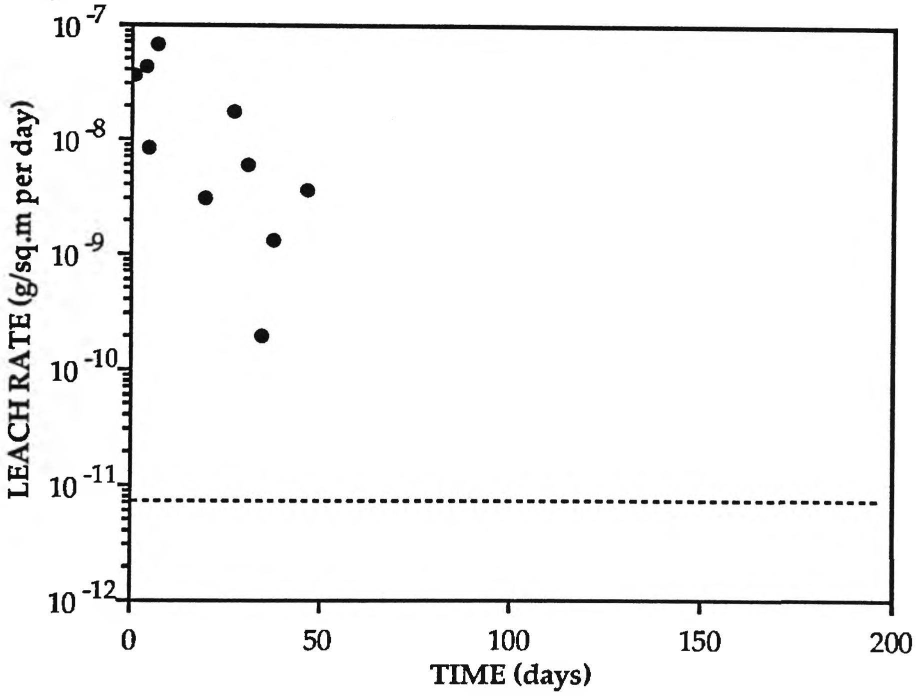

Figure 5.4.2.2.40: Leach Rate of Pb from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

Thorium and Uranium

Figures 5.4.2.2.41 to 5.4.2.2.48 show the leach rates for thorium and uranium. Leach rates in each case generally decrease with time. The Figures show that, for both elements, neither L/S ratio nor initial solution pH have an effect on leaching.

Zinc

The leach rates for zinc are shown in Figures 5.4.2.2.49 to 5.4.2.2.52. The rates decrease with time, and are similar and appear to be independent of L/S ratio and the pH of the initial solution.

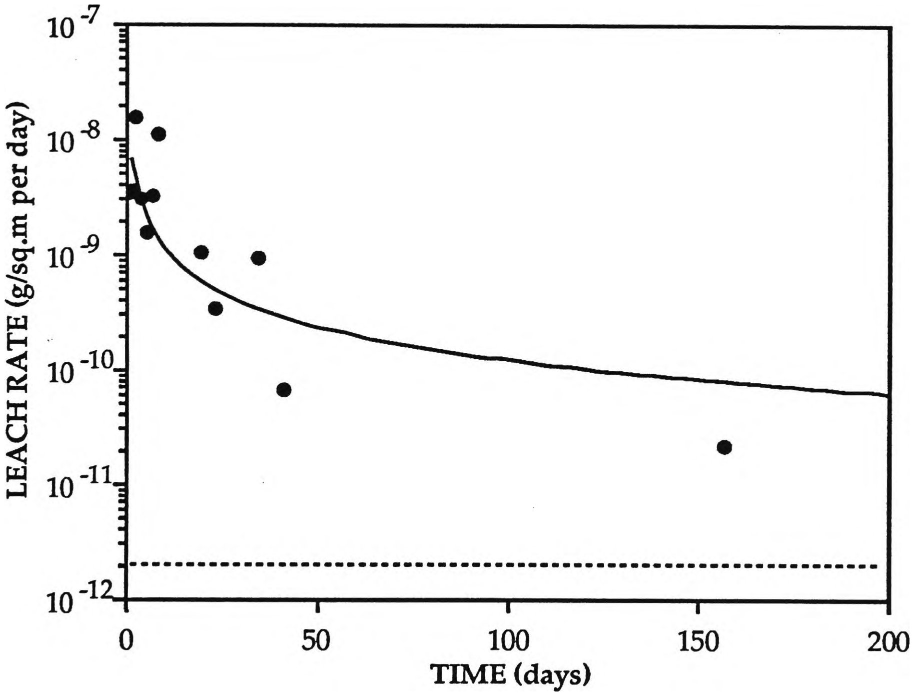

Figure 5.4.2.2.41: **Leach Rate of Th from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature**

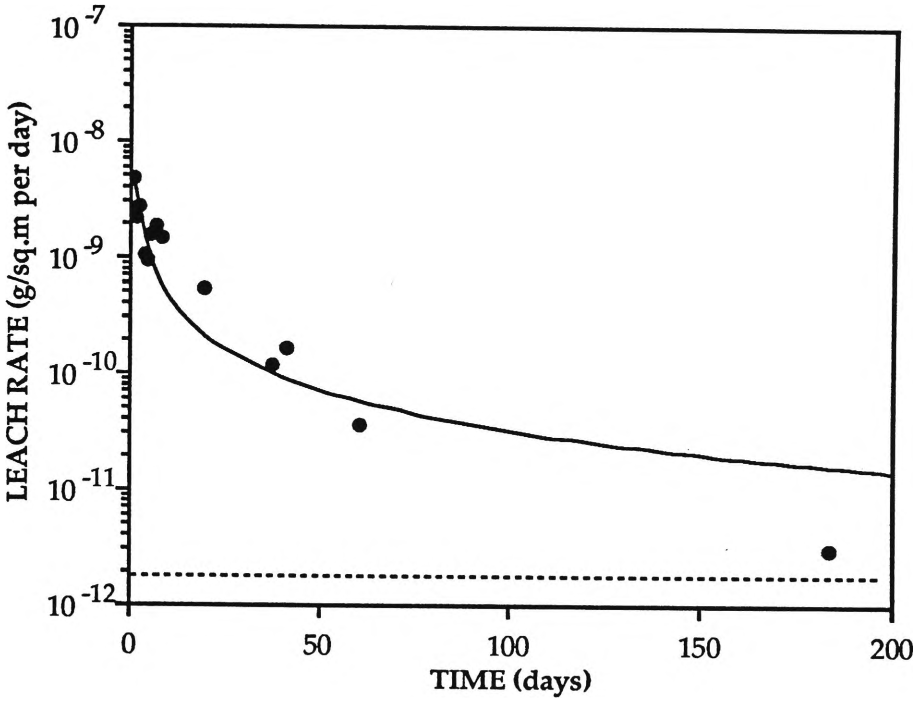

Figure 5.4.2.2.42: Leach Rate of Th from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

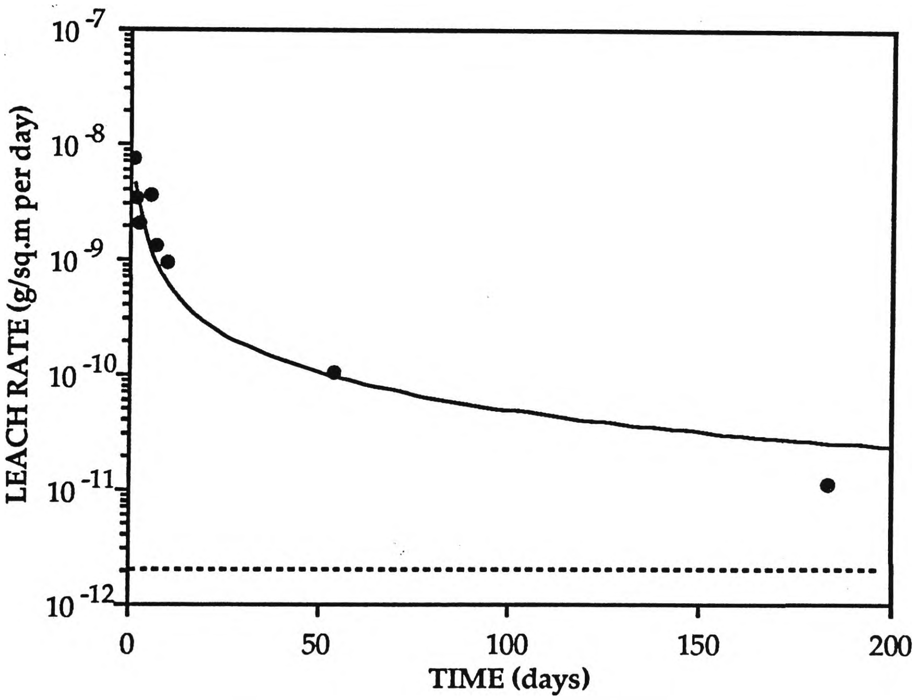

Figure 5.4.2.2.43: Leach Rate of Th from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

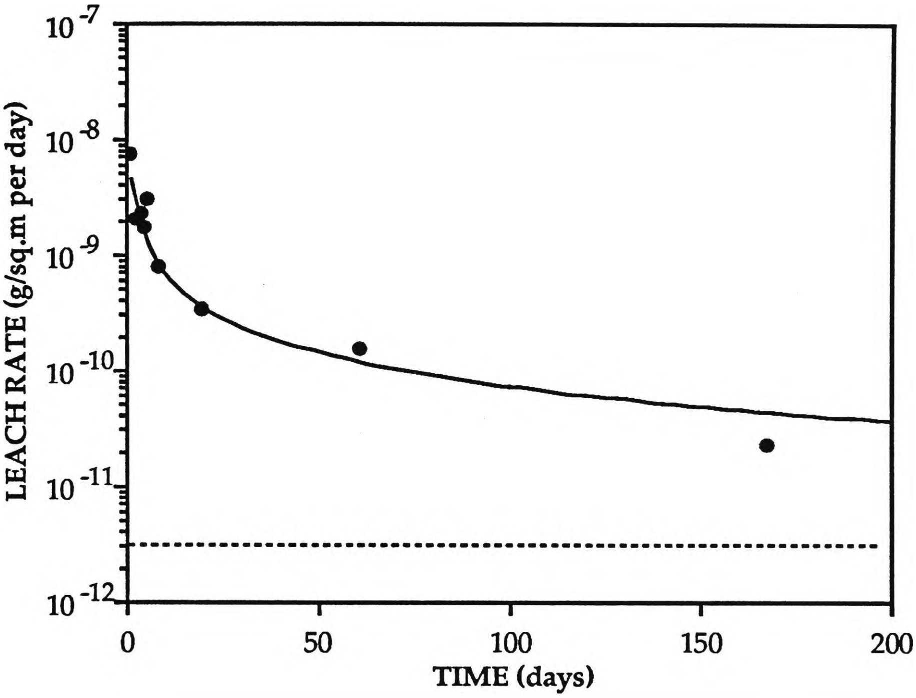

Figure 5.4.2.2.44: Leach Rate of Th from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

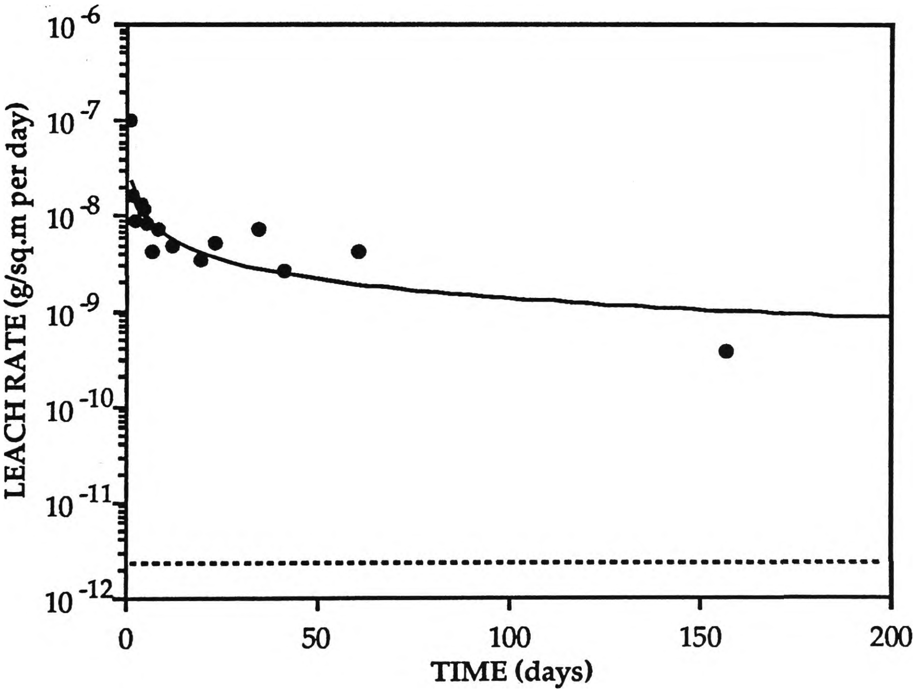

Figure 5.4.2.2.45: Leach Rate of U from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

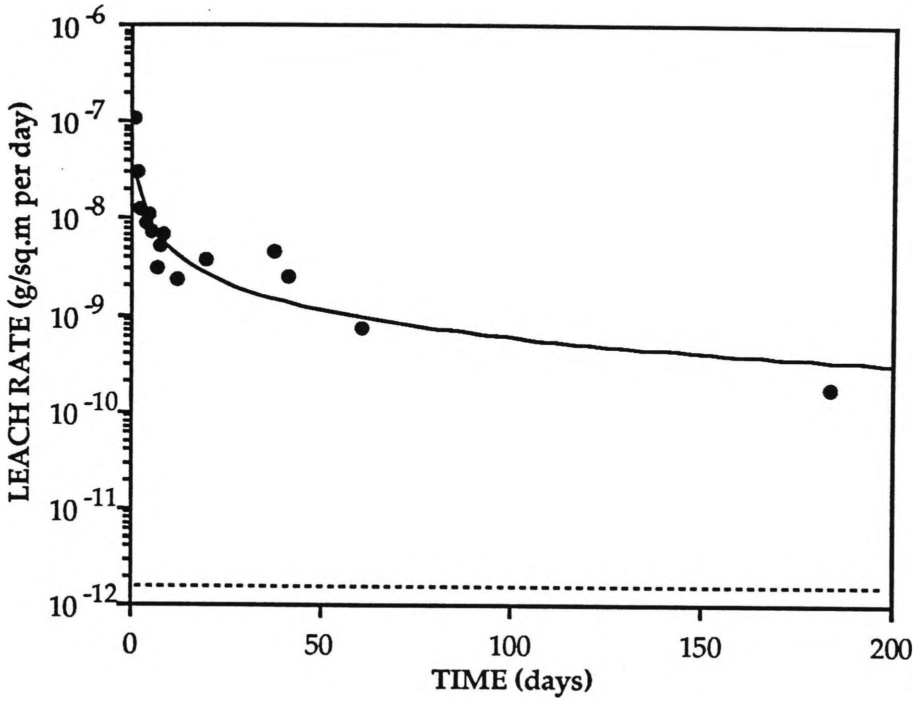

Figure 5.4.2.2.46: **Leach Rate of U from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature**

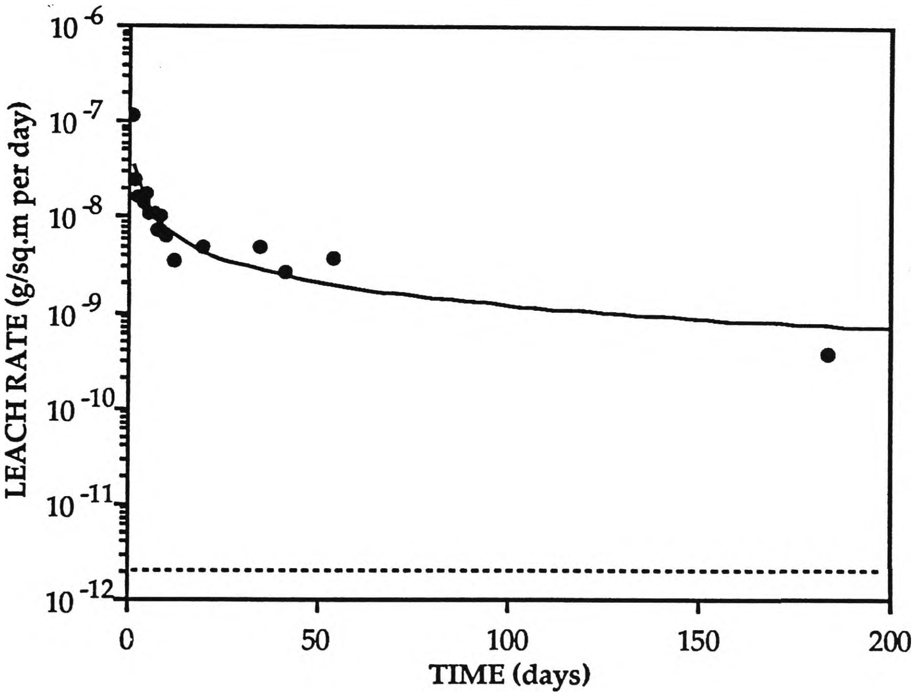

Figure 5.4.2.2.47: **Leach Rate of U from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

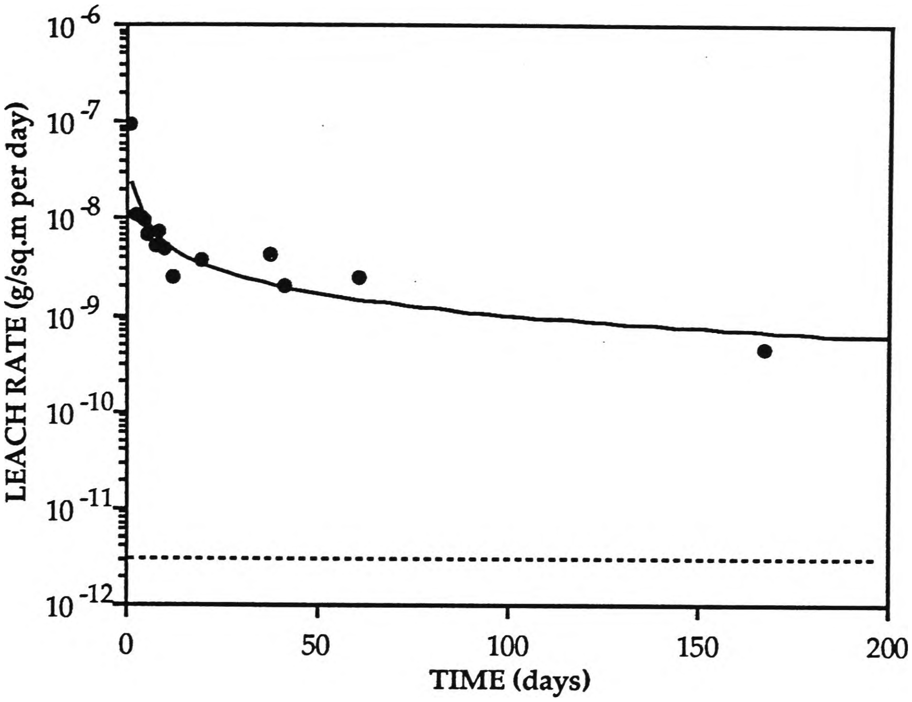

Figure 5.4.2.2.48: Leach Rate of U from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

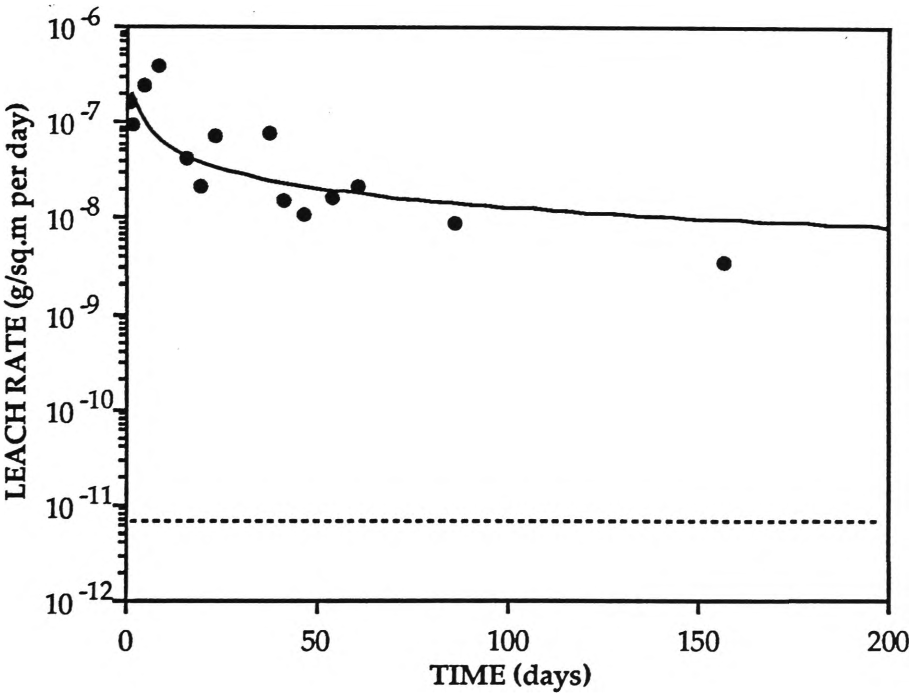

Figure 5.4.2.2.49: Leach Rate of Zn from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

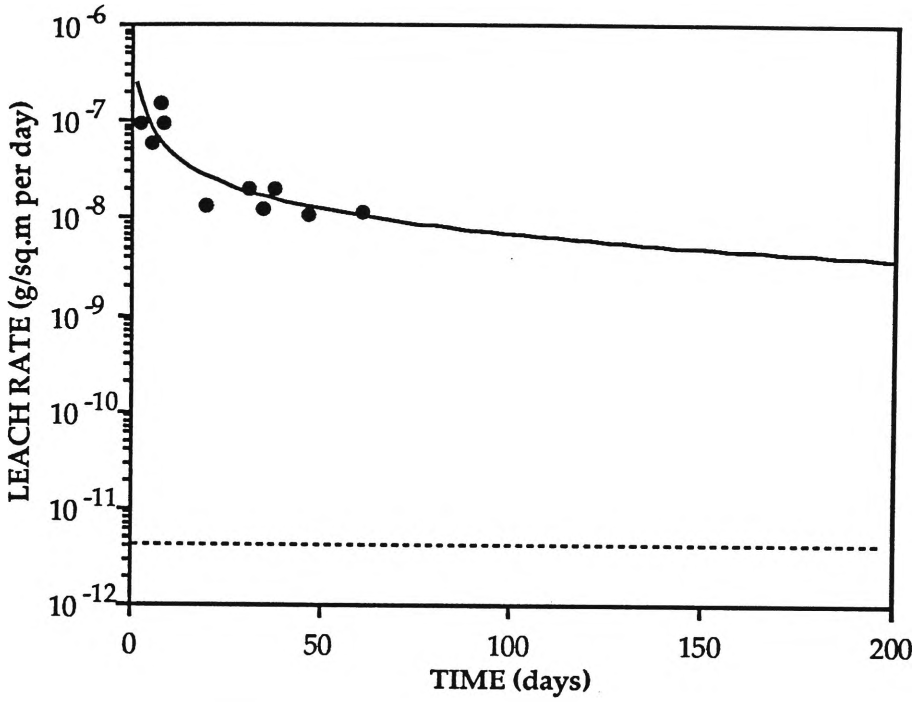

Figure 5.4.2.2.50: Leach Rate of Zn from Tailings - Initial pH 9, L/S Ratio 5:1 at Ambient Temperature

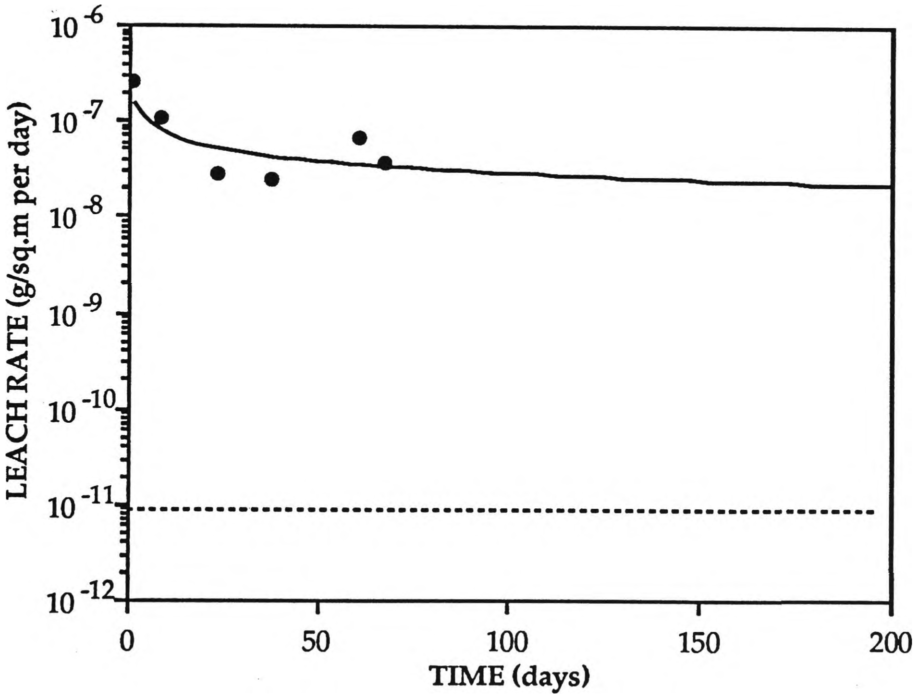

Figure 5.4.2.2.51: Leach Rate of Zn from Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

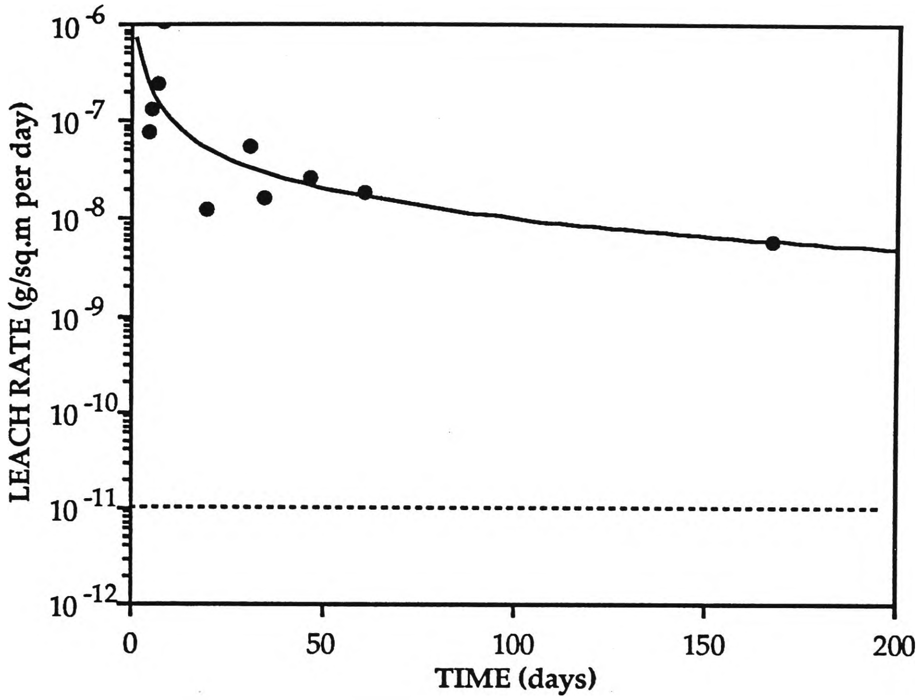

Figure 5.4.2.2.52: Leach Rate of Zn from Tailings - Initial pH 9, L/S Ratio 10:1 at Ambient Temperature

Summary of Leach Rates

The major phase of accelerated leach testing was carried out to determine the source term of four of the major elemental components, and 14 trace elements, in the tailings, from impoundments and dams containing tailings of the same, or similar, composition to those generated by West Cliff colliery. The chief findings of this series of tests were:

- pH decreases with time for each leach test. The pHs are alkaline and similar under each set of leach conditions, and are essentially independent of initial pH and L/S ratio.

- With the exception of the test carried out at L/S 5;1 and initial pH 4, the change in redox potential between tests is similar.

- Leachates in all of the tests were saturated in calcium and magnesium.

- Leachates were under-saturated with respect to aluminium and iron.

- The leaching trend for manganese is similar to that for calcium and magnesium, excepting that the leachates only appear to saturate in manganese when the leaching period is greater than 24 hours.
- Arsenic, chromium, copper, lead, thorium, uranium and zinc leach rates were not affected by initial solution pH or L/S ratio.
- Cadmium and mercury concentrations in most of the leachates were not measurable.

5.4.2.3 Leaching as a Function of L/S Ratio (According to BEOP-31 Standard)

The results presented in this section show the cumulative percentages of the elements leached from the tailings in terms of L/S ratio, according to the BEOP-31 test. To do this, the BEOP standard sums the percentages leached during each 24 hour leach period of the test, as well as the corresponding L/S ratios, and extrapolates the results to an equivalent set of L/S conditions that may prevail in the field. For example, if over five days of leaching at 5:1 L/S ratio the cumulative percentage is, say, 1%, then this would be graphed against a L/S ratio of 25:1.

The results for the most abundant elements in the tailings (aluminium, calcium, iron and magnesium) are given in the same figures, whilst those for the trace elements are given in two separate diagrams for clarity.

Aluminium, Calcium, Iron and Magnesium

The cumulative mass percentages leached of the major elements calcium, magnesium, aluminium and iron, as a function of L/S ratio, are given in Figure 5.4.2.3.1. This Figure shows that calcium and magnesium are released during each leach period. At 50:1 L/S ratio, total mass released of each element is approximately 1% and 0.4% respectively, however, these are probably under-estimated as it has been shown previously that at a L/S ratio of 5:1, the leachates are clearly saturated in both of these elements.

On the other hand, negligible proportions of aluminium and iron appear to be released above a L/S ratio of 10:1. The proportions reached at that point are 0.005% and 0.001% respectively.

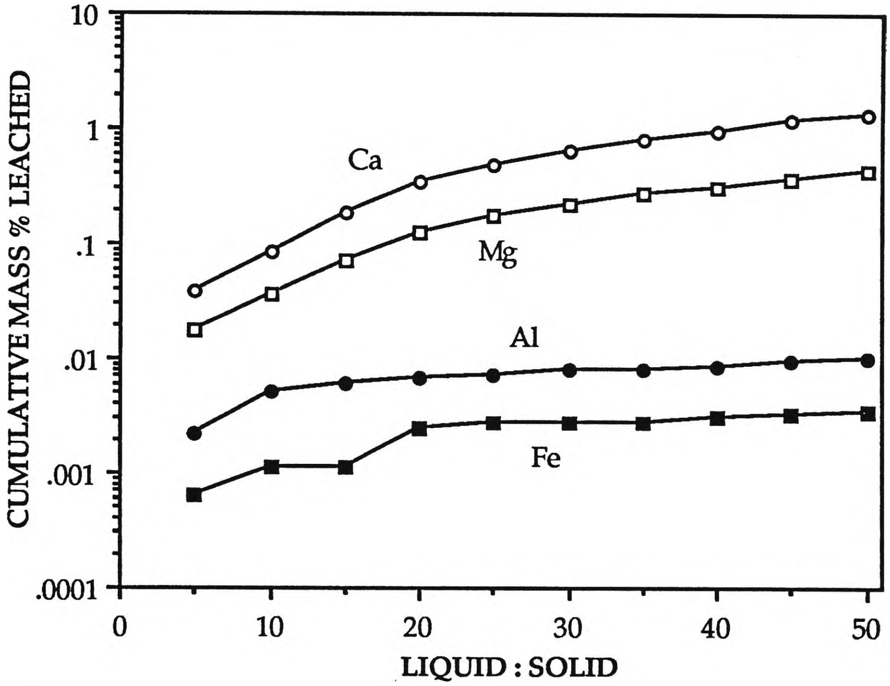

Figure 5.4.2.3.1: **Cumulative Mass Percentage of Al, Ca, Fe and Mg Leached from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature**

Trace Elements

The cumulative mass percentages leached of the trace elements are given in Figures 5.4.2.3.2 and 5.4.2.3.3. The results show that, for most of the elements, their release from the tailings is very small for a L/S ratio greater than 10:1, suggesting that above this ratio their solubility is being controlled.

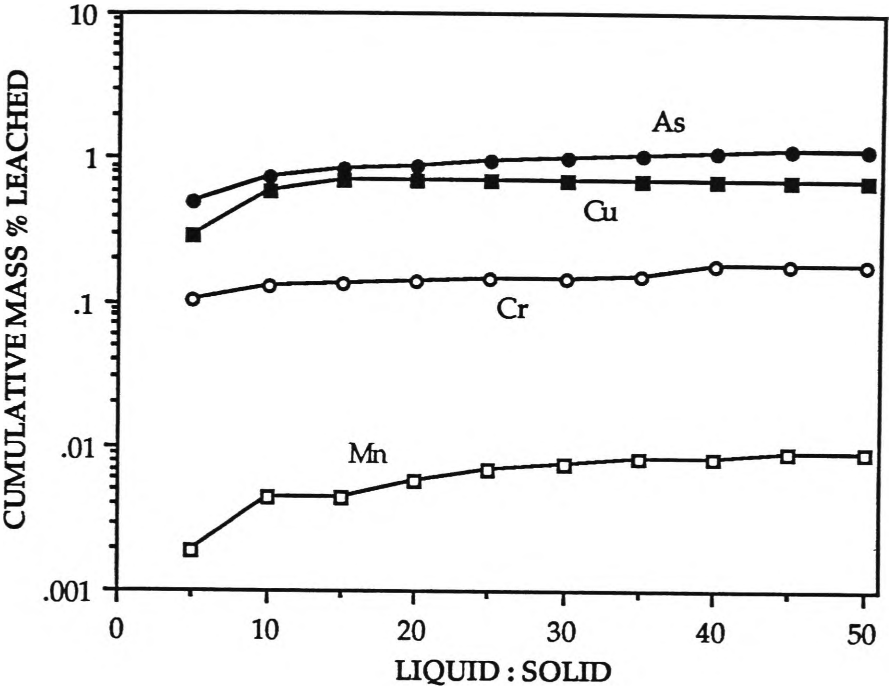

Figure 5.4.2.3.2: Cumulative Mass Percentage of As, Cr, Cu and Mn Leached from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

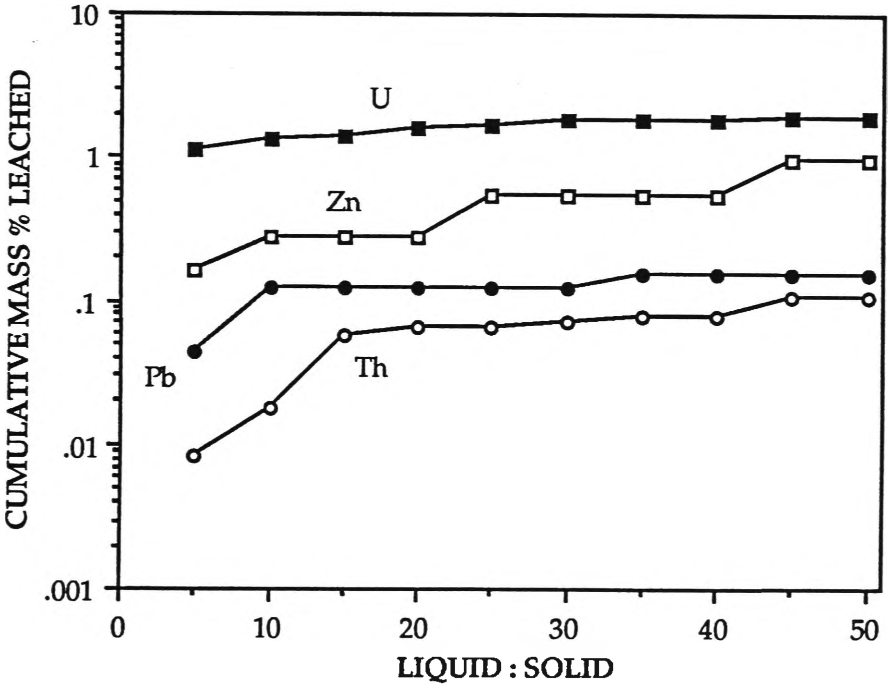

Figure 5.4.2.3.3: Cumulative Mass Percentage of Pb, Th, U and Zn Leached from Tailings - Initial pH 4, L/S Ratio 5:1 at Ambient Temperature

5.4.2.4 Relative Leachability of Tailings Under Each of the Test Conditions

The mass percentage of each of the elements leached over the entire leaching time have been calculated to determine the total elemental release from the tailings. The final leach period for the tests varied, ranging from 111 to 165 days. Up to this point each test had been carried out for a total of 101 days and the leachates had been changed with fresh solution at exactly the same times for each test.

Table 5.4.2.4 shows the amount leached up to the beginning of the final leach period i.e. after 101 days. This period was chosen as it enabled all tests to be compared for the same time and because releases in this period dominated the releases measured for the total time of the leach tests.

The relative leachability of the elements, under each of the test conditions, decrease in the order:

$$\mathrm{Ca} > \mathrm{Mg} > \mathrm{U} > \mathrm{Zn} > \mathrm{Cu} \sim \mathrm{As} > \mathrm{Mn} > \sim \mathrm{Pb} \sim \mathrm{Hg} \sim \mathrm{Cr} > \mathrm{Th} > \sim \mathrm{Al} > \mathrm{Fe}$$

The behaviour of the individual elements may be summarised as follows:

- Aluminium is one of the least leached elements from the tailings (0.014 to 0.049%). Although the amount of aluminium leached from the tailings is greater by about a factor of three at 10:1 L/S ratio than those of the 5:1 tests, leach rates for aluminium, given in the previous section of this chapter, indicated that the leachates were under-saturated with respect to this element.

- Calcium and magnesium are leached in relatively high proportions. The amount of calcium leached out at 10:1 L/S ratio is approximately 50% greater than that at 5:1. In the higher pH initial solution less calcium is released. For magnesium, the amount leached at L/S of 5:1 is about one quarter less than that at 10:1.

- Iron - Iron, like aluminium, is released in very low proportions, 0.0028 to 0.0073%. At initial pH 4, similar amounts of iron are leached at 5:1 and 10:1 L/S ratios. At initial solution pH of 9, the amount of iron released in the 10:1 test is greater than that of the 5:1 test by a factor of almost three. The amount of iron leached out at pH 9 and a 5:1 L/S ratio is half of that of the pH 4 test.

TABLE 5.4.2.4: Total Percentage Mass Leached of Each Element from the Tailings After 101 Days of Leaching

Element	Mass % Leached			
	L/S 5:1; pH 4	L/S 5:1; pH 9	L/S 10:1; pH 4	L/S 10:1; pH 9
Aluminium	0.014	0.017	0.045	0.049
Arsenic	1.0	1.4	1.6	1.8
Calcium	6.9	5.9	11.2	9.2
Cadmium*	-	-	-	-
Chromium	0.15	0.15	0.18	0.16
Copper	1.4	1.0	0.64	1.4
Iron	0.0060	0.0028	0.0056	0.0073
Mercury	0.13	0.92	0.82	2.6
Magnesium	3.7	3.6	4.8	4.8
Manganese	0.26	0.21	0.19	0.15
Lead	0.22	0.32	0.33	0.44
Thorium	0.105	0.040	0.039	0.041
Uranium	2.6	2.0	2.7	1.7
Zinc	2.0	0.69	1.1	1.8

* In solution cadmium had concentrations that were very close to detection limits and the total percentage released could not be reliably calculated.

- Manganese - The amount of manganese released is similar in each of the tests.

- Arsenic - Apart from the 5:1 L/S, initial pH 4 test, the solubility of arsenic appears to be similar in the tests. There is less arsenic leached out at the lower L/S ratio and pH.

- Cadmium - The levels of cadmium in the leachates were generally immeasurable, making comparisons of relative leachabilities between tests not possible.

- Chromium - The amount of chromium leached in each test was similar.

- Copper - Copper data were variable, and assumptions concerning the relative leachabilities are not possible.

- Mercury - There were very few measurable levels of mercury in the leachates. From the data that was obtained, it seems that there is solubility control and that there is greater solubility of mercury at higher pH.

- Lead - Dissolution of lead is controlled by both L/S ratio and pH. The amount leached under initial pH conditions of 9 is greater by about a half than leaching with an initial pH of 4. The difference in leached quantities between 5:1 and 10:1 L/S ratios is similar.

- Thorium - The amounts leached are similar, except for the test carried out at a L/S ratio of 5:1 and pH 4 which is a factor of two greater.

- Uranium - The amount leached is greater at pH 4 than pH 9 for both L/S ratio tests.

- Zinc - The proportion of zinc released from each test is variable, between 0.69 and 2.0%.

5.4.3 Leaching Tests of Oxidised Tailings

The aim of this phase of the work was to determine the effect on leaching, if any, of the exposure of the tailings to an oxidising environment. This would simulate exposure of the tailings to the atmosphere, followed by contact with water as a result of rainfall or covering by fresh, wet tailings.

The leach rates for the oxidised tailings are shown in the following Figures, and are compared to the results for the previous leach test carried out on 'fresh' tailings and at the same L/S ratio and pH.

The detection limits for calcium and magnesium were 2.9×10^{-10} and 2.9×10^{-9} g m^{-2} respectively, well below the measured values. The detection limits for the other elements are represented in each of the figures by a broken line.

Redox Potential and pH

A comparison of changes in pH and redox potential (Eh) with time, between the fresh and oxidised tailings, are given in Figures 5.4.3.1 and 5.4.3.2. Initial pH is shown by the broken line.

The pH is generally similar for both leach tests. Redox potential, however, is generally lower, albeit only slightly, for the oxidised tailings.

Aluminium

The leach rates for aluminium are shown in Figure 5.4.3.3. They indicate that leaching of aluminium from the oxidised and fresh specimens is similar, excepting for the initial period of ten days where there appears to be a lower leach rate of aluminium from the oxidised tailings.

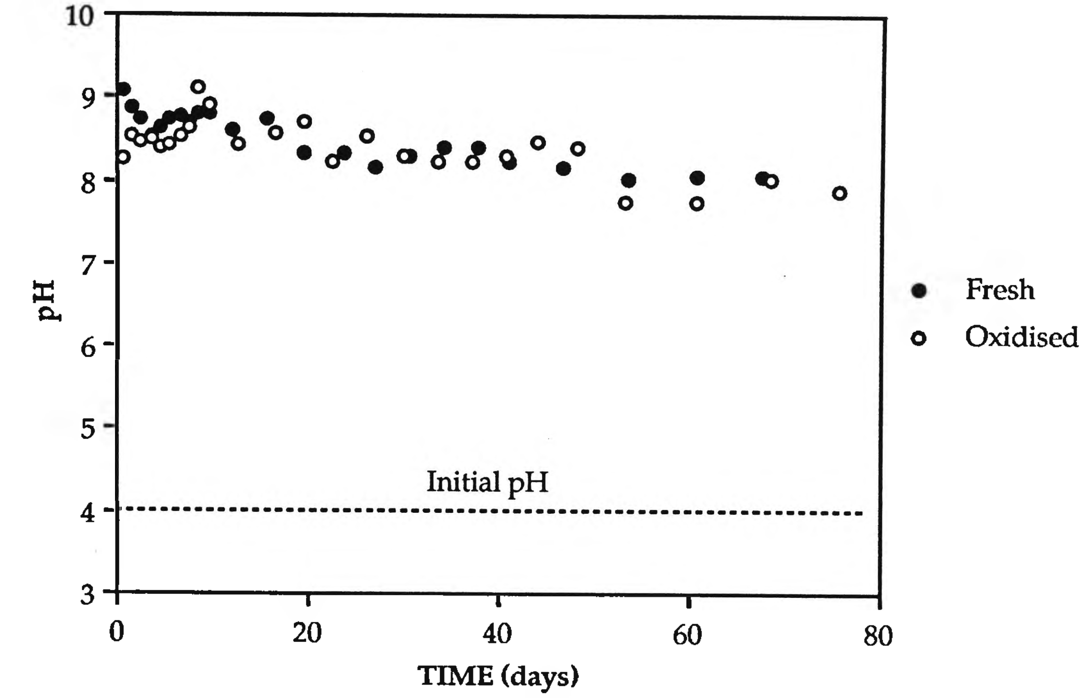

Figure 5.4.3.1: Comparison of pH in Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

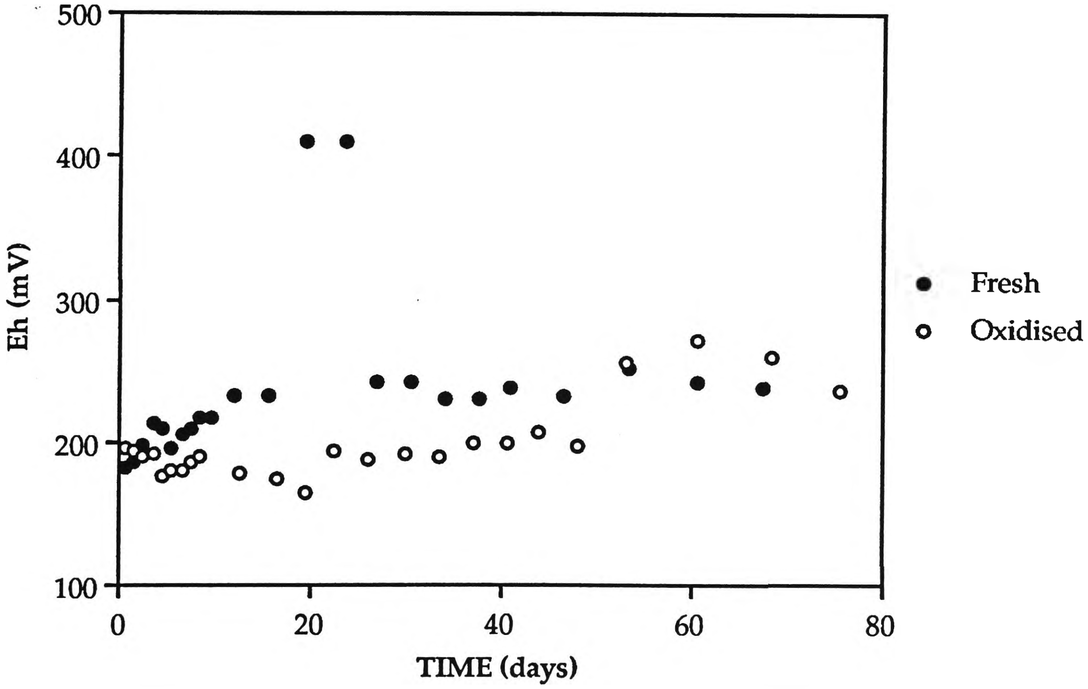

Figure 5.4.3.2: Comparison of Eh in Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

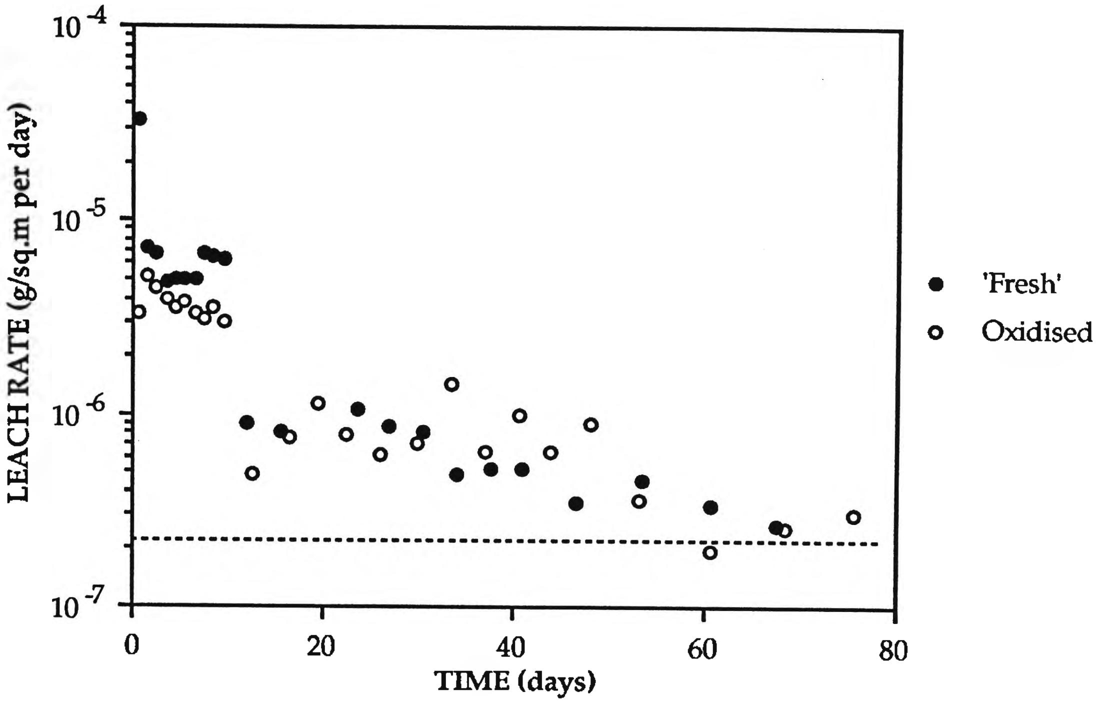

Figure 5.4.3.3: **Comparison of Al Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

Calcium

The leaching of calcium is shown in Figure 5.4.3.4. The leach rate for the fresh sample is generally slightly higher throughout leaching than that for the oxidised sample. The leach rate of the fresh sample is fairly constant for leaching times greater than 20 days at 7 x 10^{-5} g m^{-2} d^{-1}. The long-term leach rate for the oxidised sample is constant and about a factor of two to three lower than for the fresh sample.

Iron

Data for iron concentration for the oxidised specimen are few. However, Figure 5.4.3.5 shows that the leach rates measurable for iron in the oxidised specimen are similar to those for the 'fresh' sample.

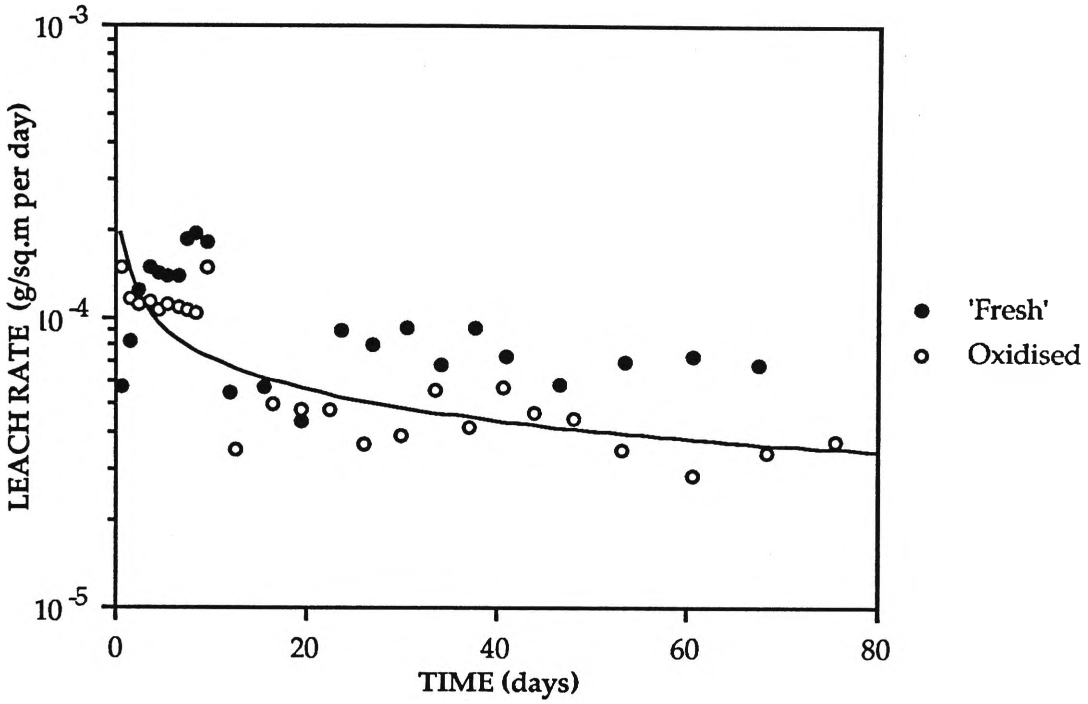

Figure 5.4.3.4: Comparison of Ca Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

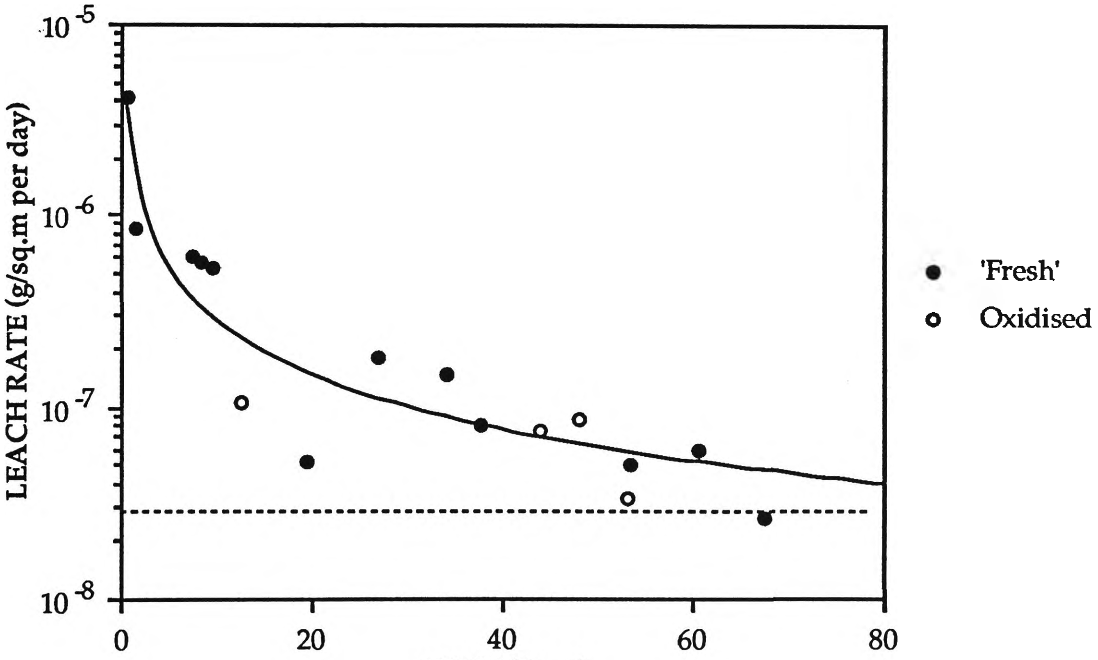

Figure 5.4.3.5: Comparison of Fe Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

Magnesium

The leaching pattern for magnesium is similar to that for calcium (see Figure 5.4.3.6), although there appears to be a greater reduction in releases of magnesium from the oxidised tailings. The rates for the oxidised specimen continues to decrease with time, whilst that for the fresh sample increases over the first ten days of leaching, then decreases by a factor of about six over the ensuing few days.

Excepting for the first two days of leaching, the leach rate for the oxidised sample is lower, sometimes by as much as a factor of eight, than that for the fresh specimen. After about 20 days, the leach rates for both specimens remain fairly constant, that for the fresh sample at 8×10^{-6} g m^{-2} d^{-1}, and that for the oxidised sample at 3×10^{-6} g m^{-2} d^{-1}.

Manganese

The leach rate of manganese is greater for the 'fresh' than the oxidised sample (see Figure 5.4.3.7) by a factor of between two and five. Leaching increases then decreases several times over the 80 day leach period. Despite the fluctuations in leach rate, the trend for both of the tailings samples is similar and can be paralleled with that for magnesium.

The leaching pattern is similar to that for calcium.

Arsenic

The leach rates for arsenic from the tailings are shown in Figure 5.4.3.8. The leach behaviour of both samples is similar but it appears that the oxidised sample has a consistently higher leach rate.

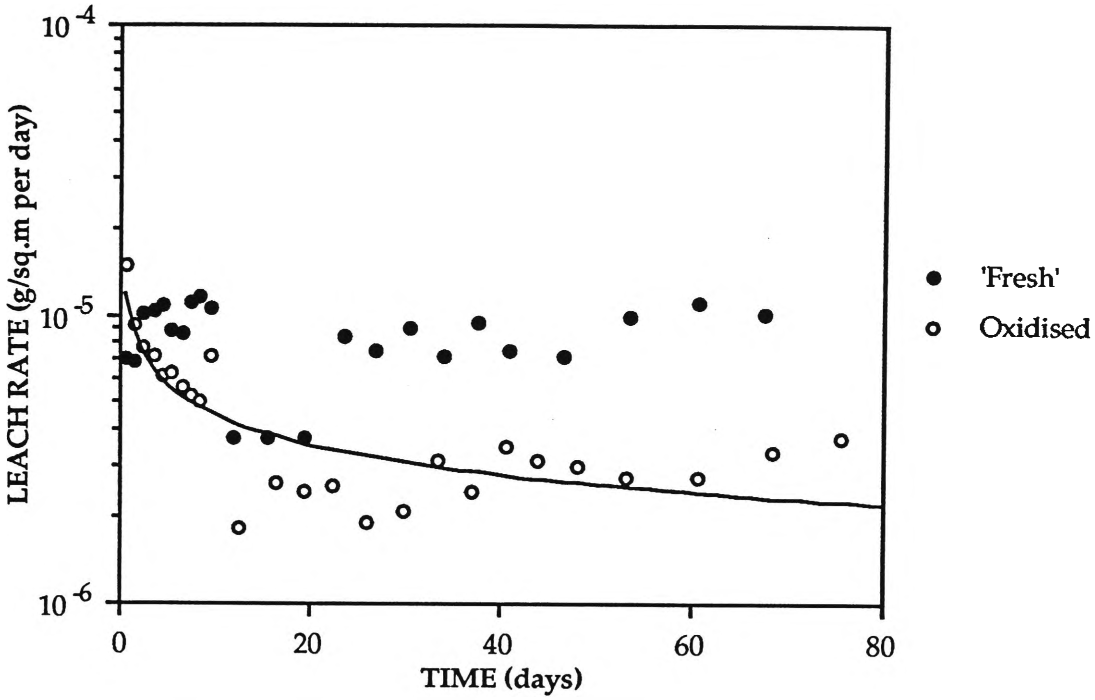

Figure 5.4.3.6: Comparison of Mg Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

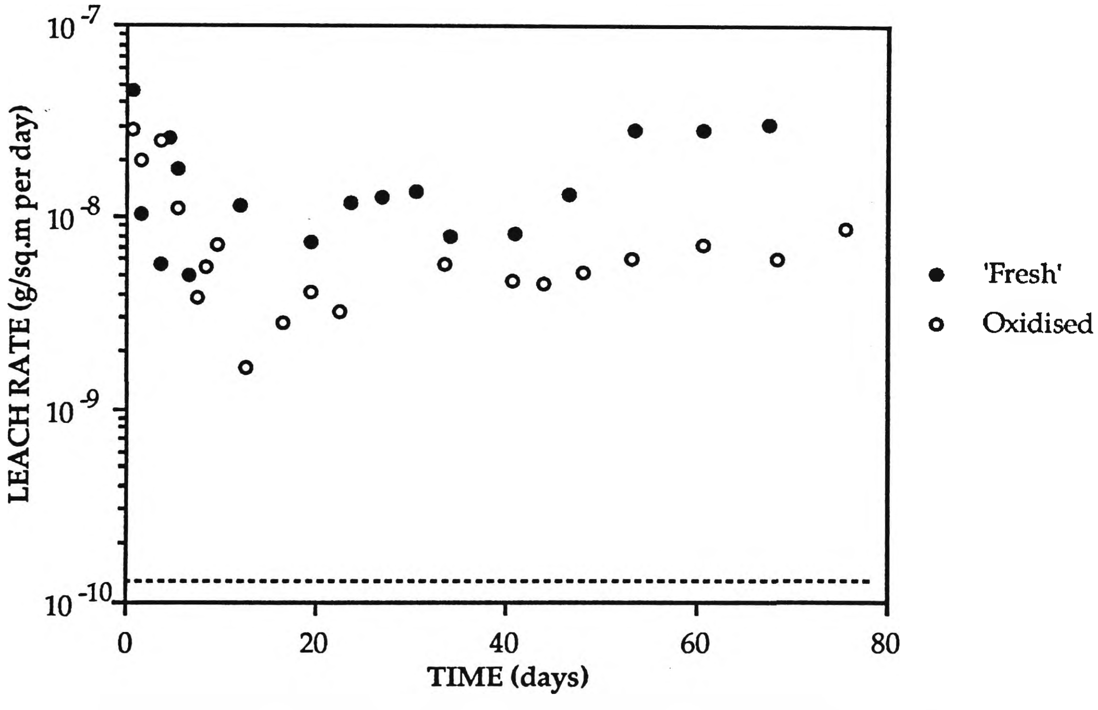

Figure 5.4.3.7: Comparison of Mn Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

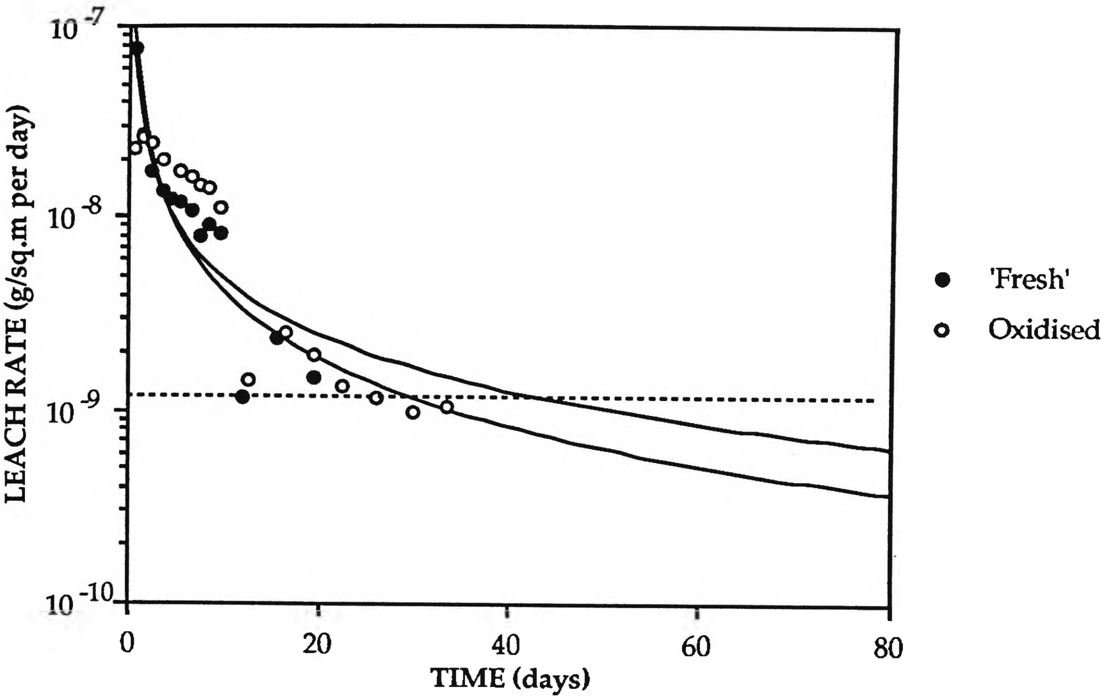

Figure 5.4.3.8: Comparison of As Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

Mercury

The leach rates for mercury are given in Figure 5.4.3.9. Generally, leach rates are only measurable during the early stages of leaching when mercury is leached out in detectable quantities. From the few data measured there is a significant increase in releases of mercury from the oxidised sample.

Lead

Lead concentrations from the leaching of the oxidised tailings were generally immeasurable and only two data points were obtained (see Figure 5.4.3.10).

Thorium

Figure 5.4.3.11 shows the leachability of thorium from the fresh and oxidised tailings. Generally, the oxidised sample gives a higher leach rate.

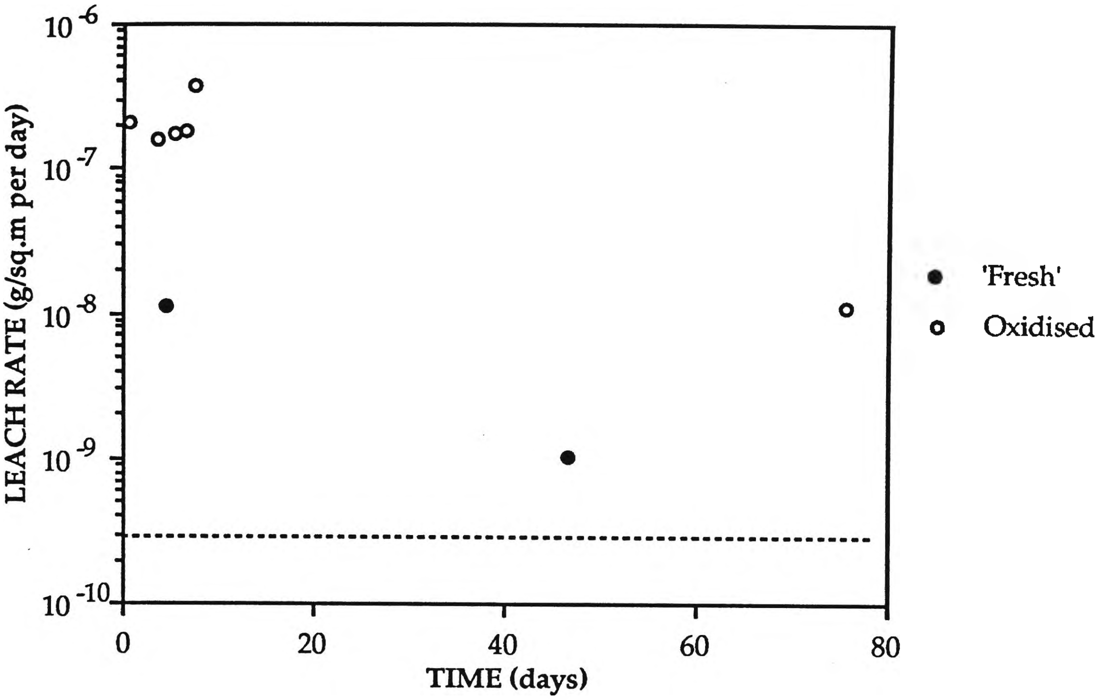

Figure 5.4.3.9: **Comparison of Hg Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

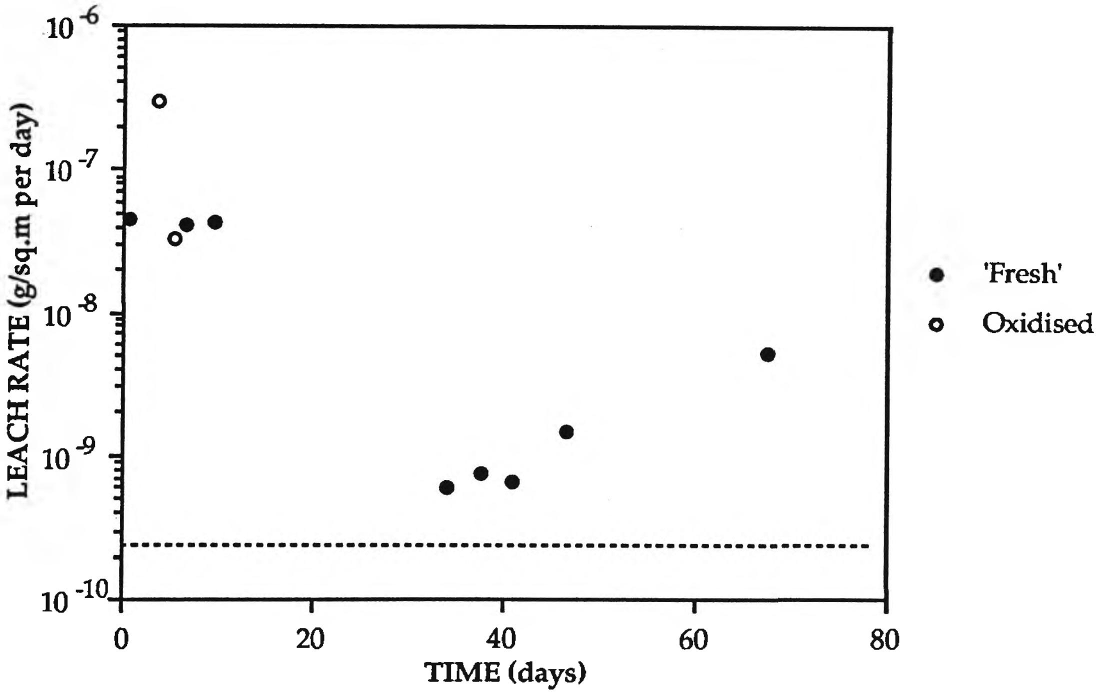

Figure 5.4.3.10: **Comparison of Pb Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

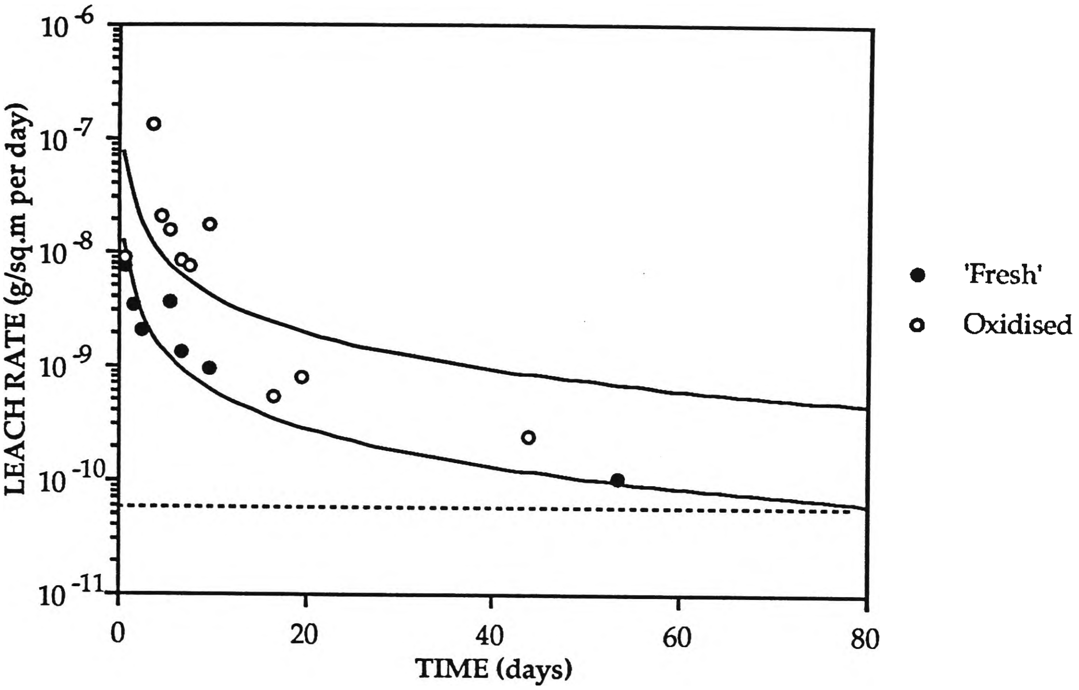

Figure 5.4.3.11: Comparison of Th Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temp.

Uranium

Leaching of uranium from the oxidised tailings and the fresh material are similar throughout the entire leach period (see Figure 5.4.3.12). After about 20 days the leach rate is generally constant at about 3 x 10^{-9} g m^{-2} d^{-1}.

Zinc

There appears to be little effect of oxidation on the leach rates of zinc from the tailings (see Figure 5.4.3.13).

Summary of Oxidation Leach Tests

There appears to be little effect of oxidation on the leaching behaviour of the elements, except for calcium, magnesium, aluminium and manganese, whose leach rates are lower from the oxidised tailings. This suggests that oxidation has caused a change in the mineralogical and/or surface properties of the tailings which has reduced the availability of these elements for leaching.

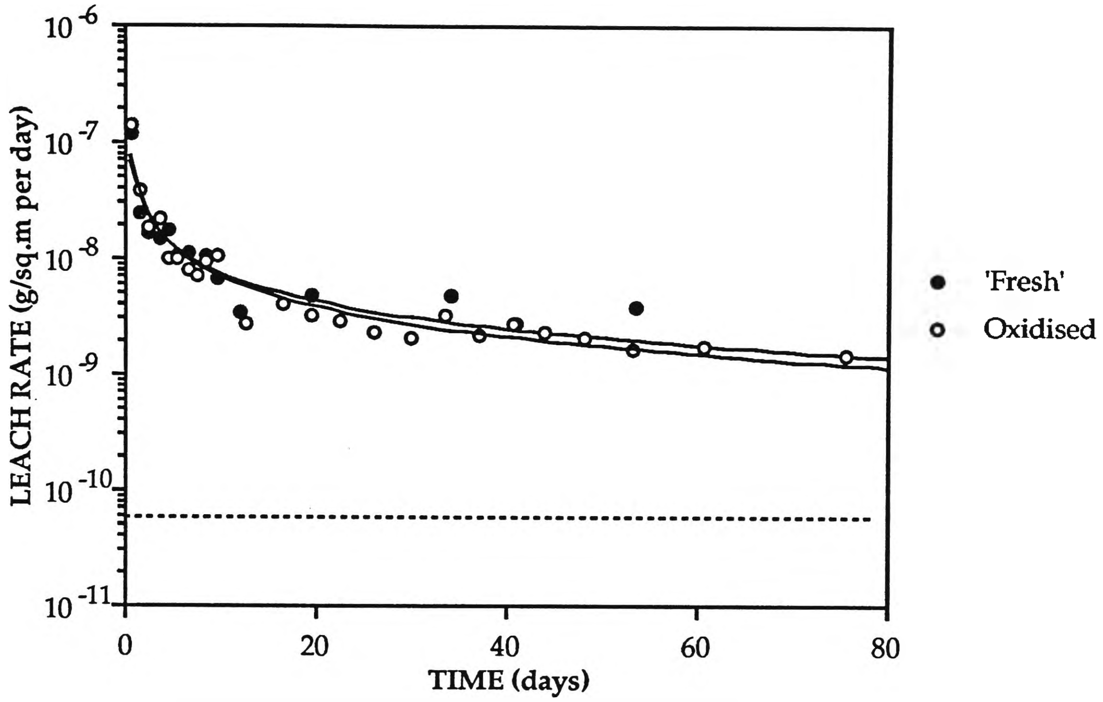

Figure 5.4.3.12: Comparison of U Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

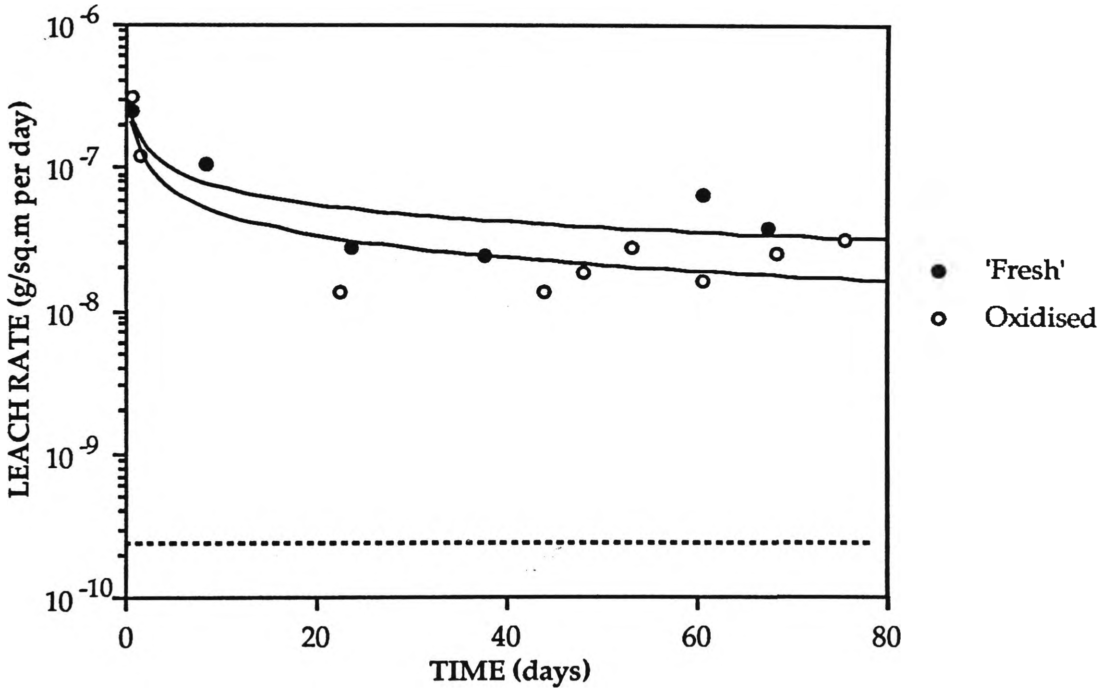

Figure 5.4.3.13: Comparison of Zn Leach Rates from Oxidised and Fresh Tailings - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

5.4.4 Effect of Leaching Time - 5 Minute to 32 Hour Leach Tests

This test was carried out to ascertain the kinetics of leaching during the first 32 hours. This work was prompted by the pH results of the previous leach tests, where pH was shown to increase from 4 to 9 in less than 24 hours, and was not originally considered in the experimental program. This extra phase of testing was considered necessary due to the importance of pH in leaching systems.

5.4.4.1 Change in pH and Eh with Time

It was clear from the beginning of the leach work carried out in this study that the pH of the leaching solution after 24 hours of leaching was approximately 9, regardless of the pH of the original leaching solution. To determine how quickly this pH was reached a series of leach tests was carried out using a geometric progression of time steps. Individual specimens were leached at a L/S ratio of 10:1 for 15 minutes, 30 minutes, one hour, two hours, four hours, eight hours, 16 hours and 32 hours. A test over 24 hours was also performed as a comparison with the first day's leaching of the previous leach tests. The results of change in pH with time are shown in Figure 5.4.4.1.1.

Even after only 15 minutes of leaching the pH was 9.35. The pH reaches a maximum of 9.41 after one hour of leaching. After 24 hours of leaching, the pH is 9.14, similar to those levels attained in the previous major phase of leach tests after one day of leaching.

The change in redox potential for the same periods are shown in Figure 5.4.4.1.2.

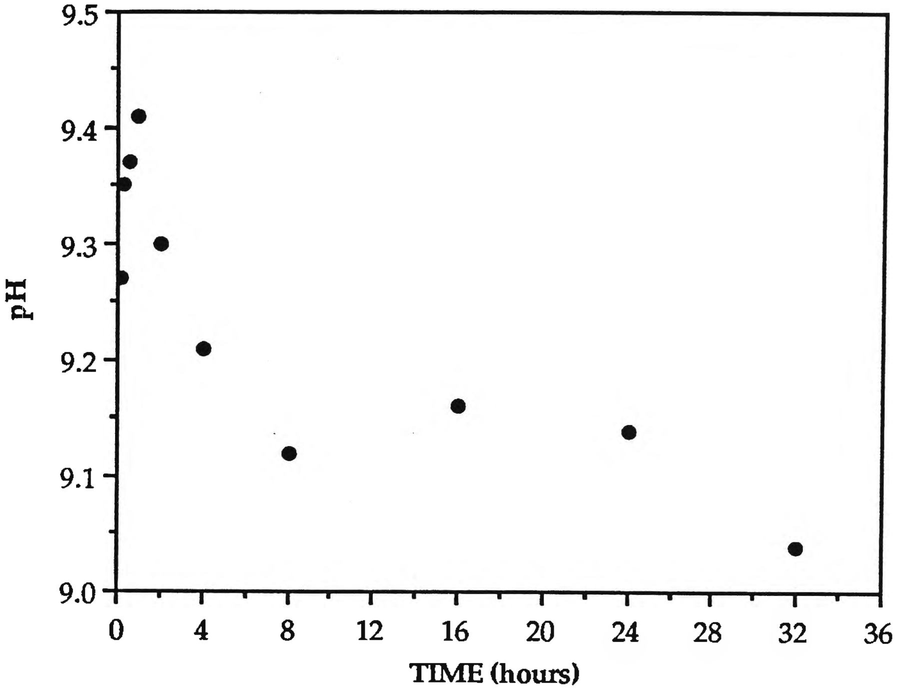

Figure 5.4.4.1.1: Leachate pH Over Different Leach Times - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

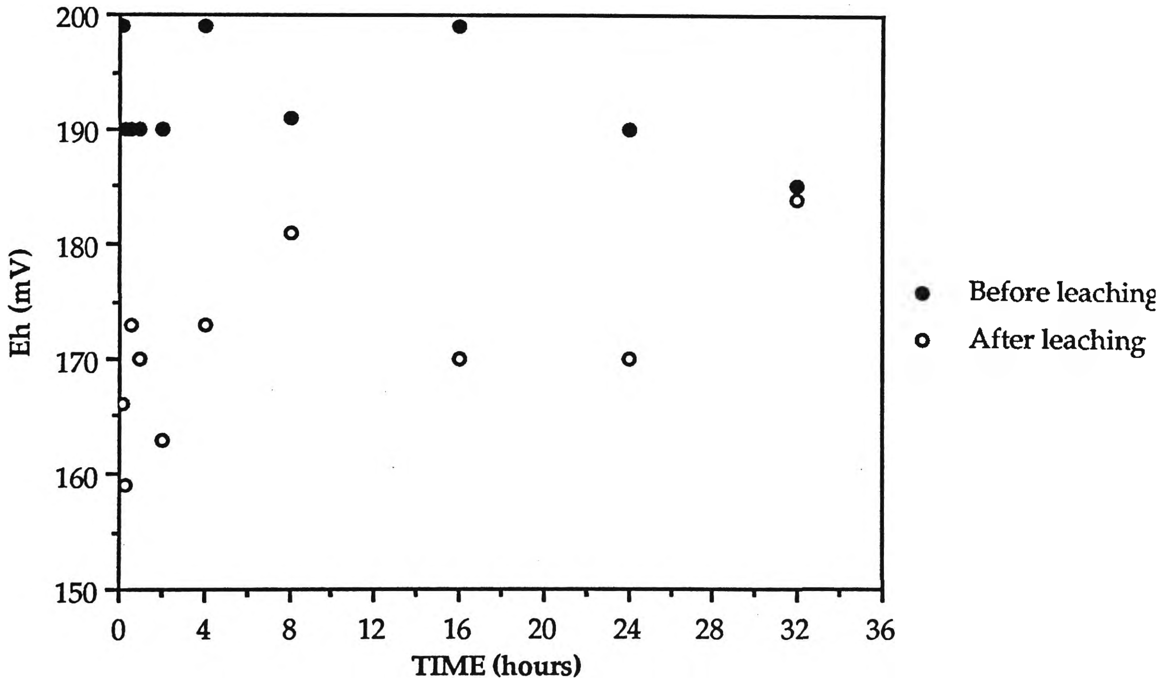

Figure 5.4.4.1.2: Change in Eh - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

Eh for each time period decreases with leaching in all cases. The Eh of the leachates reaches a minimum after 15 minutes of leaching and a maximum after eight hours of leaching. There is a slight variation in the Eh of the leaching solution so it is difficult to determine the effect of time on the leachate redox potential. Figure 5.4.4.1.3 shows the change in the redox potential, the difference between the starting Eh and the final Eh for each leach period.

The largest change in redox potential occurs during the first five minutes of leaching. The smallest change in redox potential occurs after 32 hours. The difference in Eh, however, is not a linear relationship.

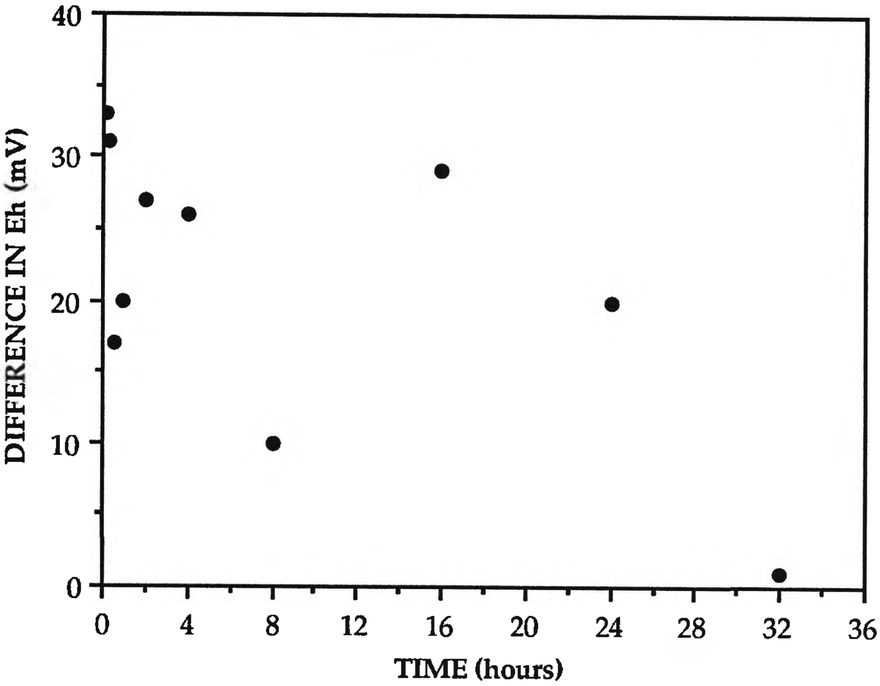

Figure 5.4.4.1.3: **Difference in Eh Between Initial Solution and Final Leachate - Initial pH 4, L/S Ratio 10:1 and Ambient Temperature**

5.4.4.2 Change in Leachate Composition with Time

Leachates from each of the kinetic tests were analysed in the usual manner. Aluminium, calcium and magnesium were analysed by ICP-OES, and the trace elements, due primarily to their extremely low concentrations, by ICP-MS. Limits of detection for all of the elements, calculated as mass leached per surface area, are given in Table 5.4.4.2.

TABLE 5.4.4.2: Detection Limits for All Elements in Terms of Mass Leached - 10:1 L/S Ratio, Initial pH 4

Element	Detection Limit (g m^{-2})
Aluminium	1.5×10^{-6}
Calcium	2.0×10^{-9}
Iron	2.0×10^{-7}
Magnesium	2.0×10^{-8}
Manganese	8.0×10^{-10}
Arsenic	8.0×10^{-9}
Chromium	4.0×10^{-10}
Copper	6.0×10^{-10}
Mercury	2.0×10^{-9}
Lead	9.9×10^{-10}
Thorium	4.0×10^{-10}
Uranium	4.0×10^{-10}
Zinc	1.6×10^{-9}

Aluminium, Calcium and Magnesium

Aluminium, calcium and magnesium were the elements with the highest concentrations in the leachates (see Figure 5.4.4.2.1).

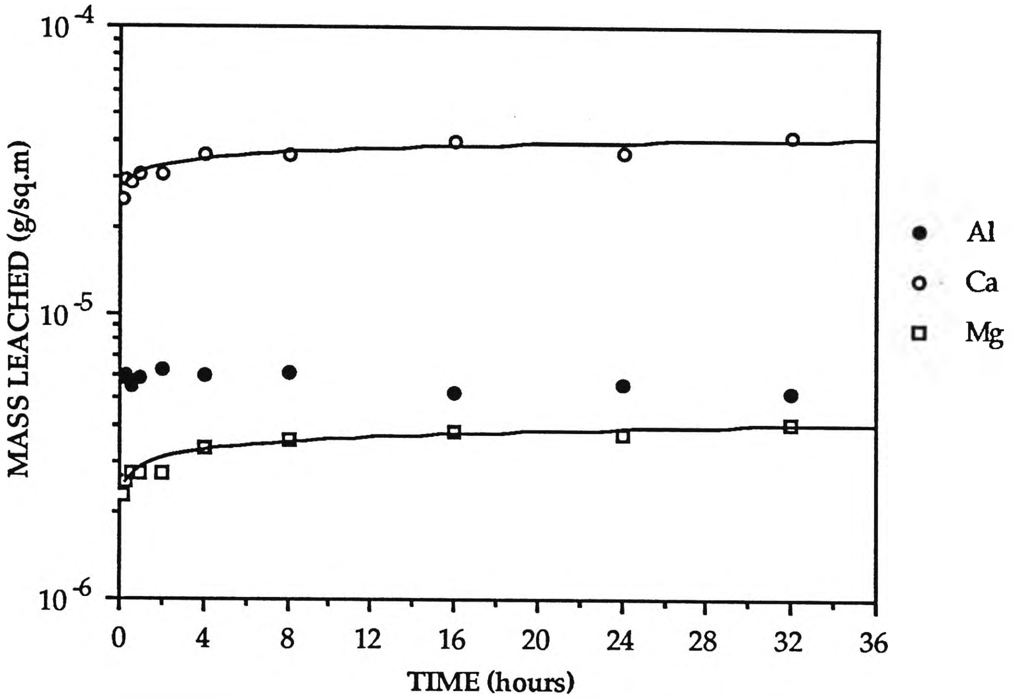

Figure 5.4.4.2.1: **Mass of Al, Ca and Mg Leached per Unit Surface Area of Tailings Over Various Leach Periods - Initial pH 4, Liquid to Solid Ratio 10:1 at Ambient Temperature**

The duration of leaching has little effect on the leachability of aluminium. The mass leached is approximately 6×10^{-6} g m^{-2}, regardless of the leaching time, suggesting that aluminium is quickly released from the solid surfaces.

For magnesium, the mass leached rises with an increase in leach period up to four hours, whereafter it remains constant at about 4×10^{-6} g m^{-2}. Similarly for calcium, where, for periods longer than two hours, the mass leached is essentially constant at about 4×10^{-5} g m^{-2}. This suggests that saturation of the leachates with respect to calcium and magnesium has occurred.

Trace Elements

The mass of manganese leached (see Figure 5.4.4.2.2) is ~ 4 x 10^{-8} g m^{-2} for the leach tests, although there is some scatter of data about this value.

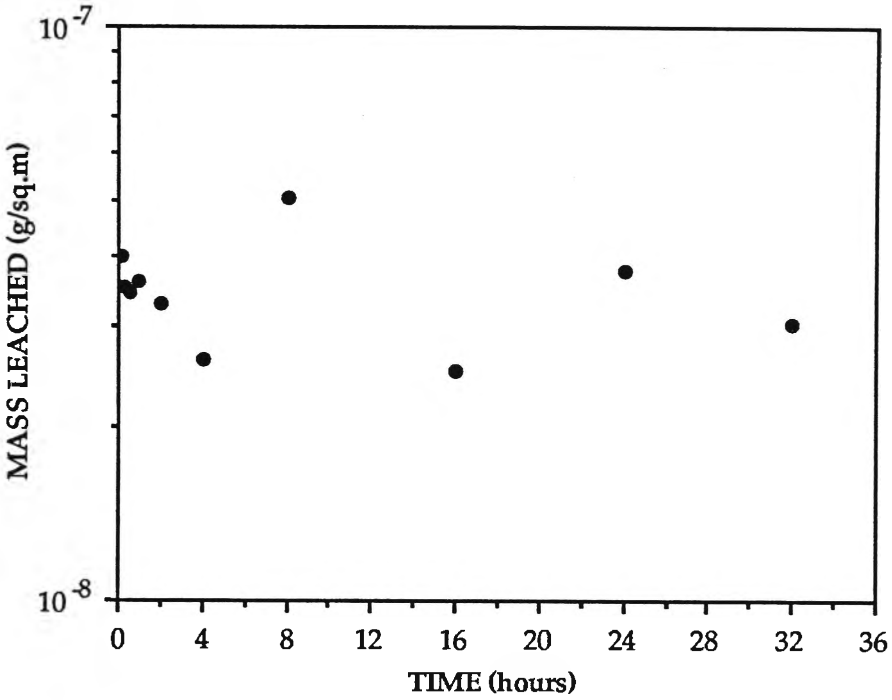

Figure 5.4.4.2.2: **Mass of Mn Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temp**

Arsenic concentration in the leachates increases with time up to 16 hours and thereafter remains constant (see Figure 5.4.4.2.3).

Chromium shows a similar relationship between leaching time and mass leached to that for arsenic (see Figure 5.4.4.2.4), mass leached increasing with increasing leaching time up to four hours, then remaining constant (at ~ 8 x 10^{-8} g m^{-2}).

The concentration of copper in the leachates is measurable in only five of the leach tests (see Figure 5.4.4.2.5). An approximate line of best fit for the data would be represented by a constant mass leached of ~ 1.5 x 10^{-7} g m^{-2}.

The mass of mercury leached (see Figure 5.4.4.2.6) is relatively constant in the tests, between 2 and 4 x 10^{-7} g m^{-2}.

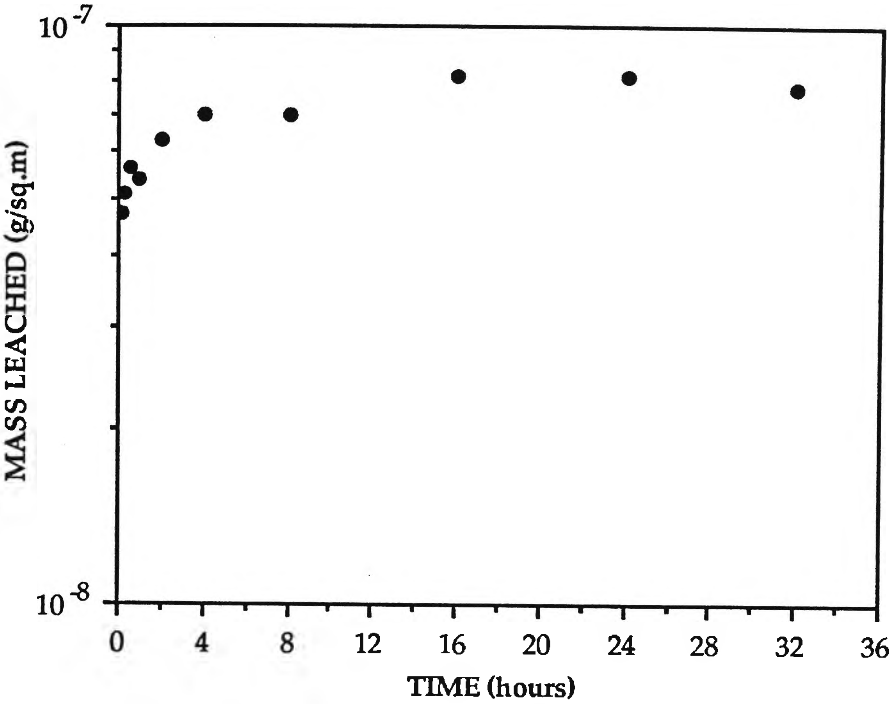

Figure 5.4.4.2.3: **Mass of As Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

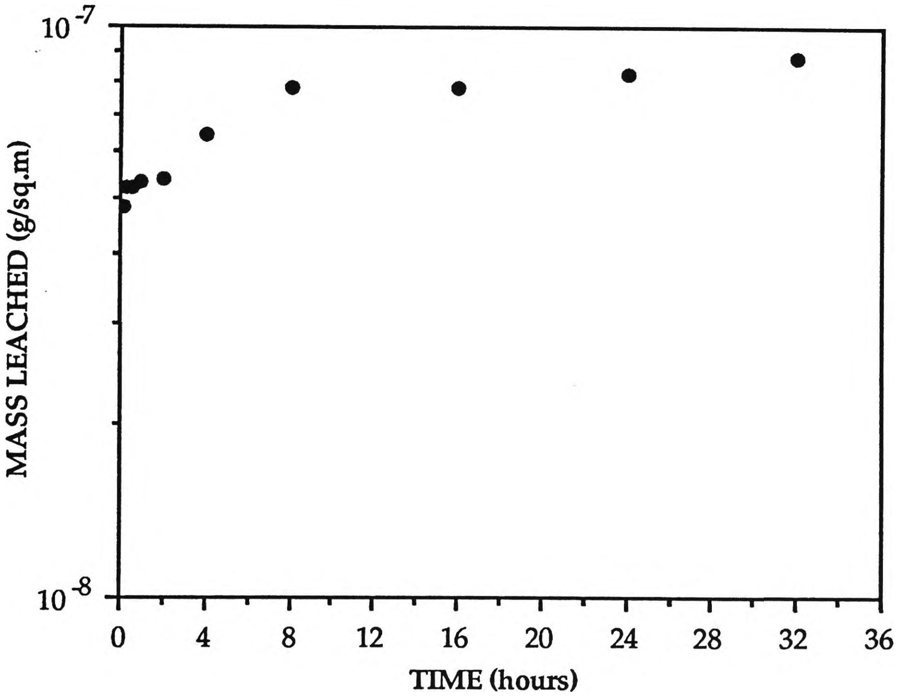

Figure 5.4.4.2.4: **Mass of Cr Leached from Tailings Over Various Leach Periods Initial pH 4, L/S Ratio 10:1 at Ambient Temperature**

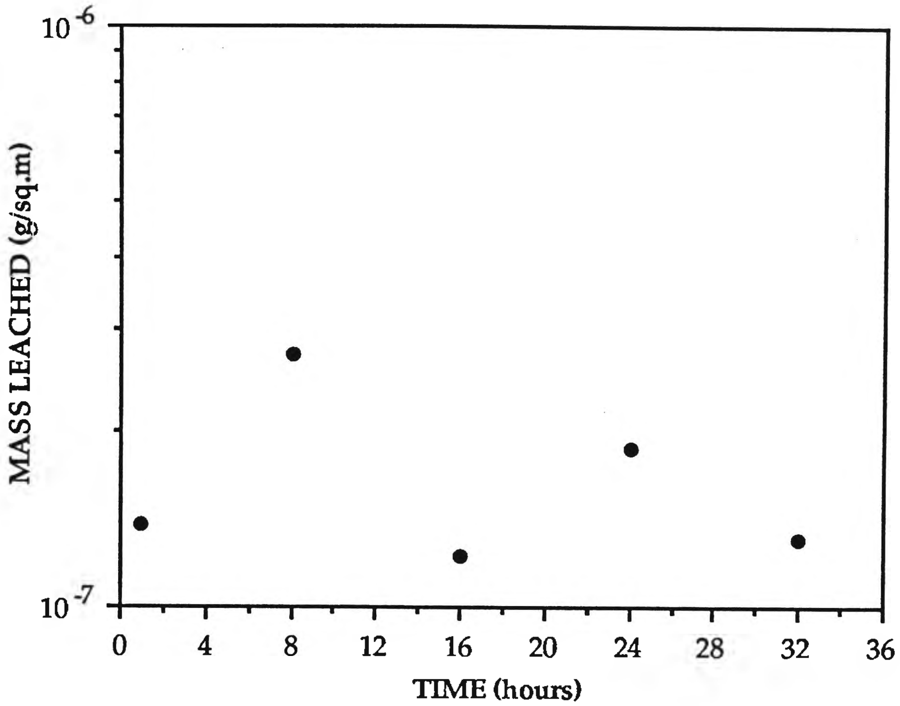

Figure 5.4.4.2.5: Mass of Cu Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

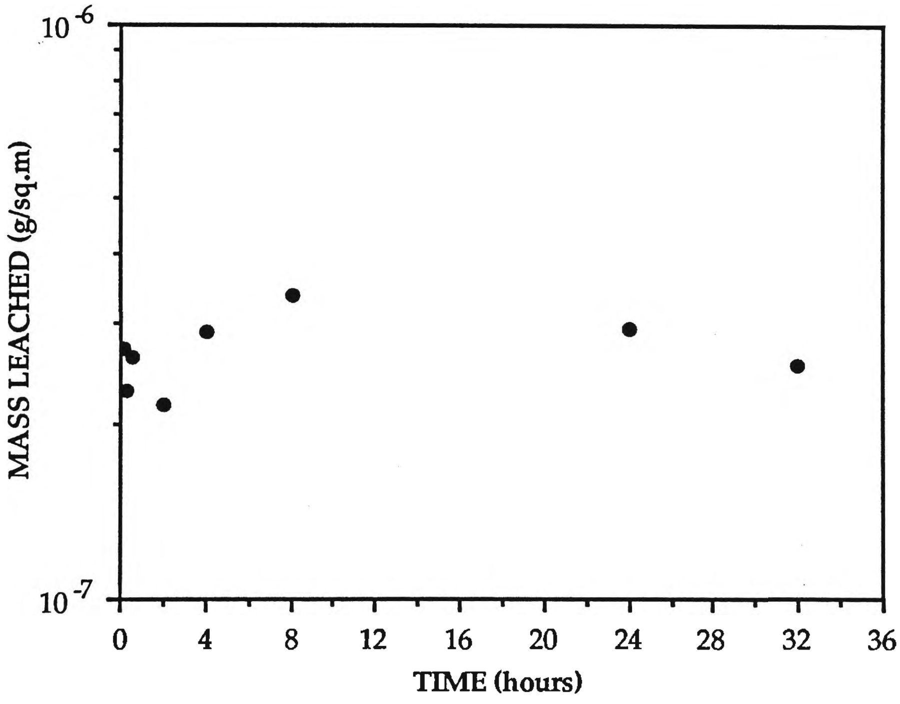

Figure 5.4.4.2.6: Mass of Hg Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

The leach data for lead are shown in Figure 5.4.4.2.7. Maximum mass is leached after eight hours of leaching.

Thorium levels in the leachates were generally not detectable.

The mass of uranium leached is similar for all leach periods at approximately 10^{-7} g m^{-2} (see Figure 5.4.4.2.8).

For zinc, the mass leached is between 1 and 3 x 10^{-7} g m^{-2} for each of the time periods except the 24 hour leach period, where it is 1 x 10^{-6} g m^{-2} (see Figure 5.4.4.2.9). There were no measurable levels of zinc for the eight and 32 hour leach periods.

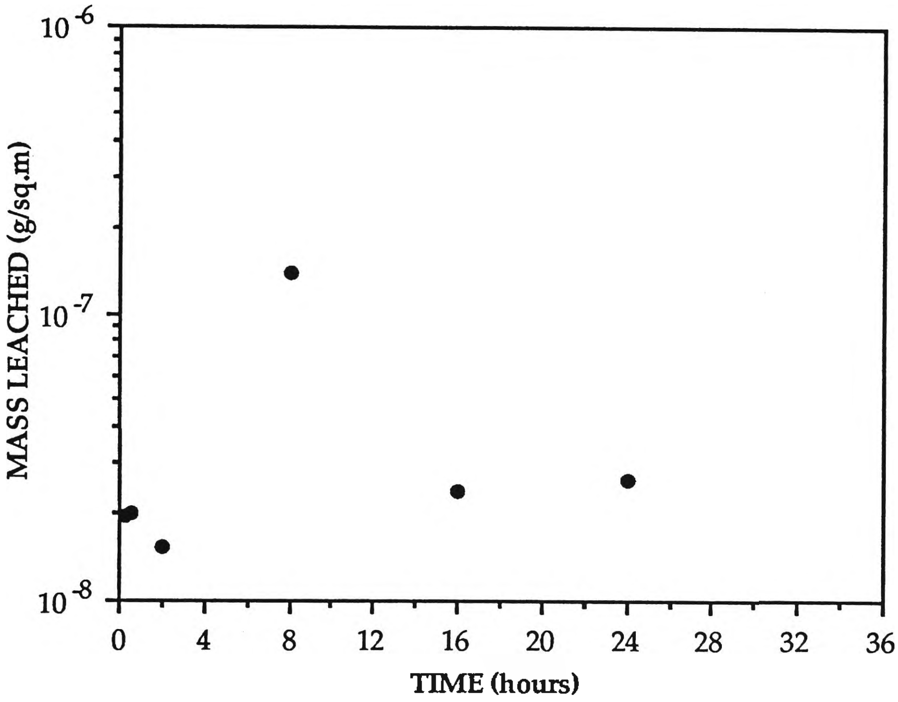

Figure 5.4.4.2.7: Mass of Pb Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

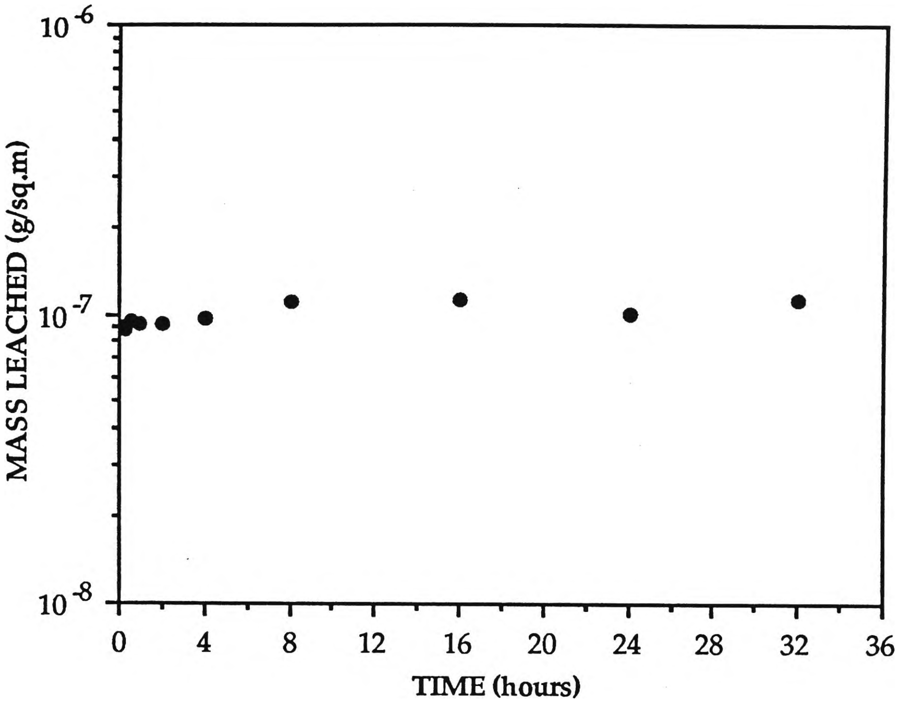

Figure 5.4.4.2.8: Mass of U Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

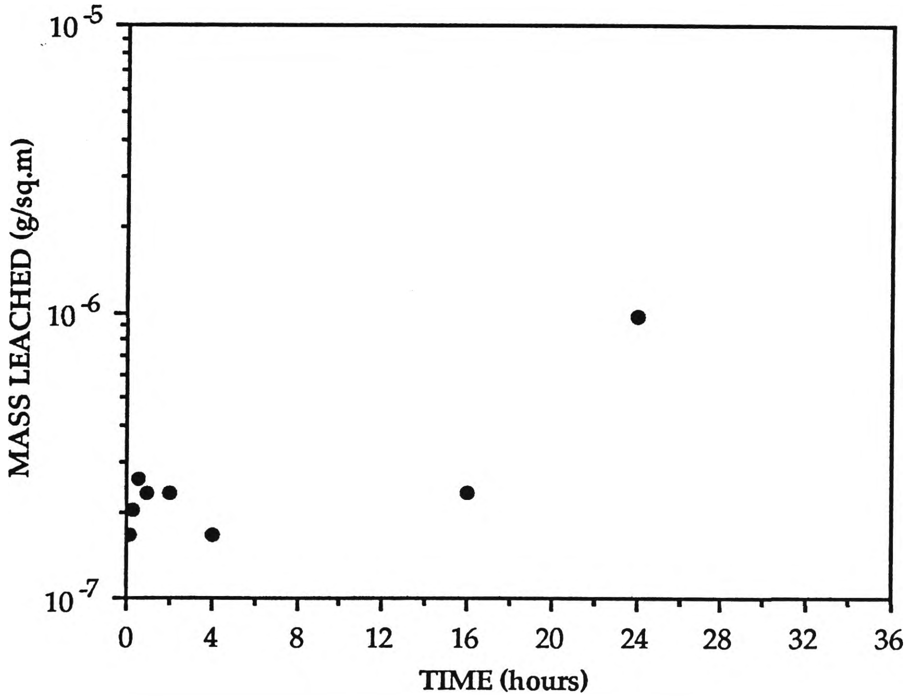

Figure 5.4.4.2.9: Mass of Zn Leached from Tailings Over Various Leach Periods - Initial pH 4, L/S Ratio 10:1 at Ambient Temperature

Summary of Kinetics Leach Tests

This series of leach tests was originally designed to determine the change in pH of the leachates with increasing leach time, from 5 minutes to 32 hours. A study of the leaching kinetics was included to see if there how leaching duration, over relatively short periods, affects the mass leached of the respective elements. The main findings were:

- Leachate pH increases from 4 to over 9 in only five minutes. The major control of pH appears to be the bicarbonate ion caused by the dissolution of calcite and the magnesium-bearing siderite.
- The change in redox potential for the tests ranges between 0 and 35 mV. There appears to be a correlation between pH and Eh.
- Mass leached of aluminium, calcium, magnesium, arsenic and chromium against time showed similar trends, increasing with increasing leaching time to about four hours, then remaining fairly constant for the longer leach periods. Calcium and magnesium are the major cations in solution and appear to control the solution chemistry.
- Mass of manganese, mercury, copper, uranium and zinc remained generally constant for all of the leach periods.
- Lead and thorium data were too few and widely scattered to draw any conclusions.
- Iron concentration in the leachates was measurable in only the 32 hour leach test.
- Cadmium levels were not detectable.

5.4.5 Geochemical Modelling

The conceptual geochemical model used in this work is equivalent to the dissolution of the minerals in unbuffered, aqueous solutions starting at pH 4 and pH 9, and initially containing the equivalent number of moles of minerals contained in the tailings, and leached with a proportional volume of solution. Data from two of the leach tests carried out were used in the model - the test carried out at pH 4 and a L/S ratio of 5:1, and the other at pH 9 and the same L/S ratio.

For the purpose of this study, the EQ3/6 model has been used to determine the predicted concentrations of the major elements in solution, and to compare them to those measured experimentally. Additionally, a comparison of measured and predicted pH has been made. Reaction time in the model has been set at one day to correspond with the first experimental 24 hour leach period. This was chosen for the following reasons:

- The leachates during experimentation were replaced completely with fresh solution on a regular basis. Complete replacement of leaching solution in this manner makes it difficult to simulate geochemical behaviour with EQ3/6 for more than one leaching period.

- It was possible to compare leach results from any of the first ten leach periods, all carried out over 24 hours, with the calculations determined by the model.

- It was clear from the rapid increase in pH during the 24 hour leach tests that there were significant reactions taking place to justify modelling of this period of leaching.

An EQ3NR run was initially made to establish the characteristics of the leaching solution and to allow the output from this run to be used as part of the input for the kinetics modelling. All the elements associated with the main minerals in the tailings were introduced in this run, namely calcium, magnesium, iron and aluminium.

The magnesium-bearing siderite mineral determined by SEM is not identified in the literature, and there is no thermodynamic database available for it. Consequently, to simulate the role of magnesium in the leaching system, magnesite was substituted in the model, proportional to the elemental magnesium concentration in the tailings.

More than fifty EQ6 kinetic runs were carried out to determine the effects of different dissolution constants, surface areas, initial pH, and suppression of certain mineral phases on modelling. Table 5.4.5.1 gives the dissolution rates, surface areas and moles of the respective minerals used in one of the first EQ6 runs. The dissolution rates are those given previously in Chapter 4, obtained from the studies of other workers. The surface areas and amount of minerals were calculated from sizing data and elemental analysis of the tailings.

TABLE 5.4.5.1: Input Data Used in EQ6 to Model Dissolution of Tailings Comprising Calcite, Siderite, Magnesite and Kaolinite

	Dissolution Rate (mol cm^{-2} s^{-1})	Surface Area (cm^2)	Moles (x 10^{-3})
Calcite	4×10^{-10}	31175	3.50
Siderite	1×10^{-8}	54525	7.74
Magnesite	1×10^{-8}	10775	1.58
Kaolinite	3×10^{-19}	279950	23.4

Table 5.4.5.2 compares the modelled and measured concentrations of aluminium, calcium, magnesium and iron in the leachates after 24 hours of leaching. The measured values represent the range of concentrations determined in the leachates for the first ten 24 hour leach periods. The pHs after leaching, measured and calculated, are shown in Table 5.4.5.3.

The results show that the model has predicted well the likely pH of tailings leached under the conditions prescribed. The model also shows reasonable agreement with the measurements made in the experimental work for calcium and magnesium.

TABLE 5.4.5.2: Comparison of Modelled and Measured Concentrations of Calcium, Iron, Magnesium and Aluminium After Leaching for 24 Hours

	Initial pH 4		Initial pH 9	
	Calculated Concentration (ppm)	Range of Measured Concentrations (ppm)	Calculated Concentration (ppm)	Range of Measured Concentrations (ppm)
Calcium	21.9	1.99 - 10.75	19.0	1.84 - 7.72
Iron	4.6×10^{-8}	0.010 - 0.217	4.6×10^{-8}	0.014 - 0.162
Magnesium	0.861	0.250 - 0.856	0.745	0.224 - 0.652
Aluminium	4.4×10^{-4}	0.075 - 0.698	3.9×10^{-4}	0.170 - 0.568

TABLE 5.4.5.3: Comparison of Modelled and Measured pHs After Leaching for 24 Hours

Initial Solution pH 4		Initial Solution pH 9	
Final pH - Calculated	Final pH Range-Measured	Final pH - Calculated	Final pH Range-Measured
8.26	8.50 - 9.09	8.29	8.70 - 9.20

The calculated results for iron and aluminium concentrations, however, are much smaller than those measured experimentally; iron by seven orders of magnitude, and aluminium about three orders of magnitude.

The simulation of the leaching of a coarser reject material from the washery was carried out using calcite and magnesite only as input parameters, as calcium and magnesium were modelled successfully by the code.

A comparison between the calculated concentrations for calcium and magnesium, and the pH, for the fines and coarser material, are given in Table 5.4.5.4.

TABLE 5.4.5.4: Comparison of Calculated Calcium and Magnesium Concentrations and pH for Simulated Leaching of Fines and Mid-sized Washery Waste

	Initial pH 4		Initial pH 9	
	< 0.5mm	0.5-12.7mm	< 0.5mm	0.5-12.7mm
Final pH	8.26	8.29	8.29	8.35
Calcium (ppm)	21.9	1.0	19.0	0.6
Magnesium (ppm)	0.9	14.4	0.75	13.9

The increase in particle size has not affected the pH of the solutions significantly, however the calcium and magnesium concentrations have changed. After one day of leaching, the calcium concentration has decreased by a factor of between 20 and 30, regardless of initial pH. Magnesium, on the other hand, increases by a similar magnitude for both simulations.

5.4.5 Kinetics of Leaching

Comparative solubilities of the main minerals in the tailings are given in Table 5.4.5.1. Of course, solubility measures how much of a substance will dissolve in a given quantity of solution. The dissolution rate determines how quickly a material will dissolve. These rates are also given in the table for the respective minerals. Magnesite has been included in the comparison as its dissolution rate was used in the geochemical modelling phase of this study.

Although there is a tendency for minerals that have high solubilities to have fast dissolution rates, this is not always the case. It does hold however for the minerals studied in this work.

TABLE 5.4.5.1: Comparison of Solubility Constants and Dissolution Rates for Calcite, Siderite, Magnesite and Kaolinite[4]

Mineral	Solubility Constant (g/100cc)	Dissolution Rate (mol cm^{-2} s^{-1})
Calcite	1.4×10^{-3}	$\sim 4 \times 10^{-10}$
Siderite	6.7×10^{-3}	$\sim 1 \times 10^{-8}$
Magnesite	10.6×10^{-3}	$\sim 1 \times 10^{-8}$
Kaolinite	0.52×10^{-3}	$\sim 3 \times 10^{-19}$

The relative solubilities generally correspond with the dissolution rates, solubilities and rates decreasing in the order:

magnesite > siderite > calcite > kaolinite

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[4] Kaolinite solubility was calculated from experimental data of Stumm and Morgan (1981). Calcite, magnesite and siderite solubilities were derived from Weast's CRC Handbook (1981). The dissolution rate of calcite is from Plummer *et al* (1978); that for magnesite from Walter and Morse (1985); for kaolinite from Carroll and Walther (1990); and for siderite from Dresel (1989). Rates were estimated from graphical information and are therefore approximate for the conditions under which the current experiments were carried out.

CHAPTER 6

DISCUSSION

A description of the mineralogy and leaching characteristics of the tailings studied in this work has been possible using the BEOP-31 standard to generate leachates, SEM and XRD for physical and chemical analysis, and ICP and γ-spectroscopy for chemical and radionuclide analysis. The following discussion focuses on the main findings of this work in terms of mineralogy, leaching behaviour and assessment of environmental impact, and outlines several ways in which results from dissolution tests may be extrapolated to depict what would occur in field situations.

6.1 Mineralogy and Dissolution Behaviour

The tailings consists basically of clays (predominantly kaolinite), carbonates and quartz. Calcite and siderite, including a magnesium-bearing siderite, were the most abundant carbonates.

The leach results from this work allow the following observations on the interaction of the tailings and water to be made:

- There is rapid dissolution of calcium and magnesium, primarily from calcite and magnesium-bearing siderite.

- The solution rapidly becomes saturated in calcium and magnesium, and until there is replacement of the leachate, there appears to be no further dissolution of calcite and magnesium-bearing siderite.

- Iron and aluminium are slowly released, and are present at very low levels, suggesting that siderite and kaolinite have low solubilities and/or the kinetics of dissolution are slow.

- With the exception of manganese, the trace elements are generally released at very low rates throughout the leaching time.

The high calcium leach rates suggest that calcite is the most readily leached mineral in the tailings. The high releases of this element will ensure that alkaline conditions will prevail in the tailings impoundments, effectively controlling the release of heavy metals into solution. Garrels and Christ (1965) found that at atmospheric conditions, viz. 25°C and a partial pressure of CO_2 of $10^{-3.5}$, that the pH of an aqueous system where calcite was in excess was 8.4 and that the molality of Ca^{2+} was about 4×10^{-4}. (Further reference is made by Garrels and Christ (1965) to the experimental work of Garrels *et al* (1960) which they believed showed excellent correspondence between their calculated pH and the observed pH for water in equilibrium with calcite and the atmosphere.) This compares well with the results of this work for all tests, where pH averaged about 8.6 and the molality of Ca^{2+} in the leachates was about 2×10^{-4} during the first ten days of leaching.

The release rates for iron in the leach tests are contrary to the known dissolution behaviour of siderite[1]. There are several possible reasons for this discrepancy, as discussed below.

Under atmospheric conditions siderite is not an equilibrium species (Garrels and Christ, 1965), and readily reacts under oxidising conditions according to the following reaction:

$$3FeCO_3 + 4H_2O = Fe_3O_4 + 3HCO_3^- + 5H^+ + 2e$$

Under these conditions, iron readily forms other relatively stable phases such as Fe-hydroxides (*pers comm* Glassley, 1992), although their exact identity in this case is not known. These iron phases probably form in situ, and as they are not very soluble, there is very little iron in solution under

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[1] From the literature, siderite is the most soluble of the primary minerals in the tailings (see Table 5.4.5.1, Chapter 5).

the conditions of the leach tests in this study. SEM analysis indicated some small areas of iron enrichment, suggesting that some iron has precipitated from solution.

Siderites are rarely pure; they often containing considerable amounts of calcium and magnesium, which are usually present in solid solution, and this can influence their solubility (Reeder, 1983). This may explain the greater solubility of the magnesium-bearing siderite, already discussed in Chapter 5. SEM examination showed that the magnesium component of siderite (magnesite) had undergone more severe attack during leaching, consistent with it being a more soluble phase.

The low dissolution rate of kaolinite is reflected in the leach rates obtained for aluminium. Over longer leach periods aluminium leach rates are several orders of magnitude lower than those for calcium and magnesium, despite aluminium having a much greater concentration in the solids. The concentration of aluminium was lower than calcium and magnesium by factors of 5 and 16 respectively.

The extremely low leach rates of the heavy metals generally reflect their low concentrations in the tailings. Apart from manganese, and occasionally chromium, heavy metals were generally not detectable in the tailings, so mineralic affinity is uncertain. The similarity between the leach trends for most of the heavy metals with those for aluminium suggest that they may be associated with the clays in the tailings. The prevalence of clays in the tailings provides silicate lattices in which heavy metals may be incorporated (Reeder, 1983).

Manganese leach rates parallel those for magnesium, and in combination with the results of SEM analysis, this suggests an association with the magnesium-bearing siderite. The proportion of manganese leached, however, was a factor of between 14 and 32 less than that for magnesium.

This suggests that manganese is associated with other minerals in the tailings in addition to siderite.

The relationship between pH and the leaching of the heavy metals over short times was measured in the 5 minutes to 32 hour leach tests. After eight hours of leaching, the second lowest pH (9.12) of the leach tests was recorded. This low leachate pH corresponded to the highest levels of copper, mercury, manganese, lead and thorium in solution. The leaching behaviour of zinc was different from the other metals in that zinc concentrations were highest at the most alkaline pHs. These results suggest that pH, even over relatively short periods of time, is important in controlling the release of most of the heavy metals from the tailings.

The oxidation leach tests showed that oxidation of the tailings had little impact on the leaching characteristics of the heavy metals, but it did suppress the leachability of calcium and magnesium, and, to a lesser degree, that of aluminium and manganese. Despite the differences in calcium and magnesium concentrations in the leachates, changes in pH with time were not significantly different between the respective tests. Redox potentials measured were different, slightly lower in the oxidised test. A possible explanation for these observations is that there may be two sources of calcium and magnesium in the fresh material, such as the carbonates and the clays. Upon heating, and subsequent oxidation, one, or both, of these phases becomes less soluble, possibly due to the irreversible partial collapse of the clay, and the overall solubility may be decreased (*pers comm* Glassley, 1992).

The results of the oxidation tests show that, even after some time exposed to the atmosphere and undergoing oxidation, leaching behaviour of the tailings is effectively the same. In particular, pH and the levels of heavy metals released do not change significantly. This is important for tailings impoundments, where tailings are often exposed to alternating dry and wet conditions, as it shows that these processes should not increase the leachability of the tailings.

6.2 Environmental Aspects

Leaching of trace elements from the tailings has been a feature of this work, and the levels released during testing are discussed and compared to criteria set by NSW State Government environmental regulatory authorities below. Also, the significance of oxidation of the tailings on the release of heavy metals is discussed.

When levels of heavy metals are sufficiently high they become potentially toxic. Under these conditions if the element is absorbed by a living organism at abnormally high concentrations, it may cause structural damage or enter cells and inhibit enzyme activities to such an extent that normal cell functioning is impaired (Purves, 1977). However, the specific toxicity of a trace element may vary widely for different species of organisms and for different groundwater chemistries.

Because base-level data and specific information covering all the major interactive and long-term health-related effectives of heavy metals have yet to be fully established and documented, specification of acceptable levels can only be made in terms of 'recommended' tolerance levels (Yong, 1988). It is for this reason that regulations set for water criteria by Government Authorities must be used pragmatically. The NSW State Pollution Control Commission (SPCC) acknowledges in its discussion paper on water criteria for aquatic ecosystems[2] (1991) that much of the information upon which their criteria are established are based on overseas studies because very little work has been carried out in Australia on toxicity of heavy metals on the various indigenous plant and animal species. For this reason comparisons

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[2] Criteria for aquatic ecosystems have been used for comparison in this work as the leachates from the tailings at mine site are most likely to affect this classification of environment.

of releases of heavy metals measured in this work are made with criteria set for potable water.

The leaching of material such as coal tailings can affect the environment through the dispersal of individual elements, particularly heavy metals. The levels of heavy metals released from the tailings in this work, however, have been shown to be not significant. For example, the leaching of mercury and cadmium, considered by Purves (1977) to be two of the most potentially toxic heavy metals, are generally below detection limits of the analytical instruments, and certainly well below the criteria set by the SPCC (1991) for potable water. Table 6.2.1 compares the concentrations of the heavy metals in the leachates generated from this study with those recommended by the SPCC.

Manganese levels in the two tests carried out at a L/S ratio of 5:1 are the only results which exceed the recommended limits. However, this is not considered to be important as:

- the levels do not exceed the limits by a large factor,
- manganese is considered by the SPCC to be a low hazard, in comparison to the other heavy metals,
- the leach tests determine the maximum leachability of the tailings, so the amount of heavy metals leached has been over-estimated, and
- any effluent discharge from the West Cliff mine site that would enter natural waterways would be diluted to beneath threshold levels.

The pH of the leachates generated from this study agree well with those regularly measured for the settling pond at West Cliff (typically 8.3 to 8.9), which captures effluent from the waste stockpile area. Overflow from the pond would not affect that of the nearby Brennan's Creek as the pH of the creek measured upstream is typically 8.7 (*pers comm* Cooney, 1992).

TABLE 6.2.1: Comparison of Heavy Metal Concentrations in Leachates With Those Given in the Water Quality Criteria for New South Wales - SPCC Discussion Paper (1991)

Element	Concentration in Leachates (mg/L)				SPCC Criterion (mg/L)
	5:1; pH 4	5:1; pH 9	10:1; pH 4	10:1; pH 9	
As	0.0006	0.0009	0.0005	0.0006	0.05
Cd	0.0008	0.0008	0.0008	0.001	0.005
Cr	0.0009	0.001	0.0007	0.0005	0.05
Cu	0.004	0.003	0.0008	0.002	1.0
Fe	0.05	0.02	0.02	0.03	0.3
Hg	0.000014	0.000096	0.000040	0.00012	0.00014
Mn	0.02	0.02	0.005	0.006	0.01
Pb	0.0006	0.001	0.0005	0.0006	0.05
U	0.002	0.001	0.004	0.0006	0.02
Zn	0.01	0.004	0.003	0.006	5

6.3 Extrapolation of Dissolution Experiment Results to Field Situations

It is extremely difficult to carry out enough laboratory work to allow an exact description of how any waste will perform under in situ conditions over very long periods of time. Consequently, a number of approaches have been developed to allow extrapolation of laboratory data to field conditions; some are simple, like the BEOP-31 standard; others, like reaction path modelling, are complex and require access to extensive computing facilities. The success with which each can be applied will be considered here, based on the experimental results of this work.

6.3.1 Mass Percentage Leached as a Function of Cumulative L/S Ratio

The BEOP-31 standard extrapolates the cumulative leaching results of a series of individual 5:1 L/S ratio leach tests to predict the results for a single test carried out at an equivalent, cumulative L/S ratio. This approach assumes that the same leaching mechanism will control releases at L/S ratios of 5:1 and for higher ratios. In this work there is strong evidence to suggest that the solutions at L/S ratios of 5:1 and 10:1 were saturated in calcium and magnesium. Furthermore, it is likely that saturation of the solutions with these elements controls the dissolution of the minerals containing calcium and magnesium. So the assumption that the summation of releases in each test to obtain calcium and magnesium releases at higher L/S ratios would be incorrect in this case, as at the higher L/S ratio solubility limits would not necessarily control dissolution to the same extent and much higher releases could occur. Representing the results in terms of mass percentage leached against L/S ratio therefore presents problems with saturated systems and extrapolation to a field situation is therefore not reasonable under these conditions.

To apply the BEOP-31 procedure to a wide range of field situations for waste dumping it is obvious that care must be taken to ascertain the mechanisms of leaching. The extrapolation technique suggested by the standard can only be applied to systems which can be shown to be unaffected by the L/S ratio. Otherwise, the leaching tests must be carried out over the range of L/S ratios expected to be encountered in the field.

6.3.2 Geochemical Modelling

The EQ3/6 geochemical model confirmed the experimental leach results in that it predicted that magnesium and calcium are leached in relatively high concentrations from the carbonate minerals. It also confirmed that pH increases rapidly to a limiting value of about 8.3 upon leaching of the tailings.

To determine the impact of the dissolution of calcite and magnesite on the pH of the simulated leachates, additional EQ6 runs were carried out including, then excluding, the presence of each of these minerals. By excluding magnesite only, the magnesium contributor to the leachates, and then calcite only, the calcium contributor, the pH predicted by both runs was similar to that measured experimentally. This confirms that the level of carbonate in the leachates is the major determinant of the pH.

The simulated increase in particle size also did not affect the pH of the solutions significantly, however the calcium and magnesium concentrations did change. The calcium concentration decreased, whilst that for magnesium increased by a similar magnitude, for both simulations i.e. at initial pH 4 and 9. This suggests that pH of the leachates is independent of the metal ion dissolving from the carbonate mineral.

EQ6 did not model the dissolution of kaolinite or siderite particularly well. In calculating leachate iron concentrations the model predicts that iron-bearing phases, viz. hematite, form as a result of siderite dissolution. It has already been established that under oxidising conditions such iron-bearing phases will precipitate. However, the geochemical code predicted that their formation occurs in greater abundance than that occurring experimentally[3], and predicted solution concentrations are correspondingly smaller.

Similarly, the model predicted much lower aluminium concentrations in the leachates than those measured. However, the model predicted that no insoluble aluminium-bearing phases formed, i.e. all the aluminium released from the kaolinite remained in solution.

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[3] The iron-bearing phases present were in concentrations not detectable by SEM.

To confirm the observations made for iron, a series of EQ6 runs were carried out suppressing the formation of iron-bearing phases i.e. total iron released would remain in solution.

With iron-bearing phases suppressed, the iron concentration in solution increased considerably - the calculated concentrations were more than three orders of magnitude greater than those measured experimentally. A comparison between the EQ6 runs with iron-bearing species being allowed to precipitate, and not to precipitate, indicates that a number of mechanisms may be occurring to explain the differences between the modelled and experimental results:

- Iron complexes are possibly precipitating during the leach tests, but not at the rate as those predicted by the code.

- The code predicted that only hematite would form, whereas it is more likely, under the conditions of the experiments performed in this current work, that other iron-bearing phases are being precipitated as well (*pers comm* Glassley, 1991). These other iron-bearing phases may be more soluble than hematite, thereby increasing the iron concentration in solution.

- The rate of iron release from the tailings is much slower than the instantaneous rate that the model uses to predict iron dissolution. This may be due to a protective iron-bearing layer, mentioned earlier, covering the surface of the siderite particles.

There are several possible reasons for the disparity between the measured and predicted values for aluminium, as follows:

- In the modelling carried out, aluminium has been assumed simply to be associated with kaolinite only. Of course, in reality, other clays and minerals containing aluminium are in the tailings (e.g. illite), albeit in much lower proportions. These minerals may have different dissolution behaviour to that of kaolinite and consequently, the release of aluminium would also be different.

- The dissolution rate for kaolinite was determined from experiments of previous workers using relatively pure kaolinite. It is unlikely that the kaolinite contained in the tailings was pure, and consequently could have a different leaching behaviour. According to May *et al* (1986), impurities are ubiquitous in clays and may affect the dissolution chemistry.

To further elucidate the dissolution of kaolinite several EQ6 runs were carried out with a higher, and a lower, prescribed dissolution rate for kaolinite to determine the effect on aluminium concentrations. It was found that, to attain aluminium levels comparable to those measured in the tailings leach experiments, a dissolution rate three orders of magnitude greater than that extrapolated from the results of Lasaga *et al* (1990) was required. This did not substantially change pH or the concentrations of the other elements.

The modelling carried out using the EQ3/6 geochemical code has shown that in order to implement the model fully, further work, beyond the scope of this thesis, is required to identify more clearly, and address the source of discrepancy, between the modelled and experimental results.

CHAPTER 7

CONCLUSIONS

The major findings of this study are summarised as follows:

- The mineralogy of the tailings investigated in this thesis has been shown to be fairly typical of that associated with many Australian coal seams. The primary minerals present were kaolinite, siderite, calcite and quartz. Minor minerals included illite and magnetite. It is not clear if magnetite was a reaction product of the leaching process, or an artefact of coal beneficiation.

- SEM analyses revealed that few of the siderite grains were pure. Many contained significant amounts of magnesium, and lesser quantities of calcium and manganese. Similarly, the clay minerals commonly contained minor proportions of other elements such as iron and magnesium.

- XRD profiles of the leached specimens showed no discernible change in the mineralogy after leaching. SEM examination similarly showed no obvious changes in mineralogy, but there were morphological changes in the minerals, e.g. signs of dissolution which were not as apparent, or as severe, in the un-leached tailings. Attack on calcite and the magnesium-bearing siderite grains was more prevalent than on the other minerals.

- Leaching tests carried out on the tailings showed that calcium and magnesium were released in relatively high proportions. The releases of these elements are associated with with the carbonate levels in solution. The carbonate concentrations, in turn, appear to be the major determinant of the leachate pH.

- Regardless of the pH of the initial solution, the pH after leaching remained above 7.5 throughout the entire leaching program for each test (212 to 266 days). In the 32 hour leach test carried out at initial pH 4 and L/S ratio of 10:1, it was shown that the pH increased from 4 to 9.4 in just one hour. At alkaline pHs, there is a subsequent low release of heavy metals, minimising potential environmental problems.

- Extrapolation of leach results to field situations, as proposed by the BEOP-31 standard, can only be applied to systems which can be shown to be unaffected by the L/S ratio. Problems occur using this extrapolation technique where the solutions are saturated in important elements such as calcium and magnesium.

- The BEOP-31 standard predicts that increasing the L/S ratio beyond 10:1 has no significant effect on the release of the heavy metals.

- Oxidation, and subsequent leaching, of the tailings, showed that the leach rates of calcium and magnesium decreased slightly. There was no corresponding decrease in leachate pH. The leach rates of all of the other elements were not affected by oxidation. The solubility of calcium and magnesium-bearing phases appear to have been reduced by oxidation, probably due to the association of these two elements with not only the carbonate minerals, but with the clays as well. Practically, this suggests that should the tailings be exposed to oxidising conditions for prolonged periods in a tailings impoundment, then the leachability of the tailings should not be affected.

- The 5 minute to 32 hour leach tests showed that the amount of copper, mercury, manganese, lead and thorium released was greatest at the most acidic pHs.

- Accelerated leaching of heavy metals from tailings caused by acid mine drainage should not be important for tailings of similar composition to those of West Cliff Colliery because of the low levels of sulphide minerals and the high-buffering capacity of the carbonates.

- The level of heavy metal release measured from the tailings in this work was extremely low, and were generally well below the criteria set for potable water by the SPCC of New South Wales. The pH of the discharges are similar to the nearby waterways, and so discharge of leachates from tailings impoundments at West Cliff would be predicted to have no serious environmental impact.

- Geochemical modelling of the leach systems was partially successful. The EQ3/6 code modelled pH and the behaviour of calcite and magnesite dissolution well, for the tests carried out at both initial pH of 4 and 9. The leaching behaviour of kaolinite and siderite was not modelled successfully, the code grossly underestimating the concentrations of aluminium and iron in the leachates. For aluminium, this was attributed to the complicated leaching behaviour of clays, whereas for iron, the major cause of discrepancy was thought to be the complex precipitation reactions that occur when siderite is placed in contact with water under oxidising conditions.

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APPENDICES

APPENDIX A

Thorium and Uranium Decay Chains

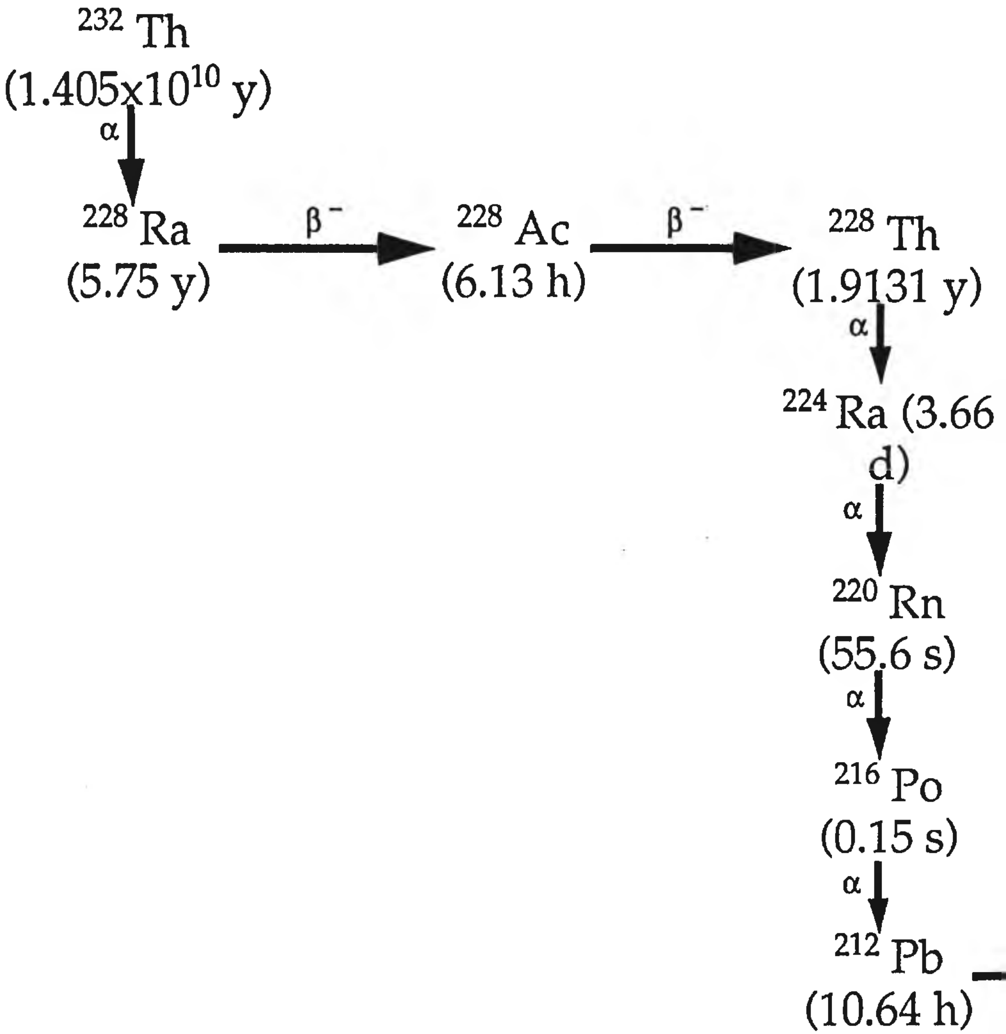
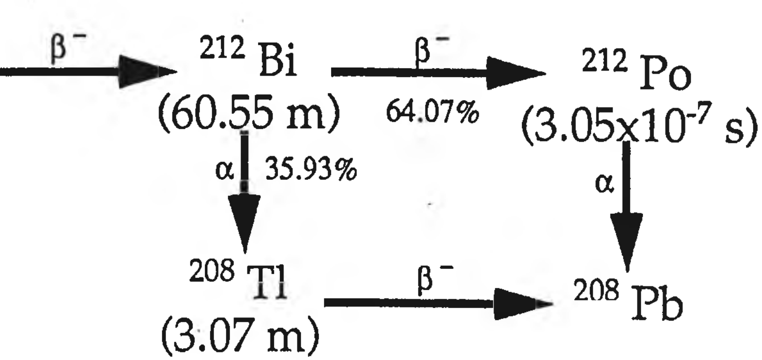


Figure A-1: Thorium Decay Series


β⁻
²¹²Bi
(60.55 m)
β⁻
64.07%
²¹²Po
(3.05x10⁻⁷ s)
α
35.93%
α
²⁰⁸Tl
(3.07 m)
β⁻
²⁰⁸Pb

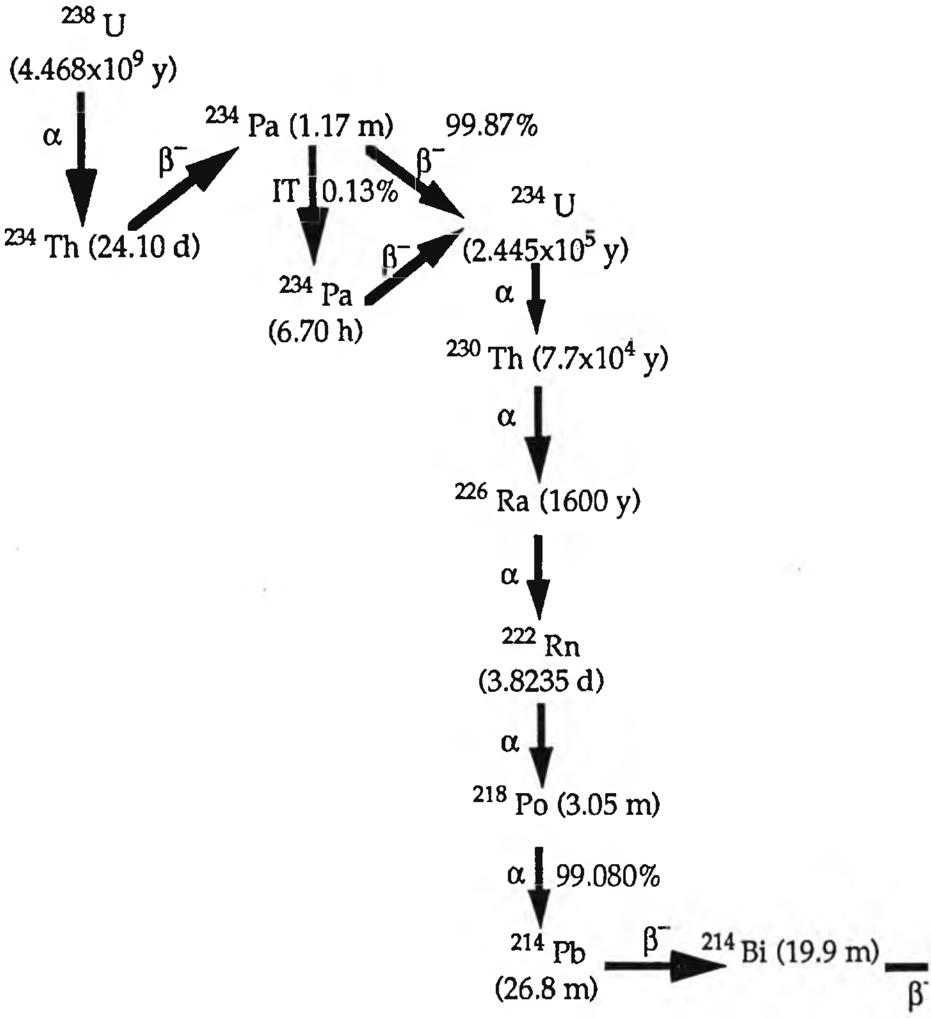
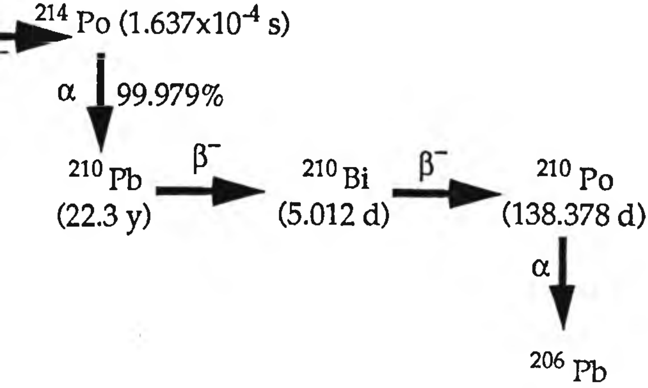


Figure A-2: Uranium Decay Series


^{214}Po (1.637x10^{-4} s)
α
99.979%
^{210}Pb
(22.3 y)
β$^-$
^{210}Bi
(5.012 d)
β$^-$
^{210}Po
(138.378 d)
α
^{206}Pb

APPENDIX B

X-Ray Diffraction (XRD) Profiles

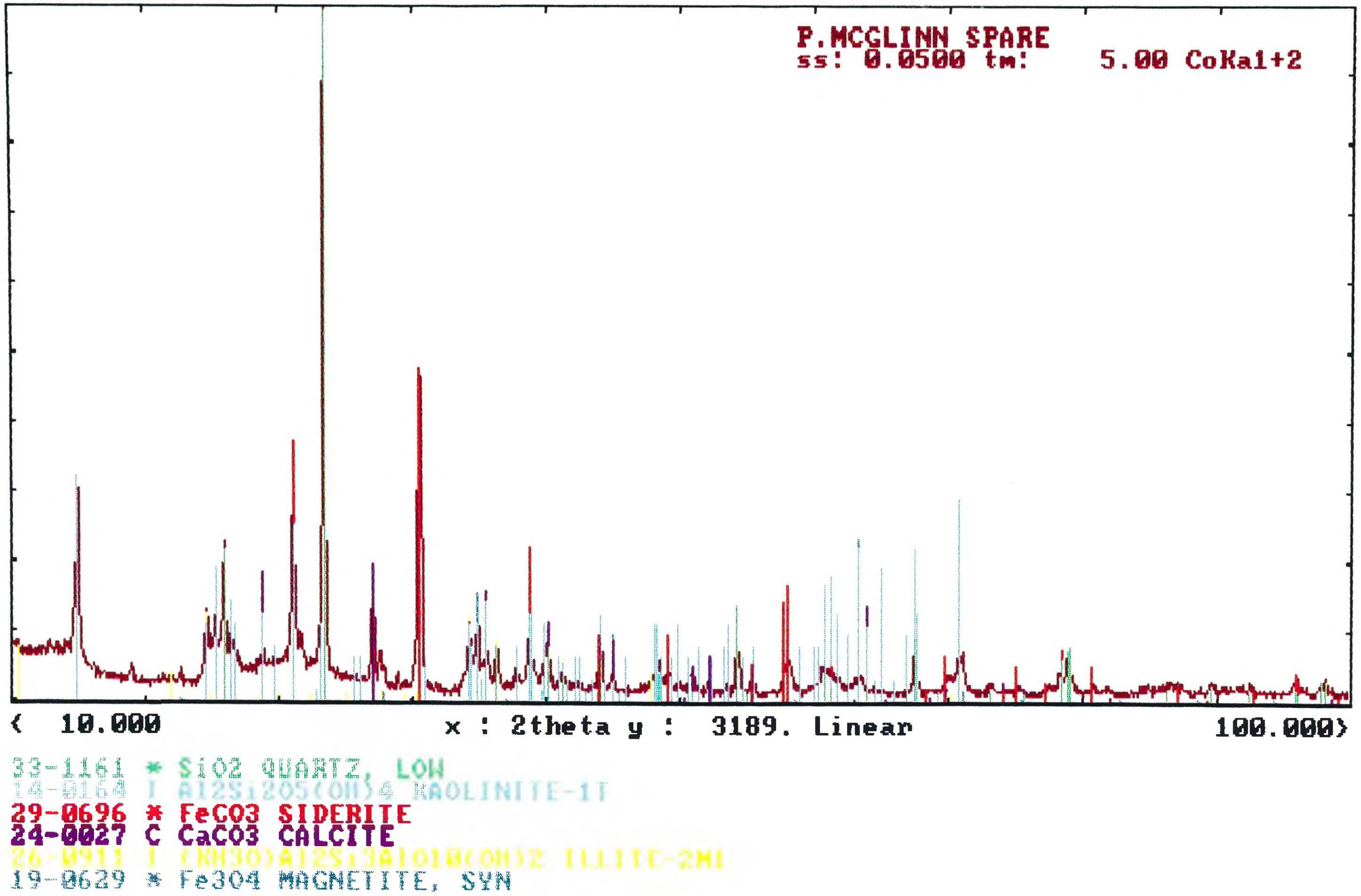


Figure B-1: X-ray Diffraction Profile of the Tailings Prior to Leaching

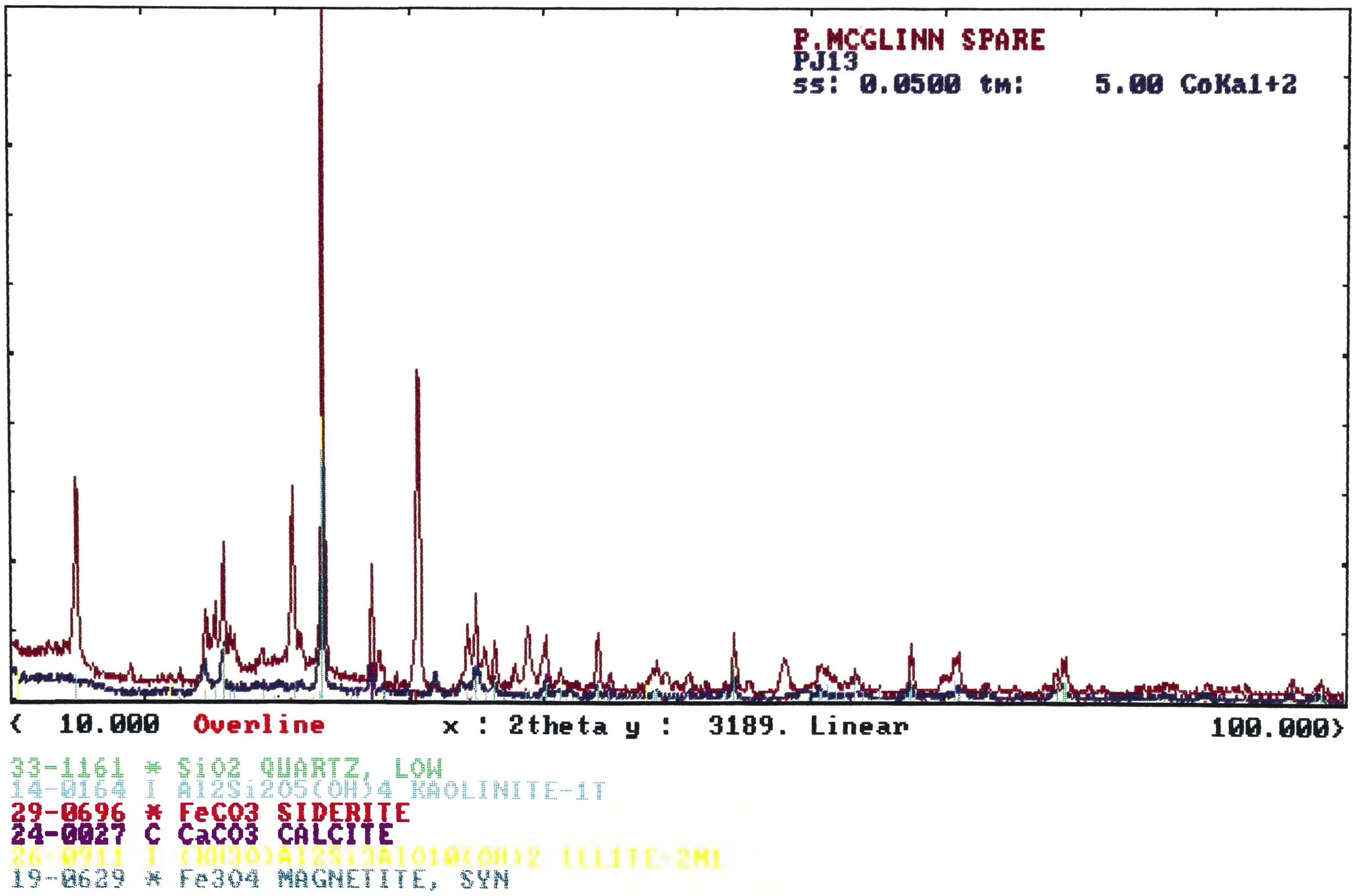


Figure B-2: Comparison of the X-ray Diffraction Profiles of Heated and Un-heated Tailings Samples for Kaolinite Identification

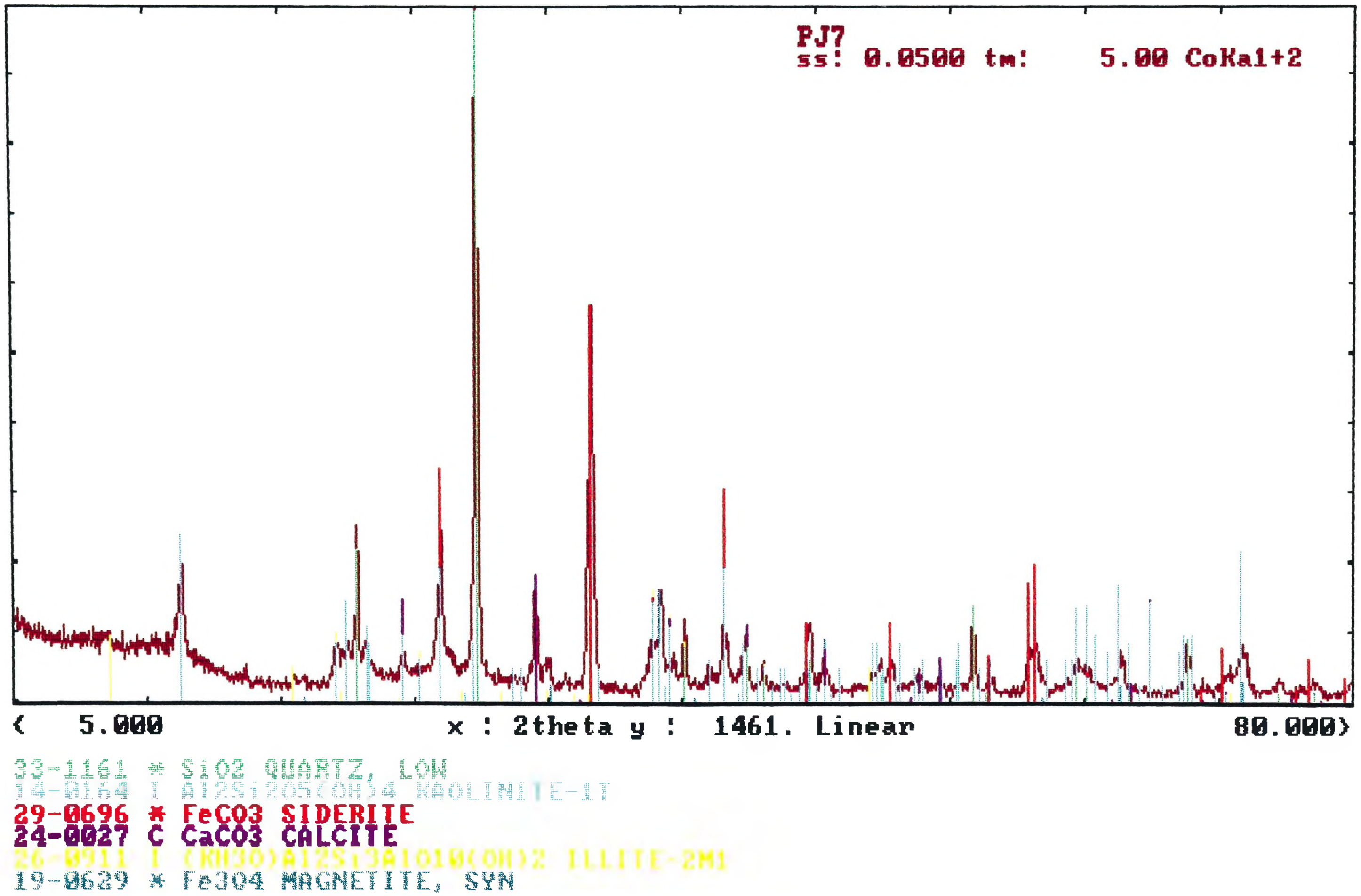


Figure B-3: X-ray Diffraction Profile of the Tailings After Leaching - L/S Ratio 5:1; pH 4

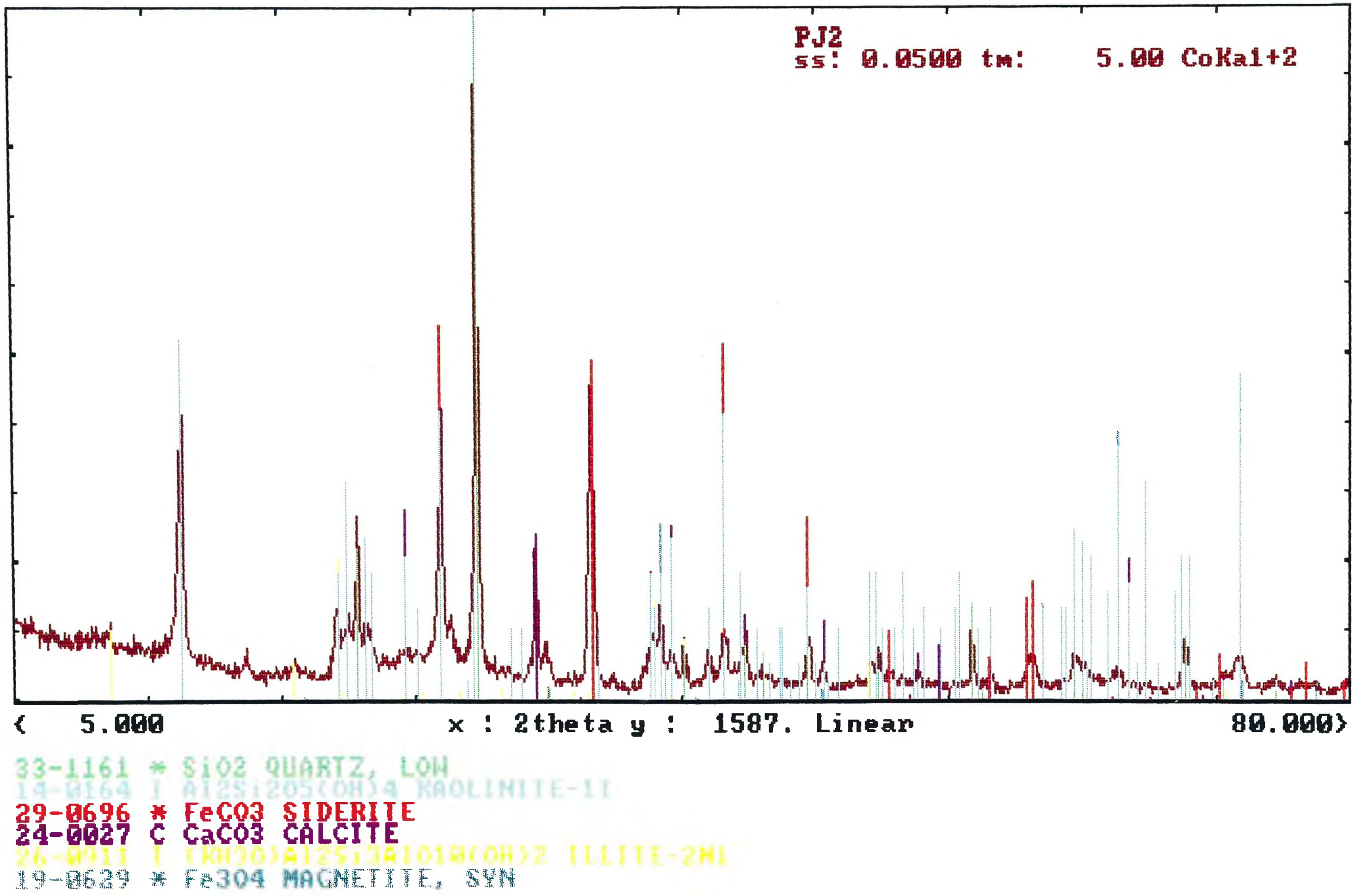


Figure B-4: X-ray Diffraction Profile of the Tailings After Leaching - L/S Ratio 5:1; pH 9

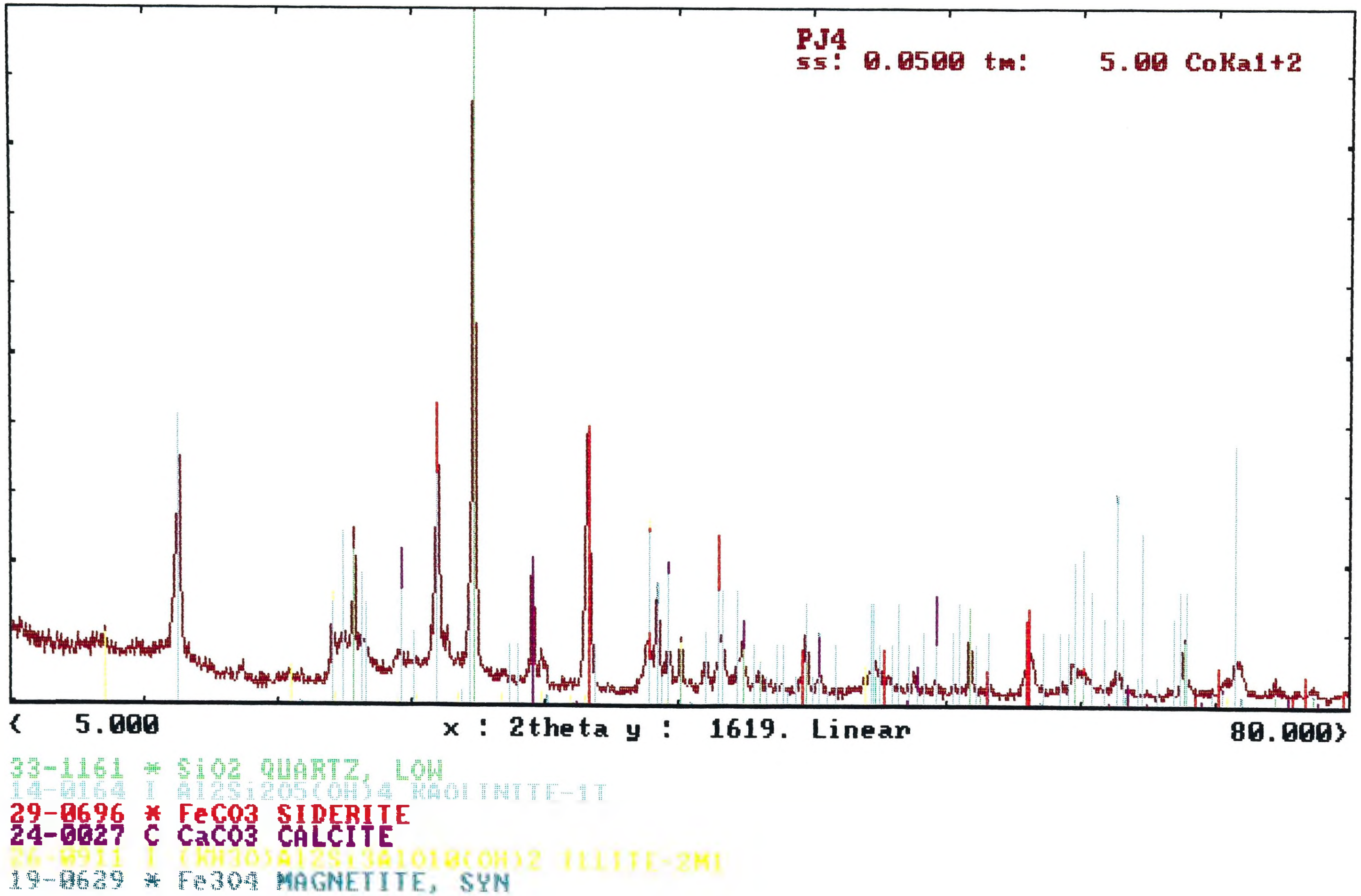


Figure B-5: X-ray Diffraction Profile of the Tailings After Leaching - L/S Ratio 10:1; pH 4

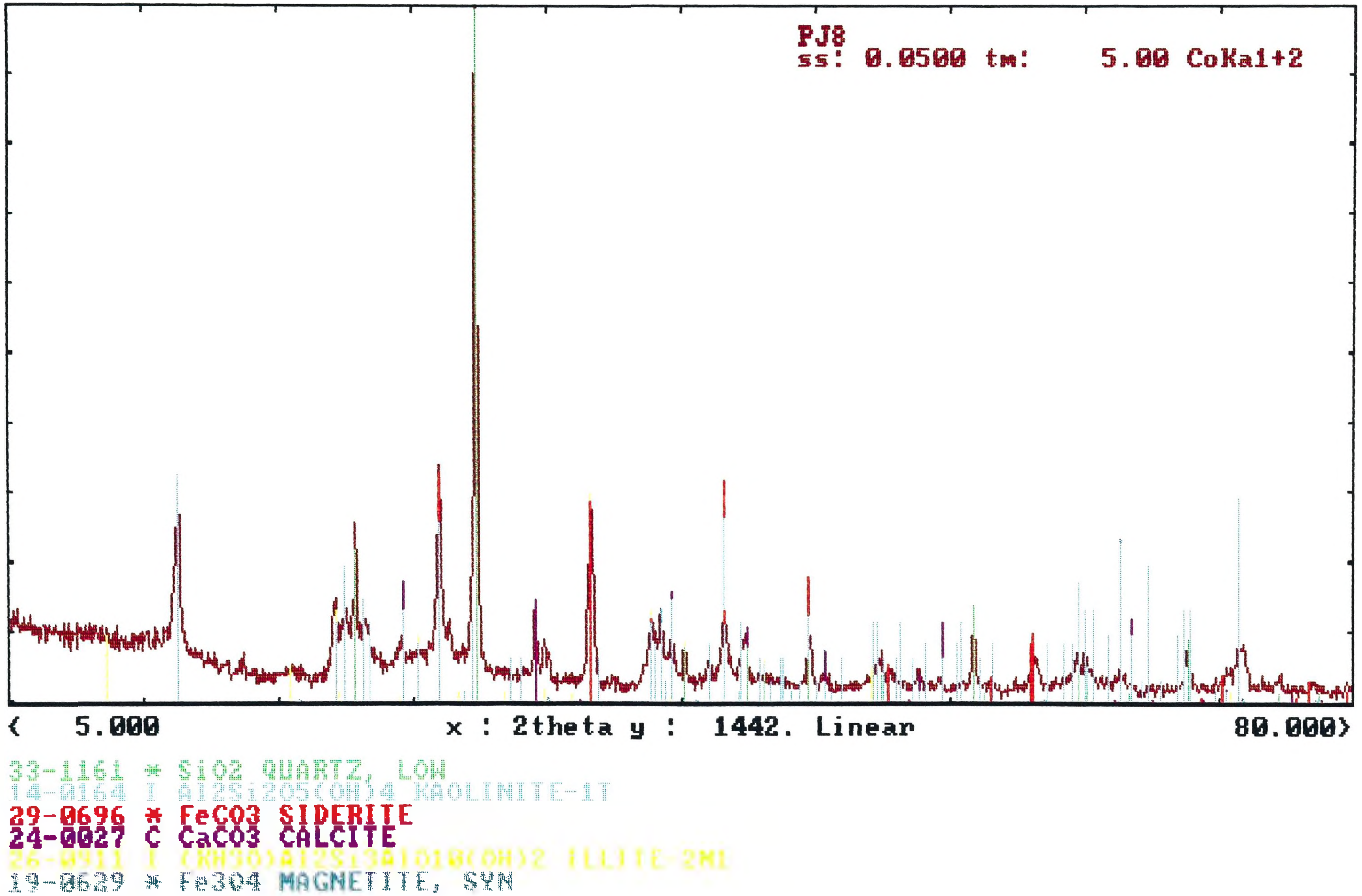


Figure B-6: X-ray Diffraction Profile of the Tailings After Leaching - L/S Ratio 10:1; pH 9

APPENDIX C

Energy Dispersive X-ray Spectrometry (EDS) Profiles

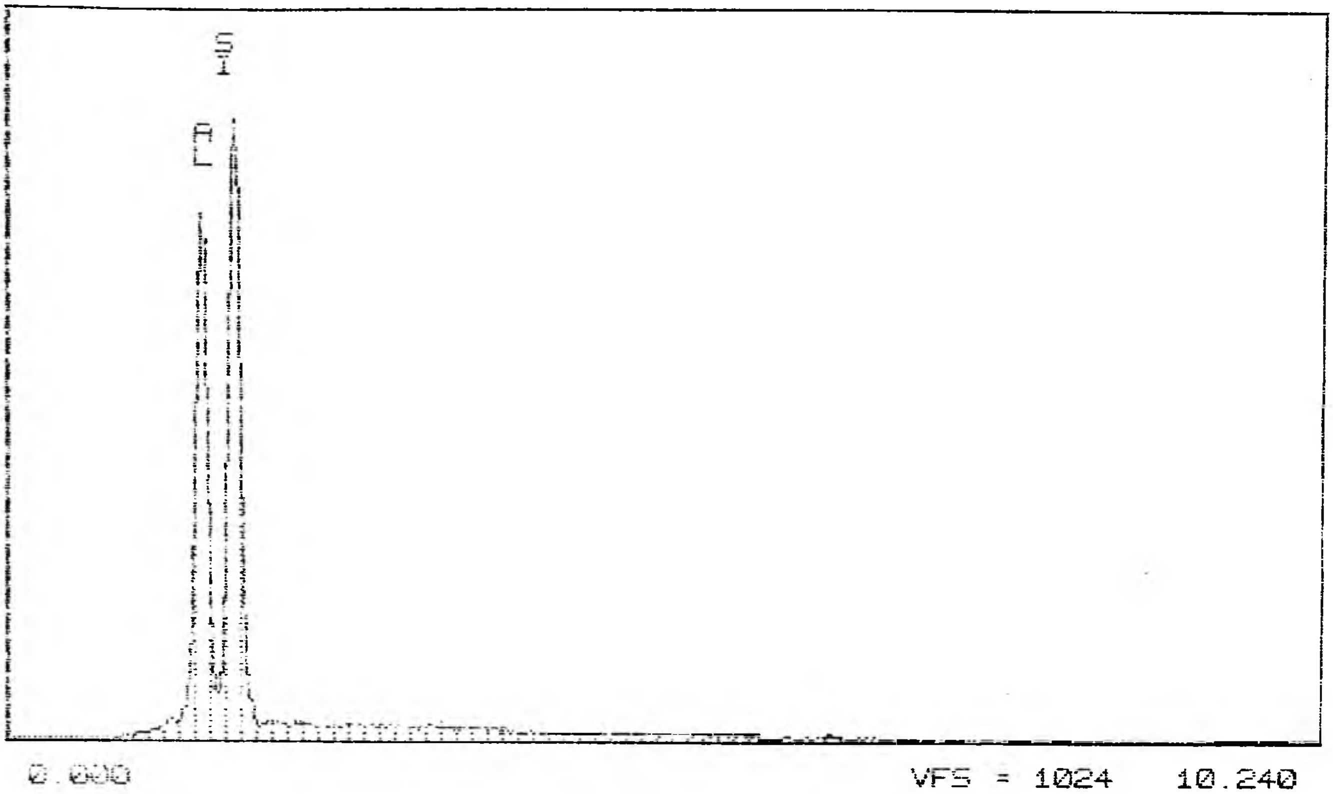


Figure C-1: Typical EDS Profile of Kaolinite in the Tailings

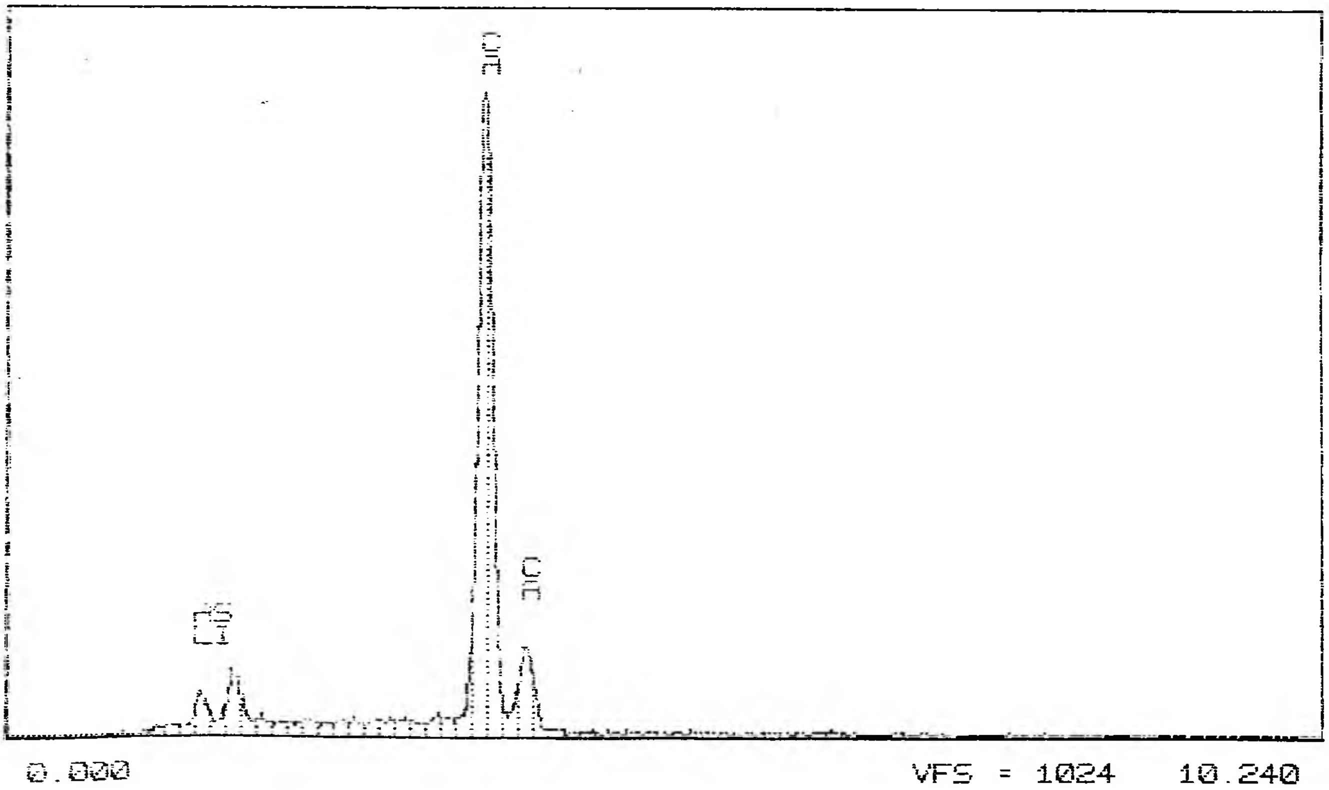


Figure C-2: Typical EDS Profile of Calcite in the Tailings

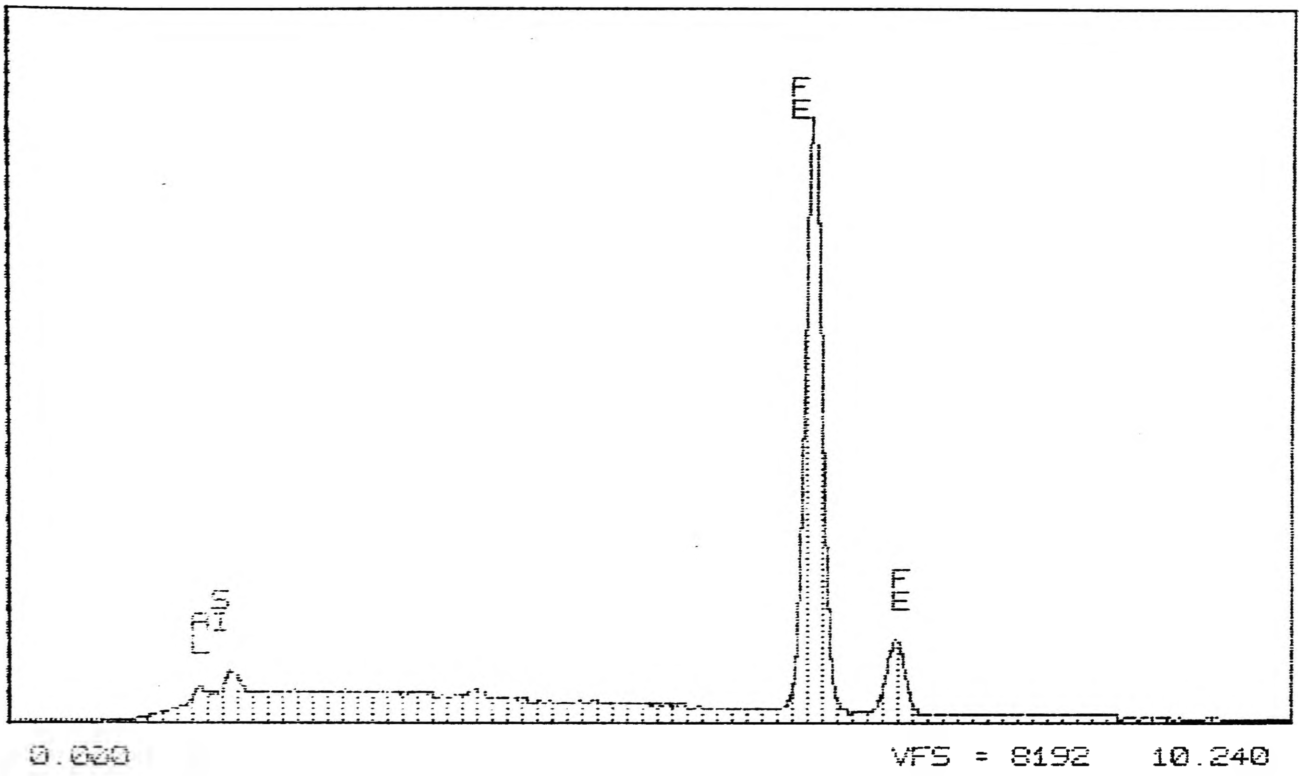


Figure C-3: Typical EDS Profile of Siderite in the Tailings

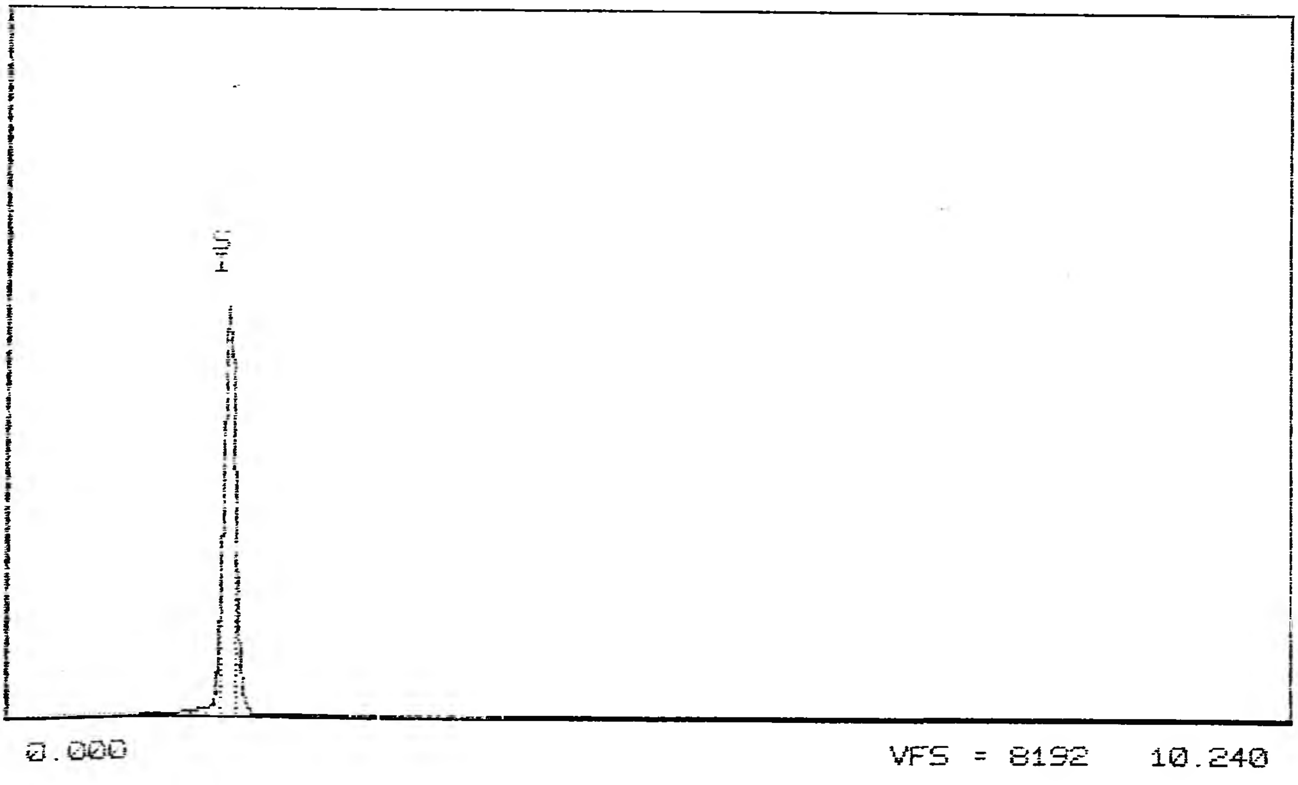


Figure C-4: Typical EDS Profile of Quartz in the Tailings

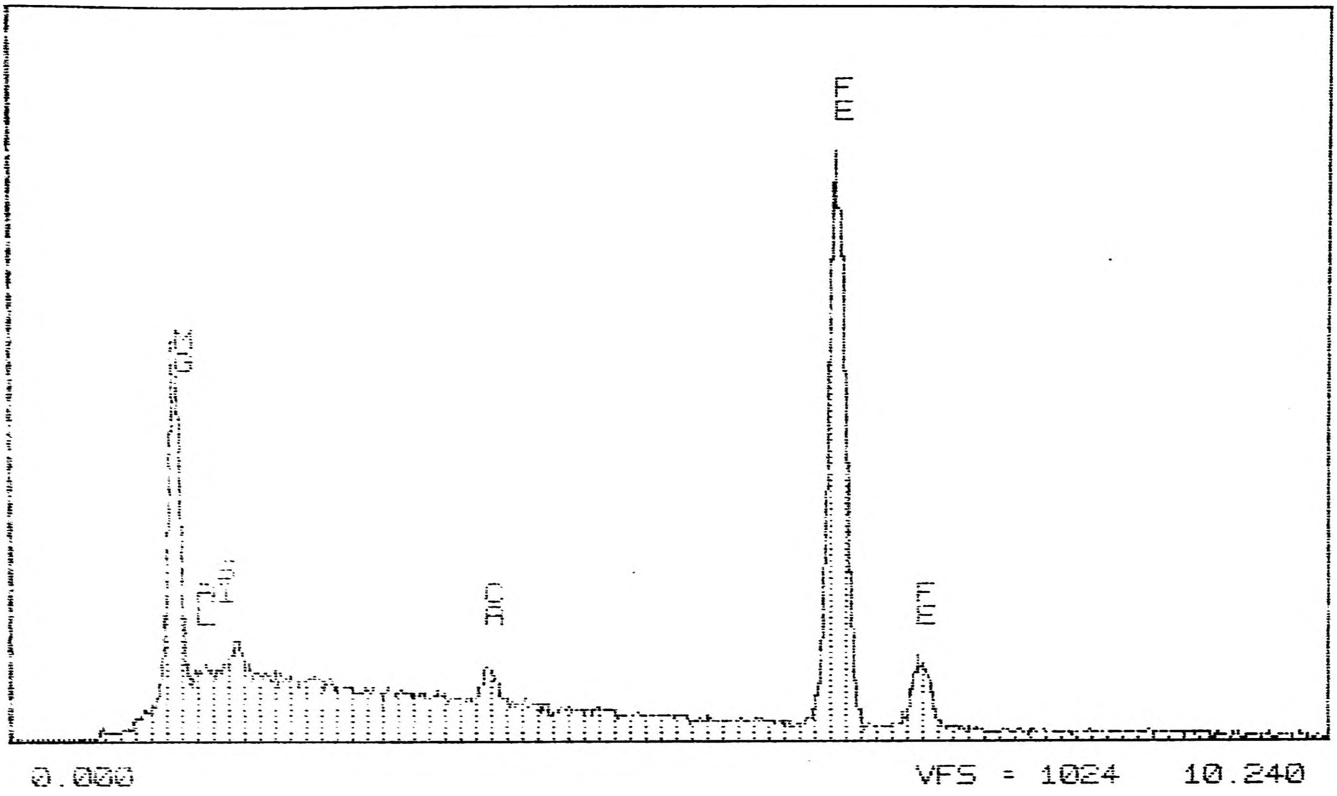


Figure C-5: Typical EDS Profile of Magnesium-bearing Siderite in the Tailings

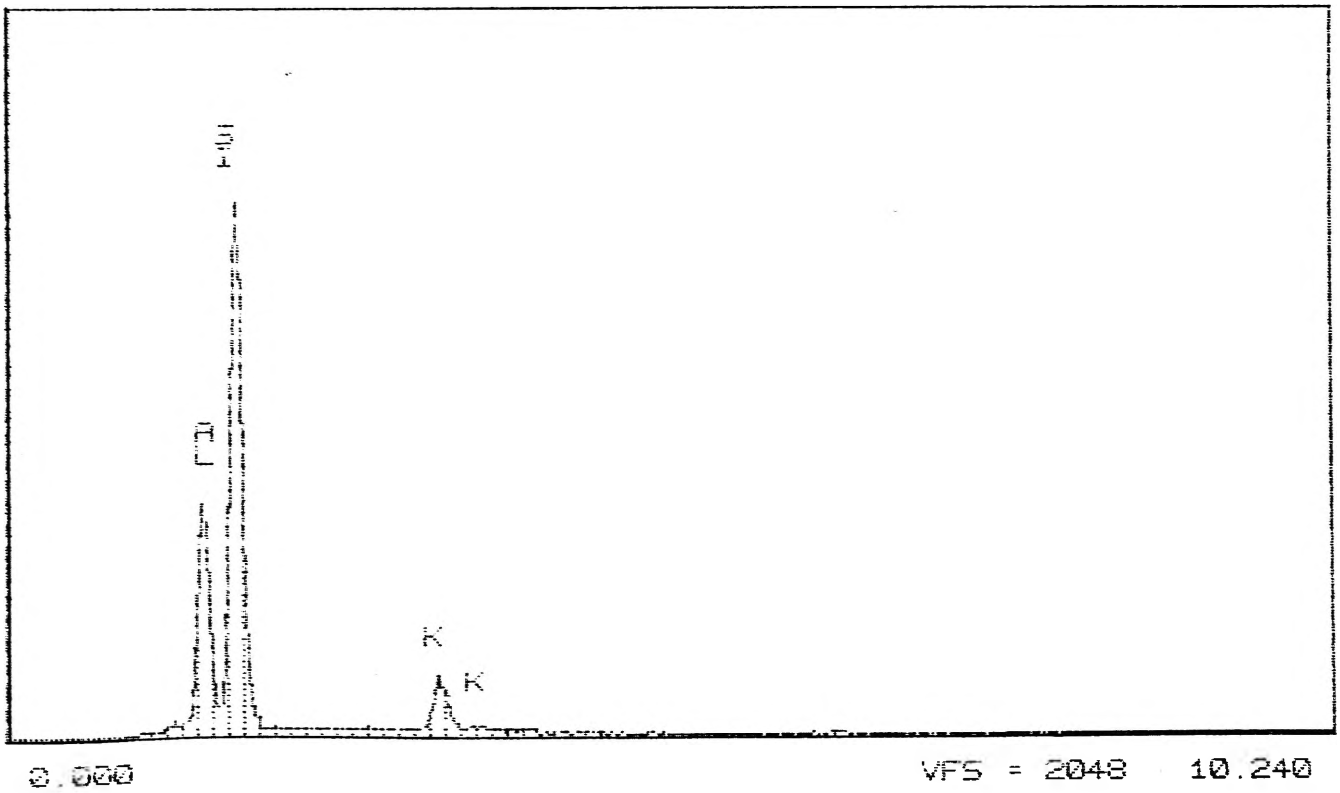


Figure C-6: Typical EDS Profile of Illite in the Tailings

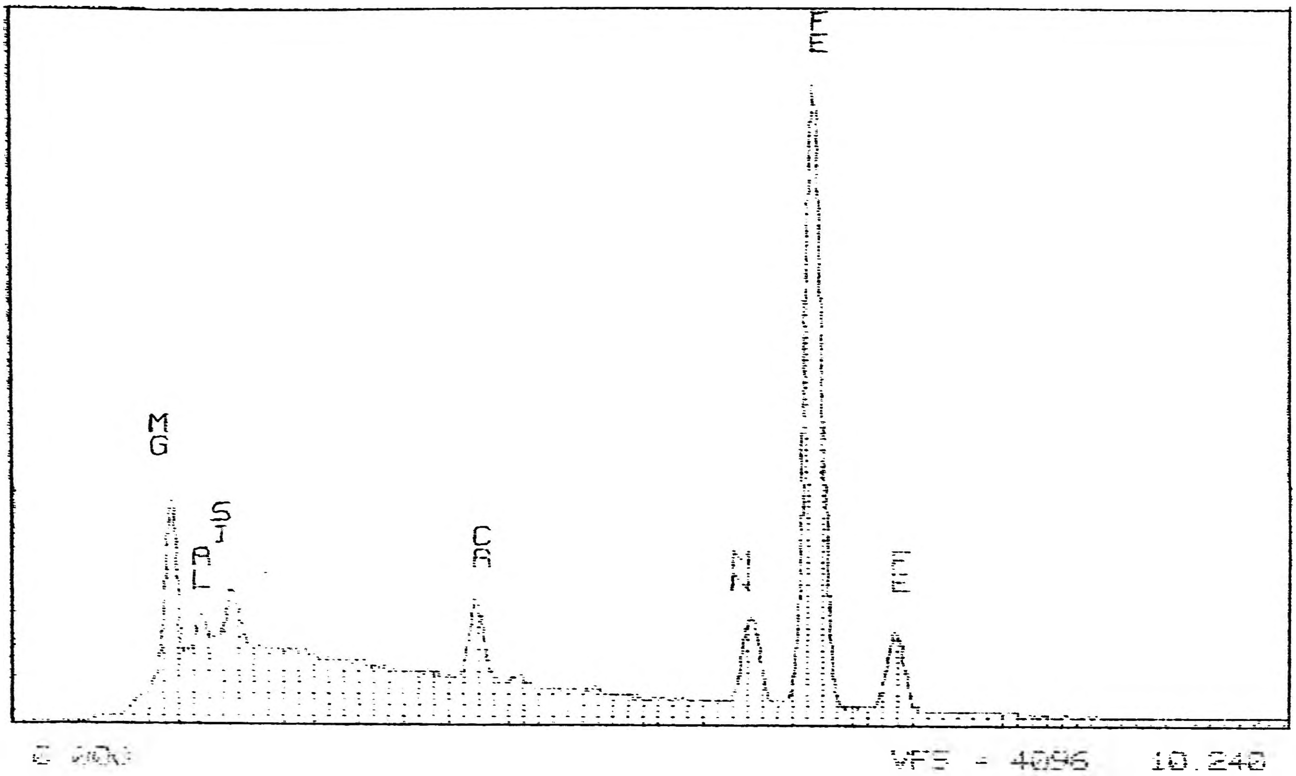


Figure C-7: EDS Profile of Siderite Grain With Significant Levels of Calcium and Manganese

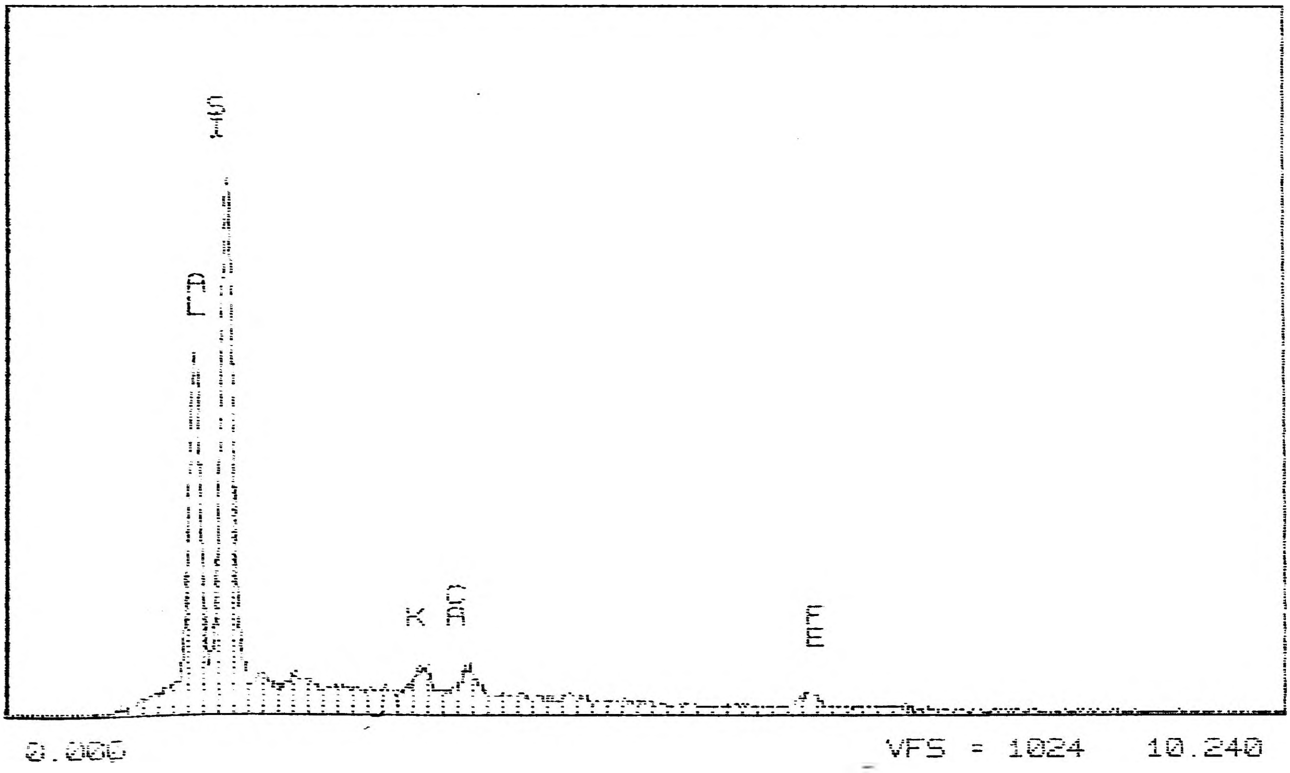


Figure C-8: EDS Profile of Clay Particle Showing Minor Proportions of Iron, Calcium and Potassium

APPENDIX D

Preliminary Leach Tests Results

PRELIMINARY LEACH TESTS

Leachates sampled for each of the liquid to solid ratios were either filtered through 1000 NMW filters or allowed to stand for several days so that the colloids could accumulate and settle, then the clear liquor decanted off for elemental analysis. Although the results do not show the extent to which the major and trace elements could occur in solution under optimum conditions (that is, completely dissolved), they do show the extent to which the elements could be bound up in the colloids. This is important, as under conditions represented by a liquid to solid ratio of less than 5:1, colloid formation obviously becomes an important consideration in trace (and major) element migration from coal refuse dumps. Results for the leach tests at the various liquid to solid ratios are given in Tables E-1 to E-11, Appendix E. The results are represented as elemental concentrations in the leachates, and leach rates have been calculated. The leach rates are shown graphically below.

The results for the preliminary test work are presented in two parts - firstly a comparison between the results of each of the leachates carried out at the various liquid to solid ratios; and secondly a comparison between the results for the acidified and non-acidified leachates. The results are discussed by element under each of these headings.

D-1 Leaching Behaviour Under Different Liquid to Solid Ratios

A comparison of the leach rates of the elements under the different liquid to solid ratios, viz 1:1, 2.5:1, 4:1 and 5:1, follows. For the preliminary test work, analyses was carried out to determine the concentrations of arsenic, cadmium, chromium, copper, mercury, lead and zinc. There were no detectable levels of cadmium and mercury in any of the leachates in this phase of the work. The 2.5:1 liquid to solid ratio leach test was carried out in duplicate.

The detection limits for the elements determined for each leach test, calculated as leach rates, are given in Table D-1. These limits apply to all of the results for the preliminary testwork.

TABLE D-1: Detection Limits for Trace Elements, Calculated as Leach Rates, for the Preliminary Leach Work

L/S Ratio	Detection Limits ($g\ m^{-2}\ d^{-1}$)				
	Arsenic	Chromium	Copper	Lead	Zinc
1:1	4.4×10^{-10}	2.2×10^{-11}	3.4×10^{-11}	5.6×10^{-11}	9.0×10^{-11}
2.5:1	1.6×10^{-9}	8.0×10^{-11}	1.2×10^{-10}	2.0×10^{-10}	3.2×10^{-10}
4:1	2.9×10^{-9}	1.4×10^{-10}	2.1×10^{-10}	3.6×10^{-10}	5.7×10^{-10}
5:1	3.5×10^{-9}	1.7×10^{-10}	2.6×10^{-10}	4.2×10^{-10}	6.9×10^{-10}

Arsenic

The leach rates of arsenic from the tailings under the four liquid to solid ratio conditions are shown in Figure D-1.1. The leach rate decreases with time for each of the tests. The rates for the 1:1 and 2.5:1 tests are consistently lower than those for the higher ratio tests. As colloidal formation increased with lower liquid to solid ratio, it appears that arsenic may have sorbed onto the colloids, leading to decreased detectable levels of that element in the leachate analysed at those liquid to solid ratios.

Chromium

The leach rates of chromium from the tailings are shown in D-1.2. The levels of chromium in the 1:1 test were not detectable. Again, the rates for the 2.5:1 test are consistently lower than those for the higher ratio tests, although the rates are similar for the first three days of leaching. The leach rates decrease with time to four days. Rates for the final leach period are similar to those for the fourth day.

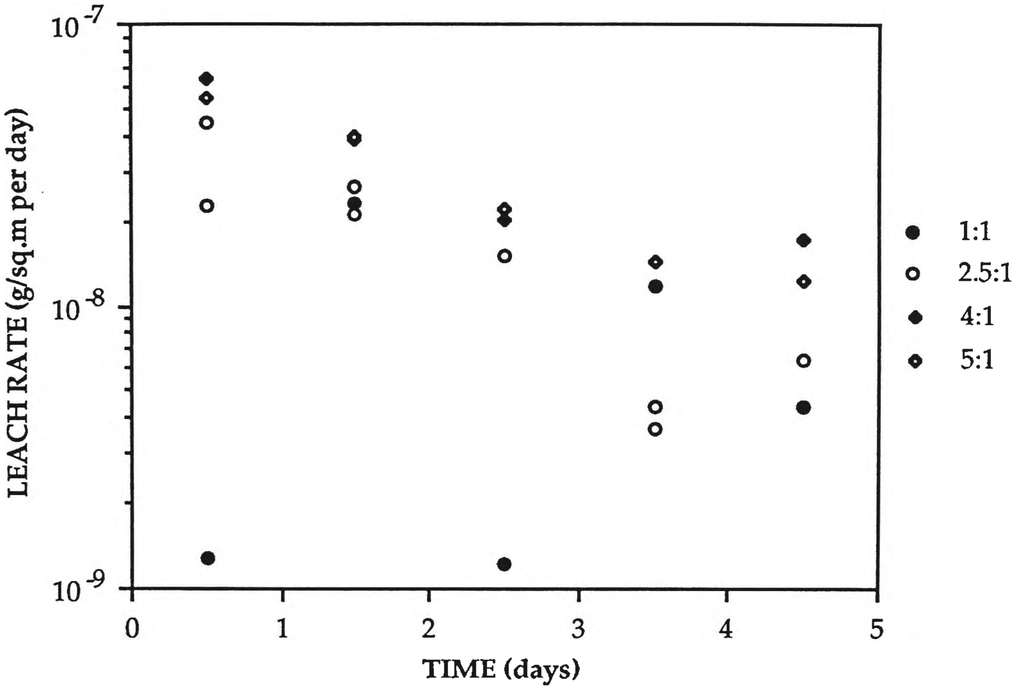


Figure D-1.1: Leach Rate of As from Tailings at Various Liquid to Solid Ratios - Initial pH 4 at Ambient Temperature

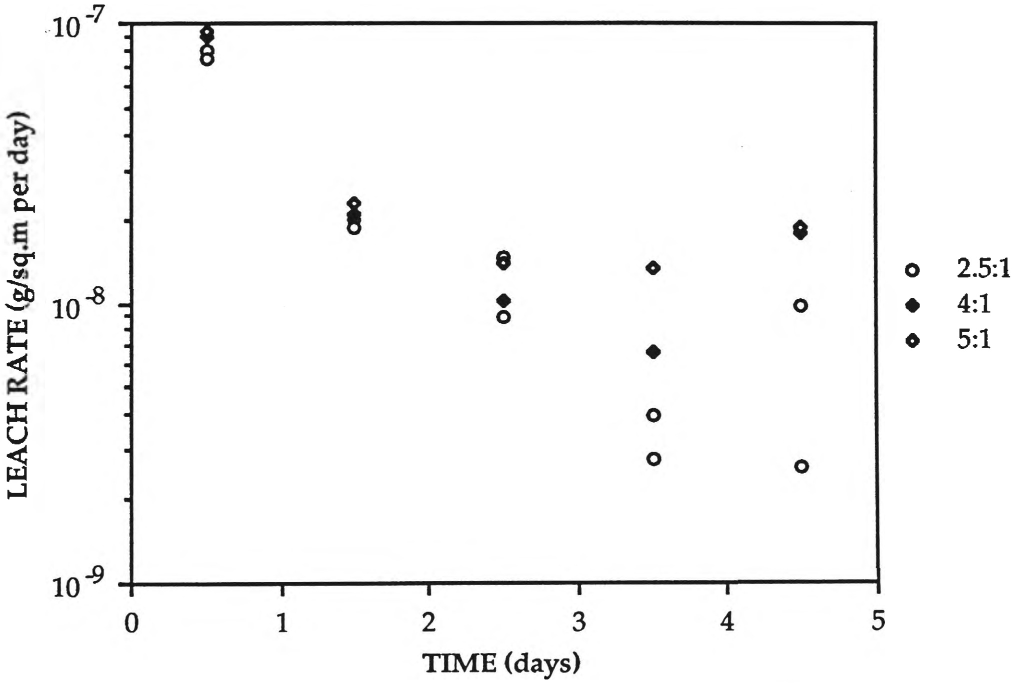


Figure D-1.2: Leach Rate of Cr from Tailings at Various Liquid to Solid Ratios - Initial pH 4 at Ambient Temperature

Copper

The leach rates of copper from the tailings are shown in D-1.3. There is a wide scatter of data between the liquid to solid ratios, but generally the rates for the lower liquid to solid ratio tests are lower than those for the 4:1 and 5:1 tests.

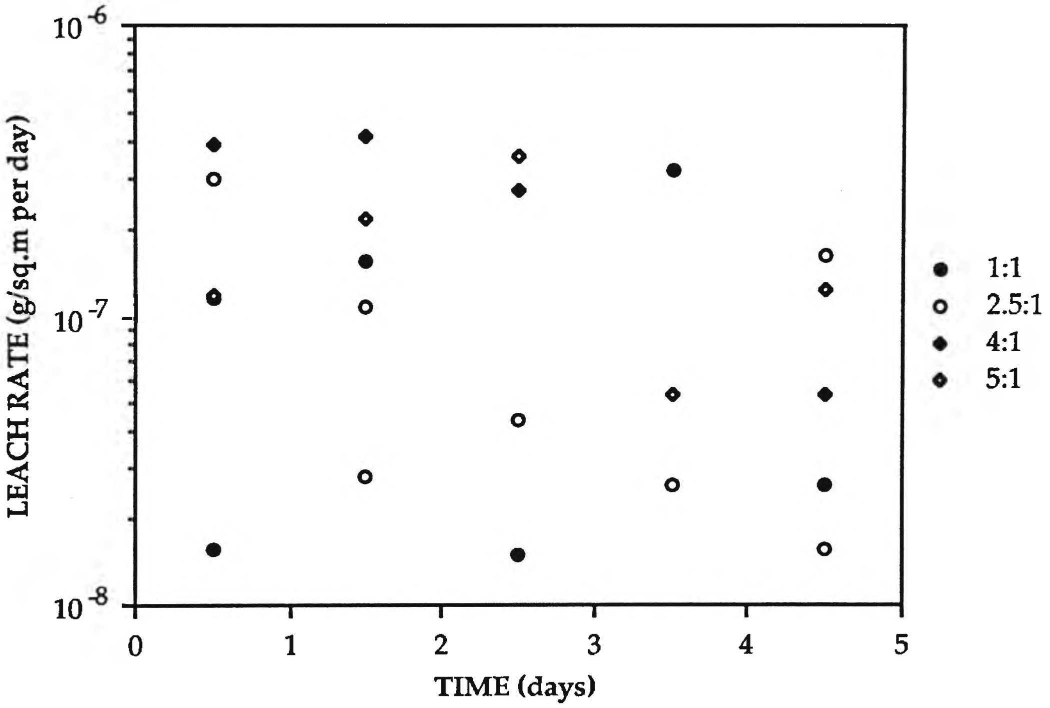


Figure D-1.3: **Leach Rate of Cu from Tailings at Various Liquid to Solid Ratios - Initial pH 4 at Ambient Temperature**

Lead

The leach rates of lead from the tailings are shown in D-1.4. Again, the rates for the lower liquid to solid ratio tests are generally lower than those for the 4:1 and 5:1 tests. The rates for each of the tests are basically uniform throughout the leaching time.

Zinc

The leach rates of zinc from the tailings are shown in D-1.5. Data for zinc are few, and a comparison between liquid to solid ratios is difficult. However, where data are sufficient for comparison, the rates for the lower

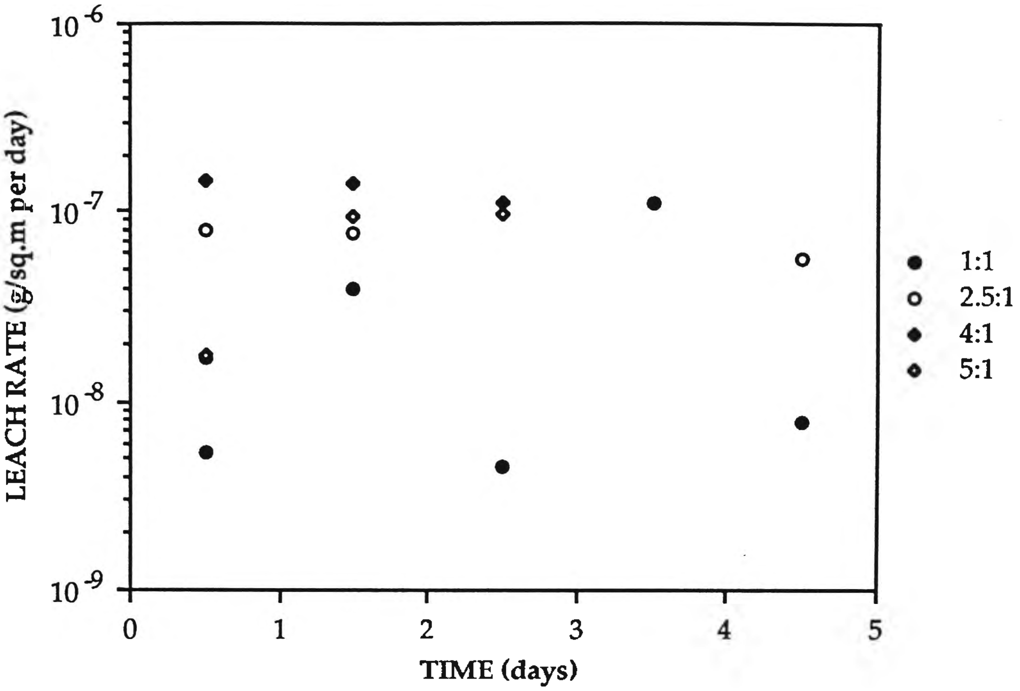


Figure D-1.4: Leach Rate of Pb from Tailings at Various Liquid to Solid Ratios - Initial pH 4 at Ambient Temperature

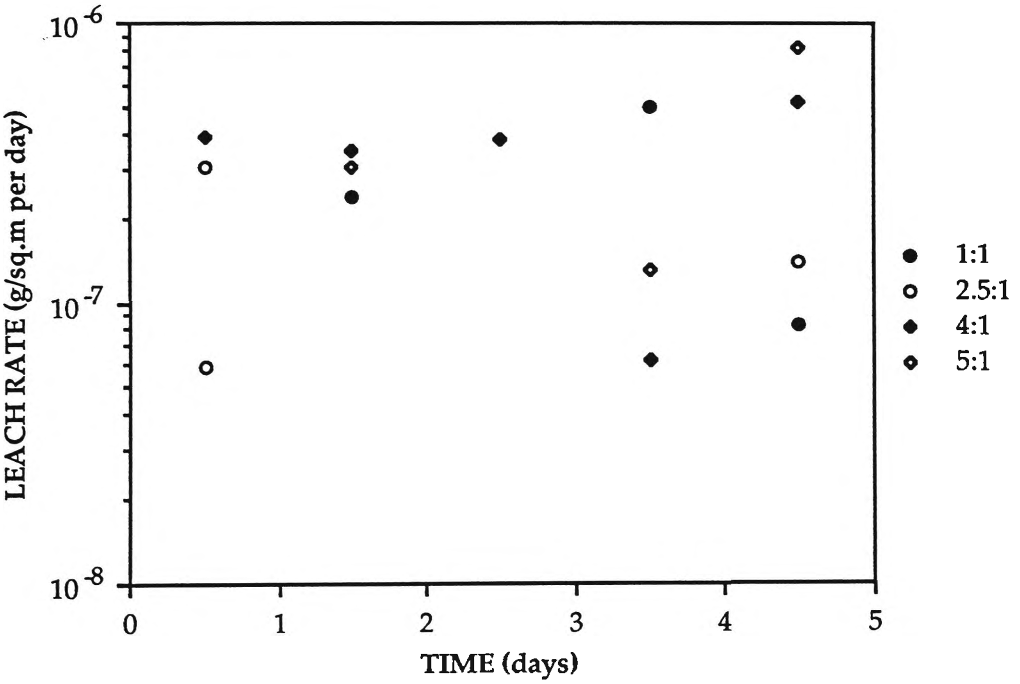


Figure D-1.5: Leach Rate of Zn from Tailings at Various Liquid to Solid Ratios - Initial pH 4 at Ambient Temperature liquid to solid ratio tests are generally lower than those for the 4:1 and 5:1 tests.

Although the data in the above Figures are generally well scattered, for each of the elements analysed, the leach rates for the tests carried out at lower liquid to solid ratios are correspondingly lower than those carried out at ratios of 4:1 and 5:1. Each of the elements appears to have the propensity to sorb onto the colloids that have formed in the leachates, colloidal formation becoming more prevalent at lower liquid to solid ratios.

D-2 Comparison of Leach Rates of Acidified and Non-acidified Leachates

The addition of nitric acid to the filtered leachates was carried out to stabilise the solutions to prevent the precipitation of any insoluble phases. To establish if the acid addition may have been the cause of colloid formation, which in turn would affect the concentration of the elements in solution, leach rates have been compared between a series of leachates which were divided into two separate samples, one acidified, as usual, and the other not acidified. This was carried out on the leachates from the 5:1 and 4:1 liquid to solid ratio leach tests.

Only arsenic, chromium, copper and lead were in detectable quantities in all of the leachates, so a comparison can only be made for these elements.

Arsenic - 5:1 Liquid to Solid Ratio

The comparison between the leach rates of arsenic in acidified and non-acidified leachates is shown in Figure D-2.1. The addition of acid to the leachate has had no obvious effect on the leach rates. The leach rate for the leachate not acidified is similar to that for the leachate with 1% nitric acid addition.

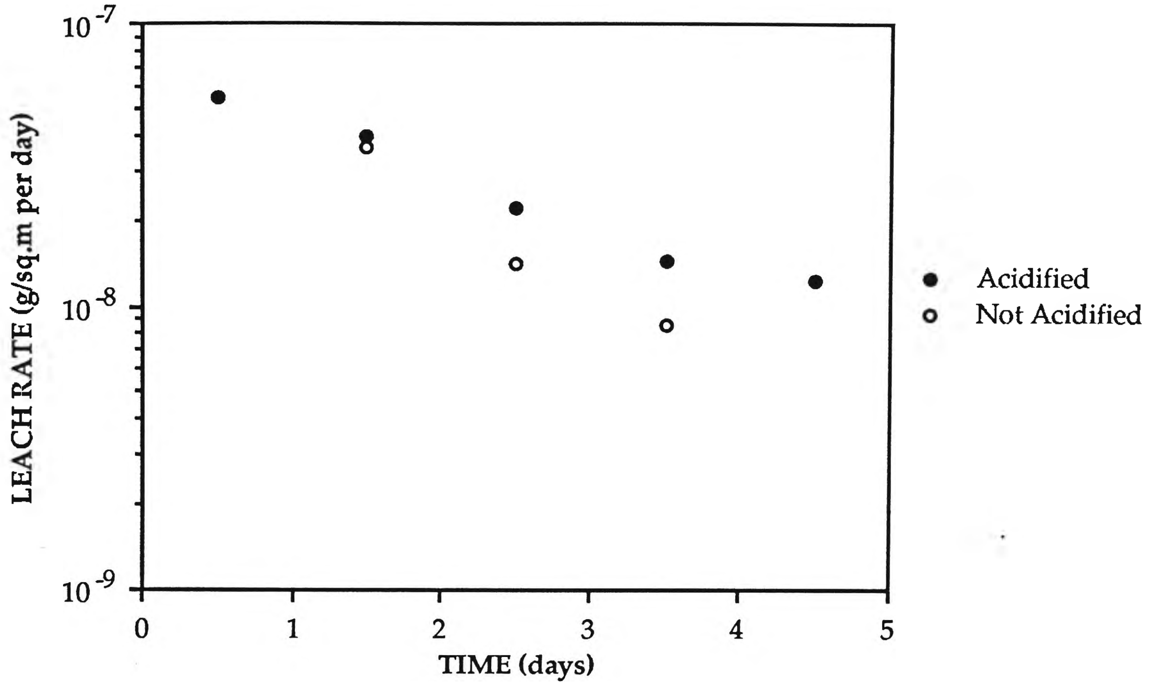


Figure D-2.1: **Leach Rate of As in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 5:1, Initial pH 4 at Ambient Temperature**

Chromium - 5:1 Liquid to Solid Ratio

The comparison between the leach rates of chromium in acidified and non-acidified leachates is shown in Figure D-2.2. Again, the addition of acid to the leachate has had no obvious effect on the leach rates. The leach rate for the leachate not acidified is similar to that for the leachate with 1% acid addition.

Copper - 5:1 Liquid to Solid Ratio

The comparison between the leach rates of copper in acidified and non-acidified leachates is shown in Figure D-2.3. Leach rates for both sets of data are similar.

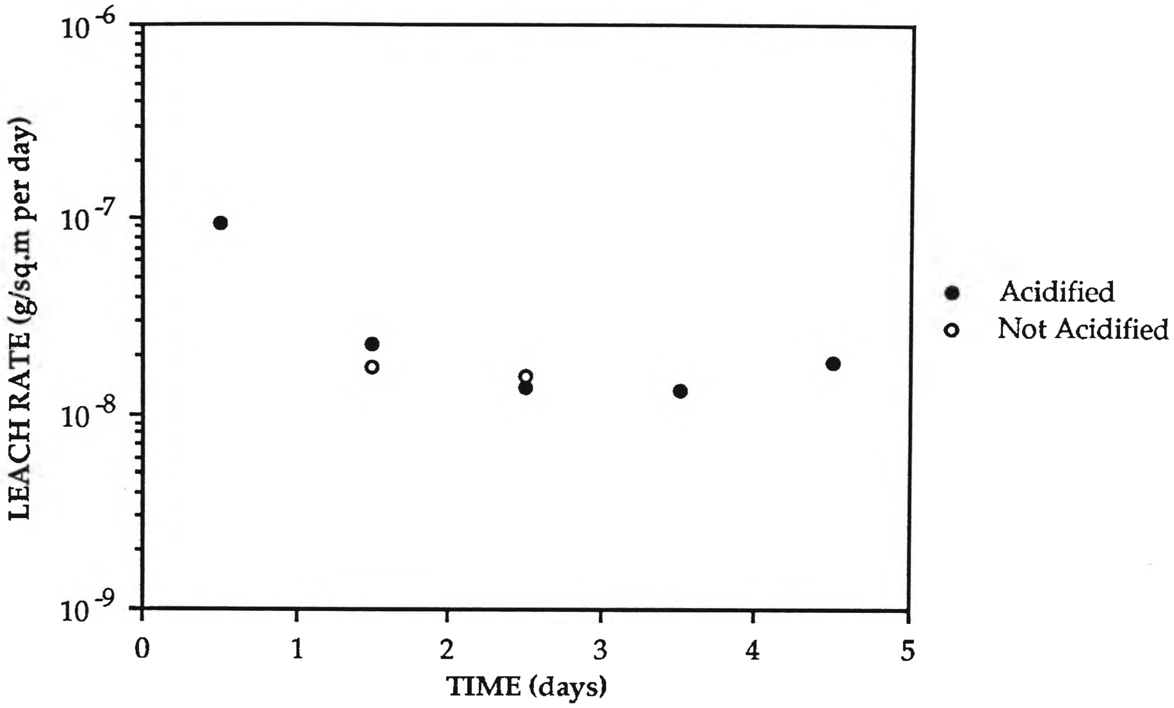


Figure D-2.2: **Leach Rate of Cr in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 5:1, Initial pH 4 at Ambient Temperature**

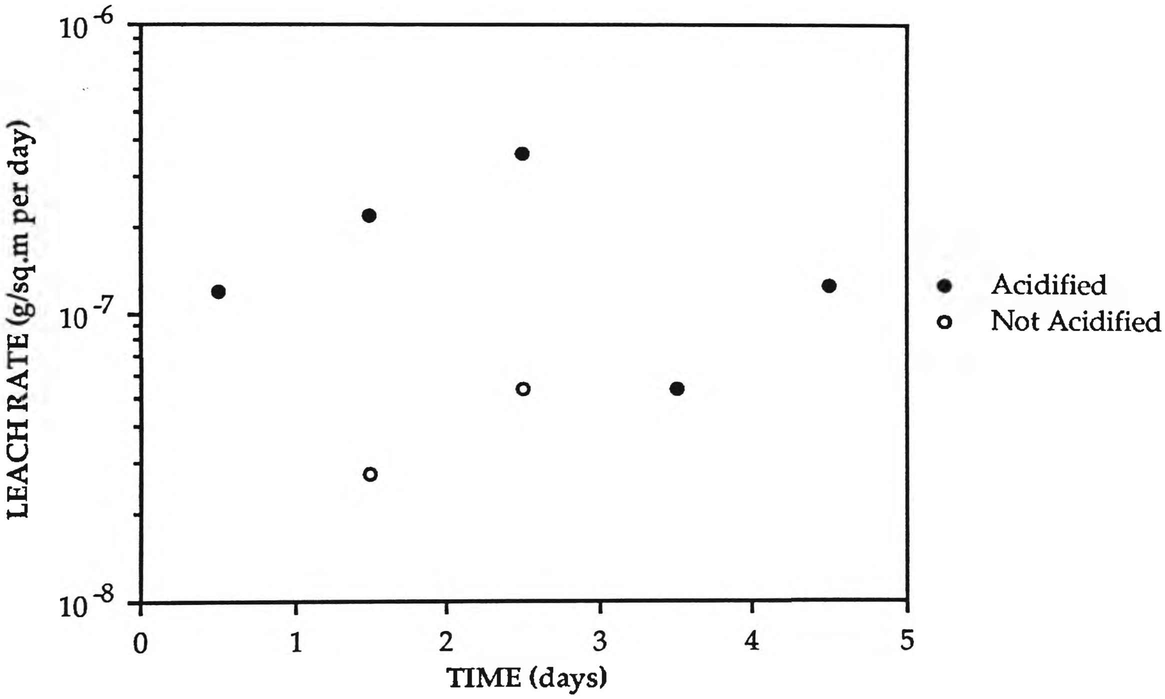


Figure D-2.3: **Leach Rate of Cu in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 5:1, Initial pH 4 at Ambient Temperature**

Lead - 5:1 Liquid to Solid Ratio

The comparison between the leach rates of lead in acidified and non-acidified leachates is shown in Figure D-2.4. For the second and third leach periods there is an order-of-magnitude difference between acidified and non-acidified leachates.

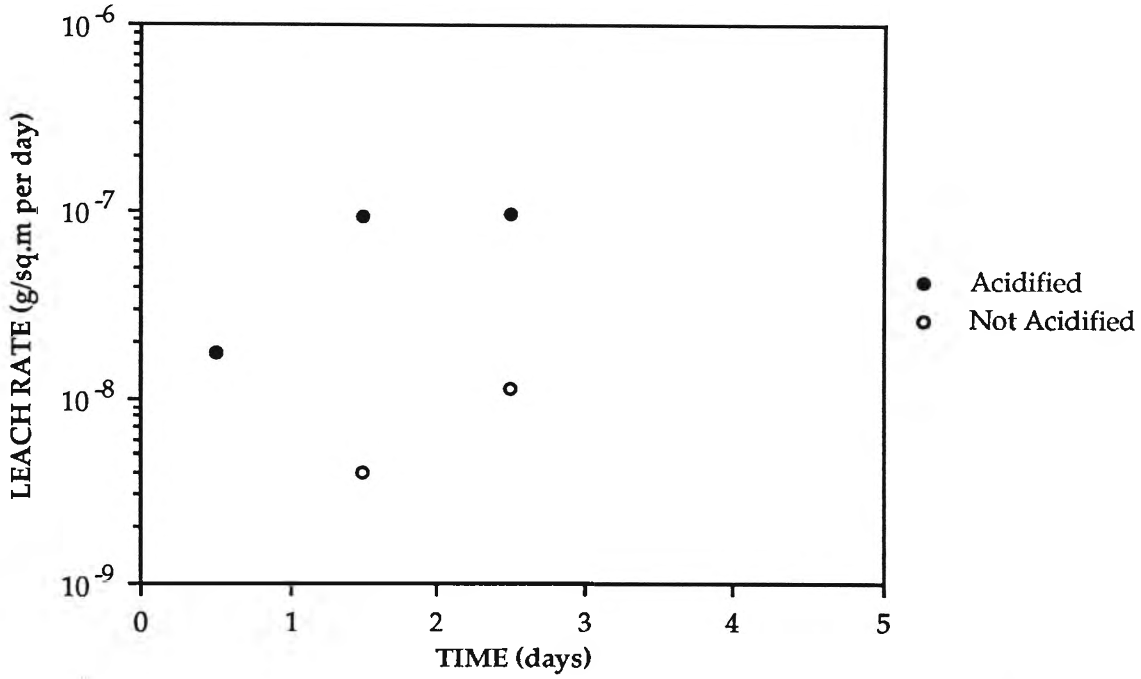


Figure D-2.4: **Leach Rate of Pb in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 5:1, Initial pH 4 at Ambient Temperature**

Arsenic - 4:1 Liquid to Solid Ratio

The comparison between the leach rates of arsenic in acidified and non-acidified leachates, at a liquid to solid ratio of 4:1, is shown in Figure D-2.5. Similar to the arsenic leach rates at a liquid to solid ratio of 5:1, the addition of acid to the leachate has had no obvious effect on the leach rates.

Chromium - 4:1 Liquid to Solid Ratio

The comparison between the leach rates of chromium in acidified and non-acidified leachates, at a liquid to solid ratio of 4:1, is shown in Figure D-2.6.

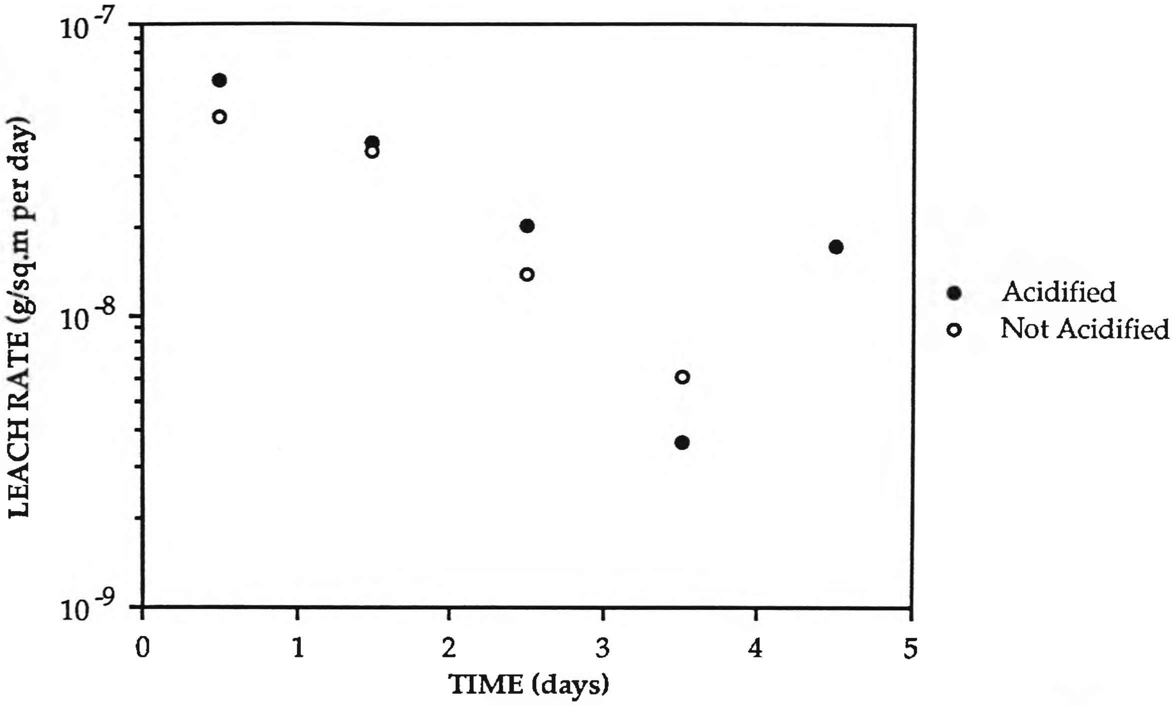


Figure D-2.5: Leach Rate of As in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 4:1, Initial pH 4 at Ambient Temperature

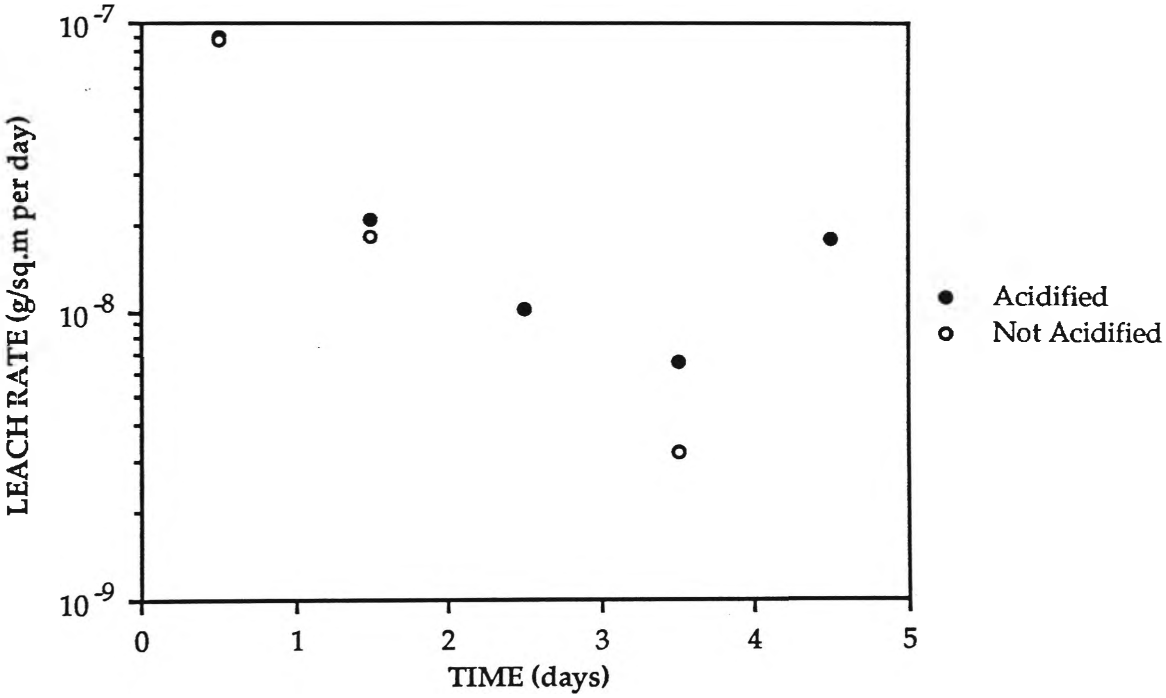


Figure D-2.6: Leach Rate of Cr in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 4:1, Initial pH 4 at Ambient Temperature

Once again, the addition of acid to the leachate has had no obvious effect on the leach rates calculated.

Copper - 4:1 Liquid to Solid Ratio

The comparison between the leach rates of copper in acidified and non-acidified leachates, at a liquid to solid ratio of 4:1, is shown in Figure D-2.7. The leach rates calculated for the acidified leachates are at least an order of magnitude greater than those for the non-acidified samples. Acidification of the leachates prior to analysis apparently inhibits sorption of copper on the colloidal fraction.

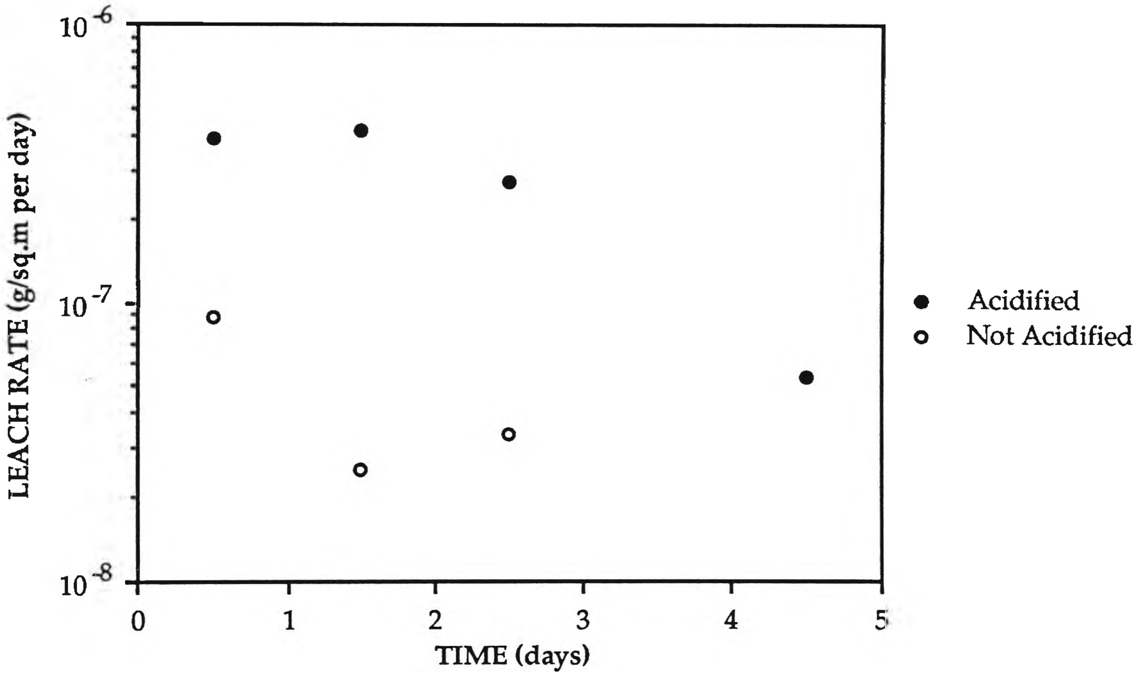


Figure D-2.7: **Leach Rate of Cu in Acidified and Non-acidified Leachates - Liquid to Solid Ratio 4:1, Initial pH 4 at Ambient Temperature**

In order to estimate the maximum release from the tailings, all leachates were subsequently acidified.

APPENDIX E

Leach Test Results

The concentrations and leach rates given in the following Tables are the net levels of the respective elements in the leachates, i.e. the total elemental concentration less background levels. Data were only considered to be significant if they were nominally a factor of five greater than the background levels. Where no values are given in the tables, those elemental concentrations were below detection limits. A number of the leachates were not analysed for thorium and uranium, and these have been indicated.

TABLE E-1: Leach Data for Preliminary Leach Test - L/S 1/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L1	1	1	4.08	8.57	210	158	21	656	1.21			14.72			5.06	
PJ02L1	1	2	4.02	8.62	250	150	16	260	24.20			162.74	12.02		41.90	250.56
PJ03L1	1	3	4.00	8.41	151	165	18	338	1.23			14.81			4.57	
PJ04L1	1	4	4.00	8.30	203	163	18	201	11.88	196.29		312.89		89.35	113.01	491.64
PJ05L1	1	5	4.02		190		15		3.95	28.11		23.53		5.81	6.90	73.77

TABLE E-2: Leach Data for Preliminary Leach Test - L/S 2.5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L2.5	1	1	4.04	8.78	211	160	16	379	10.94		19.46	72.67		14.00	19.70	75.02
PJ02L2.5	1	1	4.04	8.82	211	162	16	379	5.53		18.04	28.47		7.70	4.09	14.31
PJ03L2.5	1	2	4.00		176		26		4.98		4.62	6.63		3.19		
PJ04L2.5	1	2	4.00		176		26		6.21		4.32	25.53		6.36	17.94	
PJ05L2.5	1	3	4.04	8.39	240	159	17	139			3.55					
PJ06L2.5	1	3	4.04	8.72	240	160	17	140	3.56		2.08	10.39				
PJ07L2.5	1	4	4.04	8.61	170	164	16	102	0.84		0.89			0.87		
PJ08L2.5	1	4	4.04	8.72	170	162	16	104	1.01		0.63	6.00		0.95		
PJ09L2.5	1	5	4.08	8.37	210	168	21	111	1.48		2.22	36.86			13.05	31.43
PJ010L2.5	1	5	4.08	8.35	210	180	21	89			0.63	3.80				
PJ011L2.5	1	6	4.02	8.42	250	153	16	93	0.51		1.35	8.58			4.90	
PJ012L2.5	1	6	4.02	8.26	250	163	16	76			0.59	4.82				
PJ013L2.5	1	7	4.00	8.37	151	165	18	90				2.84				
PJ014L2.5	1	7	4.00	8.23	151	167	18	71				8.45				
PJ015L2.5	1	8	4.00	8.10	203	176	18	76		23.52	0.28			0.92		6.28
PJ016L2.5	1	8	4.00	8.30	203	164	18	71		54.08	0.73	7.65		2.88		22.52
PJ017L2.5	1	9	4.02		190		15			53.93	1.00			3.81		9.42
PJ018L2.5	1	9	4.02		190		15			196.62	1.71	6.72		1.57	7.72	15.30

TABLE E-3: Leach Data for Preliminary Leach Test - L/S 4/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L4	1	1	4.08	9.02	210	148	21	292	9.29		12.81	55.91			21.32	55.87
PJ02L4	1	2	4.02	9.14	250	139	16	133	5.6		2.97	59.87			20.45	50.14
PJ03L4	1	3	4.00	8.86	151	146	18	87	2.87		1.43	38.3			15.55	53.39
PJ04L4	1	4	4.00	8.56	203	163	18	76	0.52	29.54	0.92			0.66		8.63
PJ05L4	1	5	4.02		190		15		2.42	594.53	2.48	7.61		4.82		73.57

TABLE E-4: Leach Data for Preliminary Leach Test - Leachates Not Acidified - L/S 4/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L4na	1	1	4.08	9.02	210	148	21	292	6.84		12.58	12.76			3.75	
PJ02L4na	1	2	4.02	9.14	250	139	16	133	5.27		2.63	3.66				
PJ03L4na	1	3	4.00	8.86	151	146	18	87	1.92			4.68				
PJ04L4na	1	4	4.00	8.56	203	163	18	76	0.87		0.45			0.82		
PJ05L4na	1	5	4.02		190		15									

TABLE E-5: Leach Data for Preliminary Leach Test - L/S 5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L5	1	1	4.08	9.08	210	141	21	241	6.16		10.55	13.20			1.99	
PJ02L5	1	2	4.02	9.10	250	140	16	110	4.73		2.70	25.74			11.38	36.09
PJ03L5	1	3	4.00	8.82	151	150	18	79	2.56		1.61	41.11			11.24	
PJ04L5	1	4	4.00	8.45	203	163	18	69	1.66	111.79	1.50	6.17		1.35		14.66
PJ05L5	1	5	4.02		190		15		1.42	601.70	2.15	14.24		3.34		94.45

TABLE E-6: Leach Data for Preliminary Leach Test - Leachates Not Acidified - L/S 5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH Prior	pH After	Eh Prior (mV)	Eh After (mV)	Cond Prior (uS)	Cond After (uS)	Concentration (ug/L)							
									As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L5na	1	1	4.08	9.08	210	141	21	241								
PJ02L5na	1	2	4.02	9.10	250	140	16	110	4.36		2.06	3.30			0.48	
PJ03L5na	1	3	4.00	8.82	151	150	18	79	1.64		1.85	6.26			1.32	
PJ04L5na	1	4	4.00	8.45	203	163	18	69	0.98	0.33				0.49		11.76

TABLE E-7: Leach Rates for Preliminary Leach Test - L/S 1/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L1	1	1	1.28E-09			1.56E-08			5.37E-09	
PJ02L1	1	2	2.30E-08			1.54E-07	1.14E-08		3.98E-08	2.38E-07
PJ03L1	1	3	1.24E-09			1.49E-08			4.59E-09	
PJ04L1	1	4	1.19E-08	1.97E-07		3.14E-07		8.98E-08	1.14E-07	4.94E-07
PJ05L1	1	5	4.41E-09	3.14E-08		2.63E-08		6.49E-09	7.71E-09	8.24E-08

TABLE E-8: Leach Rates for Preliminary Leach Test - L/S 2.5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L2.5	1	1	4.48E-08		7.97E-08	2.98E-07		5.73E-08	8.07E-08	3.07E-07
PJ02L2.5	1	1	2.26E-08		7.39E-08	1.17E-07		3.15E-08	1.67E-08	5.86E-08
PJ03L2.5	1	2	2.13E-08		1.98E-08	2.84E-08		1.37E-08		
PJ04L2.5	1	2	2.66E-08		1.85E-08	1.09E-07		2.72E-08	7.68E-08	
PJ05L2.5	1	3			1.45E-08					
PJ06L2.5	1	3	1.52E-08		8.90E-09	4.45E-08				
PJ07L2.5	1	4	3.67E-09		3.89E-09			3.81E-09		
PJ08L2.5	1	4	4.42E-09		2.76E-09	2.62E-08		4.16E-09		
PJ09L2.5	1	5	6.47E-09		9.71E-09	1.61E-07			5.71E-08	1.37E-07
PJ010L2.5	1	5			2.58E-09	1.56E-08				
PJ011L2.5	1	6	2.18E-09		5.78E-09	3.67E-08			2.10E-08	
PJ012L2.5	1	6			2.53E-09	2.06E-08				
PJ013L2.5	1	7				1.27E-08				
PJ014L2.5	1	7				3.62E-08				
PJ015L2.5	1	8		1.05E-07	1.25E-09			4.11E-09		2.81E-08
PJ016L2.5	1	8		2.21E-07	2.99E-09	3.13E-08		1.18E-08		9.22E-08
PJ017L2.5	1	9		2.31E-07	4.28E-09			1.63E-08		4.03E-08
PJ018L2.5	1	9		7.87E-07	6.84E-09	2.69E-08		6.28E-09	3.09E-08	6.12E-08

TABLE E-9: Leach Rates for Preliminary Leach Test - L/S 4/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L4	1	1	6.43E-08		8.87E-08	3.87E-07			1.48E-07	3.87E-07
PJ02L4	1	2	3.88E-08		2.06E-08	4.15E-07			1.42E-07	3.47E-07
PJ03L4	1	3	2.05E-08		1.02E-08	2.74E-07			1.11E-07	3.82E-07
PJ04L4	1	4	3.72E-09	2.11E-07	6.58E-09			4.72E-09		6.17E-08
PJ05L4	1	5	1.73E-08	4.25E-06	1.77E-08	5.44E-08		3.45E-08		5.26E-07

TABLE E-10: Leach Rates for Preliminary Leach Test - Leachates Not Acidified - L/S 4/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L4na	1	1	4.74E-08		8.71E-08	8.84E-08			2.60E-08	
PJ02L4na	1	2	3.65E-08		1.82E-08	2.53E-08				
PJ03L4na	1	3	1.37E-08			3.34E-08				
PJ04L4na	1	4	6.22E-09		3.22E-09			5.86E-09		

TABLE E-11: Leach Rates for Preliminary Leach Test - L/S 5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L5	1	1	5.50E-08		9.43E-08	1.18E-07			1.78E-08	
PJ02L5	1	2	3.96E-08		2.26E-08	2.16E-07			9.53E-08	3.02E-07
PJ03L5	1	3	2.22E-08		1.39E-08	3.56E-07			9.73E-08	
PJ04L5	1	4	1.46E-08	9.83E-07	1.32E-08	5.43E-08		1.19E-08		1.29E-07
PJ05L5	1	5	1.23E-08	5.21E-06	1.86E-08	1.23E-07		2.89E-08		8.17E-07

TABLE E-12: Leach Rates for Preliminary Leach Test - Leachates Not Acidified - L/S 5/1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rate (g/sq. m per day)							
			As	Cd	Cr	Cu	Hg	Mn	Pb	Zn
PJ01L5na	1	1								
PJ02L5na	1	2	3.65E-08		1.73E-08	2.76E-08			4.02E-09	
PJ03L5na	1	3	1.42E-08		1.60E-08	5.42E-08			1.14E-08	
PJ04L5na	1	4	8.62E-09	2.90E-09				4.31E-09		1.03E-07

TABLE E-13: Eh, pH and Conductivity Data for L/S 5:1; Initial pH 4

Sample Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJ06L5	1	1	4.00	8.99	170	190	23	253
PJ08L5	1	2	4.00	8.89	206	183	22	118
PJ10L5	1	3	4.01	8.63	220	207	22	80
PJ12L5	1	4	3.98	8.58	219	236	23	73
PJ14L5	1	5	3.99	8.56	226	212	20	57
PJ16L5	1	6	3.99	8.64	216	230	21	53
PJ18L5	1	7	3.99	8.62	220	213	22	54
PJ20L5	1	8	4.00	8.5	211	214	18	58
PJ22L5	1	9	4.00	8.52	228	223	22	59
PJ24L5	1	10	4.00	8.63	224	203	22	58
PJ26L5	4	14	4.00	8.36	220	247	20	69
PJ28L5	3	17	4.00	8.41	230	246	22	74
PJ30L5	5	22	4.00	8.08	218	242	27	113
PJ32L5	3	25	3.99	8.00	210	228	25	106
PJ34L5	4	29	4.02	8.06	208	240	20	115
PJ36L5	3	32	4.02	8.11	214	248	21	117
PJ38L5	4	36	3.99	8.01	206	240	23	120
PJ40L5	3	39	3.99	7.94	203	246	23	117
PJ42L5	4	43	4.02	8.01	203	234	17	114
PJ44L5	7	50	4.03	7.85	199	236	18	138
PJ46L5	7	57	3.98	7.77	207	260	23	169
PJ48L5	7	64	4.01	7.85	231	253	17	186
PJ50L5	7	71	4.00	7.83	194	243	19	196
PJ52L5	30	101	4.00	7.63	210	220	19	378
PJ54L5	111	212	4.02	7.25	195	226	20	550

TABLE E-14: Eh, pH and Conductivity Data for L/S 5:1; Initial pH 9

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJ07L5	1	1	5.03	9.13	176	174	0	252
PJ09L5	1	2	9.00	9.01	116	186	5	114
PJ11L5	1	3	9.00	8.83	141	199	5	72
PJ13L5	1	4	9.02	8.92	133	204	4	59
PJ15L5	1	5	8.99	8.78	148	198	3	49
PJ17L5	1	6	8.99	8.88	146	200	3	48
PJ19L5	1	7	8.99	8.8	156	207	4	47
PJ21L5	1	8	9.00	8.7	138	210	2	53
PJ23L5	1	9	8.97	8.85	160	223	4	49
PJ25L5	1	10	9.03	8.77	164	214	4	50
PJ27L5	4	14	8.98	8.58	164	234	6	62
PJ29L5	3	17	9.00	8.61	170	226	3	67
PJ31L5	5	22	9.00	8.22	158	281	4	115
PJ33L5	3	25	8.99	8.15	160	300	6	103
PJ35L5	4	29	9.00	8.11	158	245	5	104
PJ37L5	3	32	9.03	8.15	162	241	6	116
PJ39L5	4	36	9.00	8.08	150	226	5	118
PJ41L5	3	39	8.98	8.03	156	232	4	112
PJ43L5	4	43	9.00	8.11	158	240	2	120
PJ45L5	7	50	9.02	7.93	160	238	10	144
PJ47L5	7	57	9.00	8	158	154	5	154
PJ49L5	7	64	9.00	7.89	168	188	7	188
PJ51L5	7	71	9.01	7.88	156	187	10	187
PJ53L5	30	101	9.01	7.63	165	228	9	373
PJ55L5	165	266	9.02	7.48	130	222	6	636

TABLE E-15: Eh, pH and Conductivity Data for L/S 10:1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJ01L10	1	1	4.00	9.09	170	181	23	164
PJ03L10	1	2	4.00	8.89	206	185	22	70
PJ05L10	1	3	4.01	8.73	220	197	22	55
PJ07L10	1	4	3.98	8.52	219	213	23	37
PJ09L10	1	5	3.99	8.64	226	209	20	47
PJ11L10	1	6	3.99	8.74	216	196	21	45
PJ13L10	1	7	3.99	8.77	220	206	22	45
PJ15L10	1	8	4.00	8.7	211	210	18	46
PJ17L10	1	9	4.00	8.81	228	218	22	47
PJ19L10	1	10	4.00	8.81	224	217	22	45
PJ21L10	4	14	4.00	8.61	220	233	20	55
PJ23L10	3	17	4.00	8.74	230	232	22	55
PJ25L10	5	22	4.00	8.34	218	410	27	86
PJ27L10	3	25	3.99	8.34	210	410	25	75
PJ29L10	4	29	4.02	8.16	208	242	20	80
PJ31L10	3	32	4.02	8.3	214	243	21	78
PJ33L10	4	36	3.99	8.41	206	230	23	78
PJ35L10	3	39	3.99	8.39	203	230	23	76
PJ37L10	4	43	4.02	8.23	203	238	17	80
PJ39L10	7	50	4.03	8.15	199	233	18	91
PJ41L10	7	57	3.98	8.03	207	253	23	114
PJ43L10	7	64	4.01	8.05	231	242	17	130
PJ45L10	7	71	4.00	8.05	194	238	19	130
PJ47L10	30	101	4.00	7.74	210	220	19	286
PJ49L10	165	266	4.02	7.57	195	227	20	507

TABLE E-16: Eh, pH and Conductivity Data for L/S 10:1; Initial pH 9

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJ02L10	1	1	5.03	9.2	176	167	0	158
PJ04L10	1	2	9.00	9.15	116	176	5	62
PJ06L10	1	3	9.00	9	141	191	5	48
PJ08L10	1	4	9.02	9.07	133	202	4	38
PJ10L10	1	5	8.99	9.11	148	200	3	38
PJ12L10	1	6	8.99	9.15	146	189	3	40
PJ14L10	1	7	8.99	9.09	156	194	4	39
PJ16L10	1	8	9.00	9.04	138	210	2	42
PJ18L10	1	9	8.97	9.11	160	203	4	41
PJ20L10	1	10	9.03	9.08	164	206	4	40
PJ22L10	4	14	8.98	8.94	164	229	6	45
PJ24L10	3	17	9.00	9.01	170	227	3	48
PJ26L10	5	22	9.00	8.52	158	373	4	73
PJ28L10	3	25	8.99	8.50	160	331	6	70
PJ30L10	4	29	9.00	8.4	158	223	5	75
PJ32L10	3	32	9.03	8.53	162	230	6	74
PJ34L10	4	36	9.00	8.47	150	220	5	76
PJ36L10	3	39	8.98	8.43	156	213	4	76
PJ38L10	4	43	9.00	8.54	158	228	2	73
PJ40L10	7	50	9.02	8.18	160	233	10	101
PJ42L10	7	57	9.00	8.04	158	233	5	109
PJ44L10	7	64	9.00	8.13	168	232	7	122
PJ46L10	7	71	9.01	8.11	156	219	10	126
PJ48L10	30	101	9.01	7.76	165	213	9	293
PJ50L10	133	234	9.02	7.69	130	220	6	390

TABLE E-17: Leachate Concentrations for L/S 5:1; Initial pH 4

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ06L5	33.5	518	5.83	1991		10.57	14.66	101		250	2.15	2.51	0.36	11.16	17.01
PJ08L5	31.0	698	2.99	2565		2.59	15.34	78		270	3.01	4.6	0.41	1.93	11.17
PJ10L5	32.0	234	1.3	5123		0.87	4.87			504			1.78	0.97	
PJ12L5	31.0	162	0.61	8254		0.8		217		754	1.55		0.35	1.54	
PJ14L5	31.0	122	0.62	7764		0.45		52		711	1.4			1.31	28.86
PJ16L5	31.0	142	0.6	8425						725	0.63		0.18	0.98	
PJ18L5	31.5		0.68	8210		0.35				681	0.7	1.95	0.37	0.48	
PJ20L5	32.0	140	0.61	8292		3.41		58		660			NA	NA	
PJ22L5	31.0	236	0.42	10175				22		856	0.95		1.3	0.85	44.31
PJ24L5	31.0	154	0.5	9888				28		792			NA	NA	
PJ26L5	31.0	196	0.33	12659			2.89			1144	1.83		0	2.26	
PJ28L5	30.0	104	0.68	12001			4.16			1126	2.01		NA	NA	14.8
PJ30L5	31.0			14828				28		1571	4.94	1.83	0.6	1.98	12.51
PJ32L5	30.0			15282			3.84	15		1825	6.1		0.12	1.87	25.74
PJ34L5	32.0	112		20254			12.01	20		2506	8.49		NA	NA	
PJ36L5	32.0			18106				61		2156	7.74		NA	NA	
PJ38L5	30.5	111	0.09	24674		0.17		32		3127	8.91	0.75	0.44	3.39	
PJ40L5	31.0	99	0.03	23939		0.17		21		3061	8.16	0.48	NA	NA	25.95
PJ42L5	31.5	142		25322		0.1	6.98			3291	7.69	0.1	0.03	1.25	6.85
PJ44L5	32.0	208		38162	1.26	0.38	3.7	341	0.34	5523	18.81	1.05	NA	NA	8.77
PJ46L5	31.5	188		37486		0.16	9.07	30		6054	35.87		NA	NA	13.49
PJ48L5	30.0	213	0.02	46637	19.45			64		7748	34.79			3.55	18.5
PJ50L5	31.0	179	0.21	39020			4.48	39		6611	43.1	0.96	NA	NA	
PJ52L5	30.5	280		69654		0.39	5.32	41		16402	185.33	1.83			32.39
PJ54L5	31.5	404		83986		0.61		11		34945	105.16		0.28	4.68	44.6

TABLE E-18: Leachate Concentrations for L/S 5:1; Initial pH 9

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ07L5	33.5	568	7.84	1841		11.83	19.69	162	1.39	247	2.83	2.84	0.51	11.67	
PJ09L5	32.0	532	3.84	2092		2.62	5.21	78		224	0.91	1.49	0.25	3.37	
PJ11L5	31.5	406	1.86	3859		0.98				357	0.71	3.03	0.32	1.42	10.58
PJ13L5	32.0	258	0.94	5639		0.46	2.42		0.6	488	0.42		0.12	0.98	
PJ15L5	33.0	304	0.72	6297		0.35		28		561	0.42		0.1	1.19	
PJ17L5	31.5	186	0.83	6593				14		528	0.48		0.18	0.82	6.89
PJ19L5	31.5	170	0.66	6478		0.32				531	0.37	1.33	0.21	0.34	
PJ21L5	31.5	228	0.53	7561		2.1		16		626	1.04	1.83		0.6	17.51
PJ23L5	31.5	234	0.54	7723			2.37			628		0.91	0.17	0.76	10.53
PJ25L5	32.5	198	0.65	7681			1.95	54		652			NA	NA	
PJ27L5	32.0	190	0.3	10428			2.43			991				1.06	
PJ29L5	30.0	92	0.33	9739						940					
PJ31L5	30.5			14003			1.35	24		1697	4.9	1.33	0.31	2.25	8.1
PJ33L5	31.0	188	0.09	15748				24		2181	5.1	1.19			
PJ35L5	31.0	154	0.12	14469				47		2153	5.19		NA	NA	
PJ37L5	31.5		0.22	15420			3.65	18		2200	5.84	5.28	NA	NA	6.9
PJ39L5	31.0	131	0.03	25064	1.21	0.12	0.9			3579	7.21	0.78	NA	NA	5.63
PJ41L5	31.0	107		22051		0.19		31		3265	6.26	1.11	0.04	1.53	6.81
PJ43L5	33.0	136		23775		0.11	4.84	22		3643	7.36		0.07	1.09	
PJ45L5	31.0	248		21148	1.34	0.2	10.39		0.32	3987	18.16	1.37	NA	NA	8.84
PJ47L5	31.0	171		31704			3.24	19		6073	23.15				
PJ49L5	31.0	171	0.09	32949	18.81	0.14	0.49	13		6715	30.5	1.29	0.03	0.61	9.45
PJ51L5	31.5	121	0.02	35430			4.54	16		6817	33.16		NA	NA	
PJ53L5	31.5	227		62985				16		16302	149.01		NA	NA	
PJ55L5	31.0	258	1.29	74371		6.17				34569	86.75	2.63	0.06	3.43	

TABLE E-19: Leachate Concentrations for L/S 10:1; Initial pH 4

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ01L10	40.0	1648	3.89	2884		5.4	6.23	212		357	2.33	2.26	0.37	5.84	12.7
PJ03L10	38.5	376	1.39	4359		0.99		44		360	0.55		0.18	1.31	
PJ05L10	38.0	363	0.93	6541						538			0.11	0.89	
PJ07L10	39.0	245	0.71	7633		0.29				530	0.29			0.75	
PJ09L10	39.0	261	0.64	7335		0.3			0.58	554	1.36			0.9	
PJ11L10	38.0	267	0.64	7416						465	0.94		0.19	0.57	
PJ13L10	38.0	265	0.58	7359		0.2				461	0.26	2.19	0.07	0.58	
PJ15L10	38.0	352	0.43	9885		0.45		32		584				0.38	
PJ17L10	38.5	345	0.48	10108				30		599				0.54	5.52
PJ19L10	39.0	330	0.43	9273				28		546		2.22	0.05	0.34	
PJ21L10	38.0	187	0.25	11804						807	2.42			0.75	
PJ23L10	38.0	130	0.38	9130			1.29			604					
PJ25L10	38.0		0.39	11759				14		1005	1.95			1.3	
PJ27L10	38.0	166		14523			1.95			1353	1.9				4.45
PJ29L10	39.0	178		16703				38		1559	2.66		NA	NA	
PJ31L10	39.0	126		14367						1404	2.14		NA	NA	
PJ33L10	38.0	102		14793		0.1		31		1528	1.71	0.13		1.02	
PJ35L10	37.5	85		15008		0.09		13		1514		0.12	NA	NA	3.92
PJ37L10	38.0	109		15526		0.09				1595	1.76	0.14		0.58	
PJ39L10	38.0	130		21910	1.13	0.13			0.38	2653	4.93	0.55	NA	NA	
PJ41L10	38.0	168		26070		0.18		19		3656	10.76		0.04	1.4	
PJ43L10	37.0	130		28081	18.53			23		4211	11.13		NA	NA	25.12
PJ45L10	38.0	97		25570		0.43	9.5	10		3778	11.36	1.96	NA	NA	13.84
PJ47L10	37.0	172		49169		2.57		43		10462	72.45	1.63	NA	NA	
PJ49L10	37.0	225	0.85	64426		6.89				24685	7.87		0.1	3.46	

TABLE E-20: Leachate Concentrations for L/S 10:1; Initial pH 9

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ02L10	40.0	1569	4.68	2686		5.59	5.24	83		337	1.24	1.84	0.38	4.77	
PJ04L10	38.0	424	1.93	3148		0.85		36		268	0.53		NA	NA	
PJ06L10	38.5	565	1.19	4824		0.36				393			0.11	0.59	
PJ08L10	38.5	288	0.87	5606		0.28			2.21	367	0.37	2.26	0.12	0.53	
PJ10L10	39.0	406	0.81	5406	4.98	0.38	0.78	20	0.64	390	0.29	0.44	0.09	0.48	3.95
PJ12L10	39.0	251	0.73	5492			3.28	30		343	0.37		0.16	0.36	7.07
PJ14L10	38.0	286	0.58	5431			3.42			344	0.33	3.5	NA	NA	12.66
PJ16L10	38.5	342	0.51	7790		0.77	3.52	27		457	0.43			0.27	
PJ18L10	39.5	338	0.42	7594				72		500			0.04	0.37	54.38
PJ20L10	38.5	422	0.46	7160						487				0.25	
PJ22L10	39.0	255	0.3	9743				16		681				0.5	
PJ24L10	38.5	146	0.2	7155						518					
PJ26L10	39.0	62		9365				15		857	0.87	0.78	0.09	0.98	3.27
PJ28L10	38.0	147	0.07	13034				244		1411	1.19				
PJ30L10	38.5	163	0.11	10948						1282	2.27	3.66	NA	NA	
PJ32L10	39.0	119		11743		0.49	6.81	30		1391	1.44	0.95	NA	NA	8.6
PJ34L10	38.5	128		13132	0.71	0.09	1.36	13		1605		0.04	NA	NA	3.54
PJ36L10	39.0	104		12817		0.16		12		1629		0.2		0.67	
PJ38L10	37.5	117	0.05	14078		0.1	1.32	16		1814	1.03			0.43	
PJ40L10	38.0	141		18131	1.19	0.2	7.03		0.22	3015	4.91	1.36	NA	NA	9.47
PJ42L10	38.0	137		19860	5.72	0.17	3.57	26		3582	7.4				
PJ44L10	37.5	142		21945	18.56	0.15	1.02	35		4090	6.93		0.06	0.95	6.84
PJ46L10	37.5	78	0.02	21588			2.98			3897	7.64		NA	NA	
PJ48L10	39.0	154	0.02	44955				17		11352	65.49		NA	NA	
PJ50L10	39.0	180	0.96	57591		3.67	8.95	28		22869	41.16		0.16	3.13	41.82

TABLE E-21: Leach Rates for L/S 5:1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rates (g/sq. m per day)													
			Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ06L5	1	1	4.84E-06	5.45E-08	1.86E-05		9.88E-08	1.37E-07	9.45E-07		2.34E-06	2.01E-08	2.35E-08	3.37E-09	1.04E-07	1.59E-07
PJ08L5	1	2	6.04E-06	2.59E-08	2.22E-05		2.24E-08	1.33E-07	6.75E-07		2.34E-06	2.60E-08	3.98E-08	3.55E-09	1.67E-08	9.67E-08
PJ10L5	1	3	2.09E-06	1.16E-08	4.58E-05		7.77E-09	4.35E-08			4.50E-06			1.59E-08	8.67E-09	
PJ12L5	1	4	1.40E-06	5.28E-09	7.14E-05		6.92E-09		1.88E-06		6.53E-06	1.34E-08		3.03E-09	1.33E-08	
PJ14L5	1	5	1.06E-06	5.37E-09	6.72E-05		3.89E-09		4.50E-07		6.15E-06	1.21E-08			1.13E-08	2.50E-07
PJ16L5	1	6	1.23E-06	5.19E-09	7.29E-05						6.27E-06	5.45E-09		1.56E-09	8.48E-09	
PJ18L5	1	7		5.98E-09	7.22E-05		3.08E-09				5.99E-06	6.16E-09	1.71E-08	3.25E-09	4.22E-09	
PJ20L5	1	8	1.25E-06	5.45E-09	7.41E-05		3.05E-08		5.18E-07		5.90E-06					
PJ22L5	1	9	2.04E-06	3.63E-09	8.81E-05				1.90E-07		7.41E-06	8.22E-09		1.13E-08	7.36E-09	3.83E-07
PJ24L5	1	10	1.33E-06	4.33E-09	8.56E-05				2.42E-07		6.85E-06					
PJ26L5	4	14	4.24E-07	7.14E-10	2.74E-05			6.25E-09			2.48E-06	3.96E-09			4.89E-09	
PJ28L5	3	17	2.90E-07	1.90E-09	3.35E-05			1.16E-08			3.14E-06	5.61E-09				4.13E-08
PJ30L5	5	22			2.57E-05				4.85E-08		2.72E-06	8.55E-09	3.17E-09	1.04E-09	3.43E-09	2.17E-08
PJ32L5	3	25			4.27E-05			1.07E-08	4.19E-08		5.09E-06	1.70E-08		3.35E-10	5.22E-09	7.19E-08
PJ34L5	4	29	2.50E-07		4.52E-05			2.68E-08	4.47E-08		5.60E-06	1.90E-08				
PJ36L5	3	32			5.39E-05				1.82E-07		6.42E-06	2.30E-08				
PJ38L5	4	36	2.36E-07	1.92E-10	5.25E-05		3.62E-10		6.81E-08		6.66E-06	1.90E-08	1.60E-09	9.37E-10	7.22E-09	
PJ40L5	3	39	2.86E-07	8.65E-11	6.91E-05		4.90E-10		6.06E-08		8.83E-06	2.35E-08	1.38E-09			7.49E-08
PJ42L5	4	43	3.12E-07		5.57E-05		2.20E-10	1.53E-08			7.23E-06	1.69E-08	2.20E-10	6.60E-11	2.75E-09	1.51E-08
PJ44L5	7	50	2.65E-07		4.87E-05	1.61E-09	4.85E-10	4.72E-09	4.35E-07	4.34E-10	7.05E-06	2.40E-08	1.34E-09			1.12E-08
PJ46L5	7	57	2.36E-07		4.71E-05		2.01E-10	1.14E-08	3.77E-08		7.61E-06	4.51E-08				1.69E-08
PJ48L5	7	64	2.55E-07	2.39E-11	5.58E-05	2.33E-08			7.66E-08		9.27E-06	4.16E-08			4.25E-09	2.21E-08
PJ50L5	7	71	2.21E-07	2.60E-10	4.82E-05			5.54E-09	4.82E-08		8.17E-06	5.33E-08	1.19E-09			
PJ52L5	30	101	7.95E-08		1.98E-05		1.11E-10	1.51E-09	1.16E-08		4.66E-06	5.26E-08	5.19E-10			9.19E-09
PJ54L5	111	212	3.20E-08		6.65E-06		4.83E-11		8.71E-10		2.77E-06	8.33E-09		2.22E-11	3.71E-10	3.53E-09

TABLE E-22: Leach Rates for L/S 5:1; Initial pH 9

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rates (g/sq. m per day)													
			Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ07L5	1	1	5.31E-06	7.33E-08	1.72E-05		1.11E-07	1.84E-07	1.52E-06	1.30E-08	2.31E-06	2.65E-08	2.66E-08	4.77E-09	1.09E-07	
PJ09L5	1	2	4.75E-06	3.43E-08	1.87E-05		2.34E-08	4.65E-08	6.97E-07		2.00E-06	8.13E-09	1.33E-08	2.23E-09	3.01E-08	
PJ11L5	1	3	3.57E-06	1.64E-08	3.39E-05		8.62E-09				3.14E-06	6.24E-09	2.66E-08	2.81E-09	1.25E-08	9.30E-08
PJ13L5	1	4	2.30E-06	8.40E-09	5.04E-05		4.11E-09	2.16E-08		5.36E-09	4.36E-06	3.75E-09		1.07E-09	8.75E-09	
PJ15L5	1	5	2.80E-06	6.63E-09	5.80E-05		3.22E-09		2.58E-07		5.17E-06	3.87E-09		9.21E-10	1.10E-08	
PJ17L5	1	6	1.64E-06	7.30E-09	5.80E-05				1.23E-07		4.64E-06	4.22E-09		1.58E-09	7.21E-09	6.06E-08
PJ19L5	1	7	1.49E-06	5.80E-09	5.70E-05		2.81E-09				4.67E-06	3.25E-09	1.17E-08	1.85E-09	2.99E-09	
PJ21L5	1	8	2.00E-06	4.66E-09	6.65E-05		1.85E-08		1.41E-07		5.50E-06	9.15E-09	1.61E-08		5.28E-09	1.54E-07
PJ23L5	1	9	2.06E-06	4.75E-09	6.79E-05			2.08E-08			5.52E-06		8.00E-09	1.49E-09	6.68E-09	9.26E-08
PJ25L5	1	10	1.80E-06	5.90E-09	6.97E-05			1.77E-08	4.90E-07		5.92E-06					
PJ27L5	4	14	4.24E-07	6.70E-10	2.33E-05			5.43E-09			2.21E-06				2.37E-09	
PJ29L5	3	17	2.57E-07	9.21E-10	2.72E-05						2.62E-06					
PJ31L5	5	22			2.38E-05			2.30E-09	4.09E-08		2.89E-06	8.34E-09	2.26E-09	5.28E-10	3.83E-09	1.38E-08
PJ33L5	3	25	5.42E-07	2.60E-10	4.54E-05				6.92E-08		6.29E-06	1.47E-08	3.43E-09			
PJ35L5	4	29	3.33E-07	2.60E-10	3.13E-05				1.02E-07		4.66E-06	1.12E-08				
PJ37L5	3	32		6.45E-10	4.52E-05			1.07E-08	5.28E-08		6.45E-06	1.71E-08	1.55E-08			2.02E-08
PJ39L5	4	36	2.83E-07	6.49E-11	5.42E-05	2.62E-09	2.60E-10	1.95E-09			7.74E-06	1.56E-08	1.69E-09			1.22E-08
PJ41L5	3	39	3.09E-07		6.36E-05		5.48E-10		8.94E-08		9.42E-06	1.81E-08	3.20E-09	1.15E-10	4.41E-09	1.96E-08
PJ43L5	4	43	3.13E-07		5.48E-05		2.53E-10	1.11E-08	5.07E-08		8.39E-06	1.70E-08		1.61E-10	2.51E-09	
PJ45L5	7	50	3.07E-07		2.61E-05	1.66E-09	2.47E-10	1.28E-08		3.96E-10	4.93E-06	2.25E-08	1.69E-09			1.09E-08
PJ47L5	7	57	2.11E-07		3.92E-05			4.01E-09	2.35E-08		7.51E-06	2.86E-08				
PJ49L5	7	64	2.11E-07	1.11E-10	4.07E-05	2.33E-08	1.73E-10	6.06E-10	1.61E-08		8.30E-06	3.77E-08	1.59E-09	3.71E-11	7.54E-10	1.17E-08
PJ51L5	7	71	1.52E-07	2.51E-11	4.45E-05			5.70E-09	2.01E-08		8.56E-06	4.17E-08				
PJ53L5	30	101	6.66E-08		1.85E-05				4.69E-09		4.78E-06	4.37E-08				
PJ55L5	165	266	1.35E-08	6.77E-11	3.90E-06		3.24E-10				1.81E-06	4.55E-09	1.38E-10	3.15E-12	1.80E-10	

TABLE E-23: Leach Rates for L/S 10:1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rates (g/sq. m per day)													
			Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ01L10	1	1	3.27E-05	7.72E-08	5.73E-05		1.07E-07	1.24E-07	4.21E-06		7.09E-06	4.63E-08	4.49E-08	7.35E-09	1.16E-07	2.52E-07
PJ03L10	1	2	7.19E-06	2.66E-08	8.33E-05		1.89E-08		8.41E-07		6.88E-06	1.05E-08		3.44E-09	2.50E-08	
PJ05L10	1	3	6.85E-06	1.75E-08	1.23E-04						1.01E-05			2.08E-09	1.68E-08	
PJ07L10	1	4	4.74E-06	1.37E-08	1.48E-04		5.61E-09				1.03E-05	5.61E-09			1.45E-08	
PJ09L10	1	5	5.05E-06	1.24E-08	1.42E-04		5.81E-09			1.12E-08	1.07E-05	2.63E-08			1.74E-08	
PJ11L10	1	6	5.04E-06	1.21E-08	1.40E-04						8.77E-06	1.77E-08		3.58E-09	1.08E-08	
PJ13L10	1	7	5.00E-06	1.09E-08	1.39E-04		3.77E-09				8.70E-06	4.91E-09	4.13E-08	1.32E-09	1.09E-08	
PJ15L10	1	8	6.64E-06	8.11E-09	1.86E-04		8.49E-09		6.04E-07		1.10E-05				7.17E-09	
PJ17L10	1	9	6.59E-06	9.17E-09	1.93E-04				5.73E-07		1.14E-05				1.03E-08	1.06E-07
PJ19L10	1	10	6.39E-06	8.33E-09	1.80E-04				5.42E-07		1.06E-05		4.30E-08	9.68E-10	6.58E-09	
PJ21L10	4	14	8.82E-07	1.18E-09	5.57E-05						3.81E-06	1.14E-08			3.54E-09	
PJ23L10	3	17	8.18E-07	2.39E-09	5.74E-05			8.11E-09			3.80E-06					
PJ25L10	5	22		1.47E-09	4.44E-05				5.28E-08		3.79E-06	7.36E-09			4.91E-09	
PJ27L10	3	25	1.04E-06		9.13E-05			1.23E-08			8.51E-06	1.19E-08				2.80E-08
PJ29L10	4	29	8.62E-07		8.09E-05				1.84E-07		7.55E-06	1.29E-08				
PJ31L10	3	32	8.13E-07		9.27E-05						9.06E-06	1.38E-08				
PJ33L10	4	36	4.81E-07		6.98E-05		4.72E-10		1.46E-07		7.21E-06	8.06E-09	6.13E-10		4.81E-09	
PJ35L10	3	39	5.27E-07		9.31E-05		5.59E-10		8.07E-08		9.40E-06		7.45E-10			2.43E-08
PJ37L10	4	43	5.14E-07		7.32E-05		4.24E-10				7.52E-06	8.30E-09	6.60E-10		2.74E-09	
PJ39L10	7	50	3.50E-07		5.90E-05	3.05E-09	3.50E-10			1.02E-09	7.15E-06	1.33E-08	1.48E-09			
PJ41L10	7	57	4.53E-07		7.03E-05		4.85E-10		5.12E-08		9.85E-06	2.90E-08		1.08E-10	3.77E-09	
PJ43L10	7	64	3.41E-07		7.37E-05	4.86E-08			6.04E-08		1.11E-05	2.92E-08				6.59E-08
PJ45L10	7	71	2.61E-07		6.89E-05		1.16E-09	2.56E-08	2.70E-08		1.02E-05	3.06E-08	5.28E-09			3.73E-08
PJ47L10	30	101	1.05E-07		3.01E-05		1.57E-09		2.63E-08		6.41E-06	4.44E-08	9.98E-10			
PJ49L10	165	266	2.50E-08	9.46E-11	7.17E-06		7.67E-10				2.75E-06	8.76E-10		1.11E-11	3.85E-10	

TABLE E-24: Leach Rates for L/S 10:1; Initial pH 9

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rates (g/sq. m per day)													
			Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ02L10	1	1	3.11E-05	9.29E-08	5.33E-05		1.11E-07	1.04E-07	1.65E-06		6.69E-06	2.46E-08	3.65E-08	7.54E-09	9.47E-08	
PJ04L10	1	2	8.00E-06	3.64E-08	5.94E-05		1.60E-08		6.79E-07		5.05E-06	9.99E-09				
PJ06L10	1	3	1.08E-05	2.27E-08	9.22E-05		6.88E-09				7.51E-06			2.10E-09	1.13E-08	
PJ08L10	1	4	5.50E-06	1.66E-08	1.07E-04		5.35E-09			4.22E-08	7.01E-06	7.07E-09	4.32E-08	2.29E-09	1.01E-08	
PJ10L10	1	5	7.86E-06	1.57E-08	1.05E-04	9.64E-08	7.35E-09	1.51E-08	3.87E-07	1.24E-08	7.55E-06	5.61E-09	8.52E-09	1.74E-09	9.29E-09	7.64E-08
PJ12L10	1	6	4.86E-06	1.41E-08	1.06E-04			6.35E-08	5.81E-07		6.64E-06	7.16E-09		3.10E-09	6.97E-09	1.37E-07
PJ14L10	1	7	5.39E-06	1.09E-08	1.02E-04			6.45E-08			6.49E-06	6.22E-09	6.60E-08			2.39E-07
PJ16L10	1	8	6.53E-06	9.74E-09	1.49E-04		1.47E-08	6.73E-08	5.16E-07		8.73E-06	8.22E-09			5.16E-09	
PJ18L10	1	9	6.63E-06	8.23E-09	1.49E-04				1.41E-06		9.80E-06			7.84E-10	7.25E-09	1.07E-06
PJ20L10	1	10	8.06E-06	8.79E-09	1.37E-04						9.30E-06				4.78E-09	
PJ22L10	4	14	1.23E-06	1.45E-09	4.71E-05				7.74E-08		3.29E-06				2.42E-09	
PJ24L10	3	17	9.30E-07	1.27E-09	4.56E-05						3.30E-06					
PJ26L10	5	22	2.40E-07		3.62E-05				5.81E-08		3.32E-06	3.37E-09	3.02E-09	3.48E-10	3.79E-09	1.27E-08
PJ28L10	3	25	9.24E-07	4.40E-10	8.19E-05				1.53E-06		8.87E-06	7.48E-09				
PJ30L10	4	29	7.79E-07	5.25E-10	5.23E-05						6.12E-06	1.08E-08	1.75E-08			
PJ32L10	3	32	7.68E-07		7.58E-05		3.16E-09	4.39E-08	1.94E-07		8.97E-06	9.29E-09	6.13E-09			5.55E-08
PJ34L10	4	36	6.11E-07		6.27E-05	3.39E-09	4.30E-10	6.50E-09	6.21E-08		7.67E-06		1.91E-10			1.69E-08
PJ36L10	3	39	6.71E-07		8.27E-05		1.03E-09		7.74E-08		1.05E-05		1.29E-09		4.32E-09	
PJ38L10	4	43	5.44E-07	2.33E-10	6.55E-05		4.65E-10	6.14E-09	7.44E-08		8.44E-06	4.79E-09			2.00E-09	
PJ40L10	7	50	3.80E-07		4.88E-05	3.21E-09	5.39E-10	1.89E-08		5.93E-10	8.12E-06	1.32E-08	3.66E-09			2.55E-08
PJ42L10	7	57	3.69E-07		5.35E-05	1.54E-08	4.58E-10	9.62E-09	7.00E-08		9.65E-06	1.99E-08				
PJ44L10	7	64	3.77E-07		5.83E-05	4.93E-08	3.99E-10	2.71E-09	9.30E-08		1.09E-05	1.84E-08		1.60E-10	2.53E-09	1.82E-08
PJ46L10	7	71	2.07E-07	5.32E-11	5.74E-05			7.92E-09			1.04E-05	2.03E-08				
PJ48L10	30	101	9.93E-08	1.29E-11	2.90E-05				1.10E-08		7.32E-06	4.22E-08				
PJ50L10	133	234	2.62E-08	1.40E-10	8.38E-06		5.34E-10	1.30E-09	4.07E-09		3.33E-06	5.99E-09		2.33E-11	4.55E-10	6.09E-09

TABLE E-25: Cumulative % Leached Against L/S Ratio - L/S 5:1; Initial pH 4

L/S Ratio	Duration of Leaching (Days)	Cumulative % Leached													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
5	1	2.19E-03	4.86E-01	3.78E-02		1.02E-01	2.93E-01	6.24E-04		1.72E-02	1.84E-03	4.33E-02	8.18E-03	1.12E+00	1.64E-01
10	1	5.14E-03	7.35E-01	8.65E-02		1.27E-01	6.00E-01	1.11E-03		3.58E-02	4.43E-03	1.23E-01	1.75E-02	1.31E+00	2.71E-01
15	1	6.13E-03	8.43E-01	1.84E-01		1.35E-01	6.97E-01	1.11E-03		7.06E-02	4.43E-03	1.23E-01	5.80E-02	1.41E+00	2.71E-01
20	1	6.81E-03	8.94E-01	3.41E-01		1.43E-01	6.97E-01	2.45E-03		1.23E-01	5.75E-03	1.23E-01	6.59E-02	1.56E+00	2.71E-01
25	1	7.32E-03	9.46E-01	4.88E-01		1.47E-01	6.97E-01	2.77E-03		1.72E-01	6.96E-03	1.23E-01	6.59E-02	1.69E+00	5.48E-01
30	1	7.92E-03	9.96E-01	6.48E-01		1.47E-01	6.97E-01	2.77E-03		2.21E-01	7.50E-03	1.23E-01	7.00E-02	1.79E+00	5.48E-01
35	1	7.92E-03	1.05E+00	8.04E-01		1.50E-01	6.97E-01	2.77E-03		2.68E-01	8.10E-03	1.56E-01	7.84E-02	1.84E+00	5.48E-01
40	1	8.52E-03	1.10E+00	9.61E-01		1.83E-01	6.97E-01	3.12E-03		3.14E-01	8.10E-03	1.56E-01	7.84E-02	1.84E+00	5.48E-01
45	1	9.51E-03	1.14E+00	1.15E+00		1.83E-01	6.97E-01	3.26E-03		3.73E-01	8.91E-03	1.56E-01	1.08E-01	1.92E+00	9.75E-01
50	1	1.02E-02	1.18E+00	1.34E+00		1.83E-01	6.97E-01	3.43E-03		4.27E-01	8.91E-03	1.56E-01	1.08E-01	1.92E+00	9.75E-01

TABLE E-26: Cumulative % Leached Against L/S Ratio - L/S 5:1; Initial pH 9

L/S Ratio	Duration of Leaching (Days)	Cumulative % Leached													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
5	1	2.40E-03	6.53E-01	3.50E-02		1.14E-01	3.94E-01	1.00E-03	6.95E-01	1.70E-02	2.43E-03	4.90E-02	1.16E-02	1.17E+00	
10	1	4.65E-03	9.73E-01	7.47E-02		1.39E-01	4.98E-01	1.48E-03	6.95E-01	3.25E-02	3.21E-03	7.47E-02	1.73E-02	1.50E+00	
15	1	6.36E-03	1.13E+00	1.48E-01		1.48E-01	4.98E-01	1.48E-03	6.95E-01	5.71E-02	3.82E-03	1.27E-01	2.45E-02	1.65E+00	1.02E-01
20	1	7.45E-03	1.21E+00	2.55E-01		1.53E-01	5.46E-01	1.48E-03	9.95E-01	9.07E-02	4.18E-03	1.27E-01	2.73E-02	1.74E+00	1.02E-01
25	1	8.74E-03	1.27E+00	3.75E-01		1.56E-01	5.46E-01	1.65E-03	9.95E-01	1.29E-01	4.54E-03	1.27E-01	2.95E-02	1.86E+00	1.02E-01
30	1	9.52E-03	1.34E+00	5.00E-01		1.56E-01	5.46E-01	1.74E-03	9.95E-01	1.66E-01	4.95E-03	1.27E-01	3.36E-02	1.95E+00	1.68E-01
35	1	1.02E-02	1.39E+00	6.23E-01		1.59E-01	5.46E-01	1.74E-03	9.95E-01	2.02E-01	5.27E-03	1.50E-01	3.84E-02	1.98E+00	1.68E-01
40	1	1.12E-02	1.44E+00	7.66E-01		1.79E-01	5.46E-01	1.84E-03	9.95E-01	2.45E-01	6.16E-03	1.81E-01	3.84E-02	2.04E+00	3.36E-01
45	1	1.22E-02	1.48E+00	9.13E-01		1.79E-01	5.94E-01	1.84E-03	9.95E-01	2.89E-01	6.16E-03	1.97E-01	4.23E-02	2.12E+00	4.38E-01
50	1	1.30E-02	1.53E+00	1.06E+00		1.79E-01	6.33E-01	2.17E-03	9.95E-01	3.34E-01	6.16E-03	1.97E-01	4.23E-02	2.12E+00	4.38E-01

TABLE E-27: Cumulative % Leached Against L/S Ratio - L/S 10:1; Initial pH 4

L/S Ratio	Duration of Leaching (Days)	Cumulative % Leached													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
10	1	1.39E-02	6.48E-01	1.10E-01		1.04E-01	2.49E-01	2.62E-03		4.92E-02	4.00E-03	7.79E-02	1.68E-02	1.17E+00	2.44E-01
20	1	1.71E-02	8.80E-01	2.75E-01		1.23E-01	2.49E-01	3.16E-03		9.88E-02	4.94E-03	7.79E-02	2.50E-02	1.43E+00	2.44E-01
30	1	2.02E-02	1.04E+00	5.23E-01		1.23E-01	2.49E-01	3.16E-03		1.73E-01	4.94E-03	7.79E-02	3.00E-02	1.61E+00	2.44E-01
40	1	2.22E-02	1.15E+00	8.13E-01		1.28E-01	2.49E-01	3.16E-03		2.46E-01	5.44E-03	7.79E-02	3.00E-02	1.76E+00	2.44E-01
50	1	2.44E-02	1.26E+00	1.09E+00		1.34E-01	2.49E-01	3.16E-03	5.80E-01	3.22E-01	7.77E-03	7.79E-02	3.00E-02	1.94E+00	2.44E-01
60	1	2.67E-02	1.37E+00	1.37E+00		1.34E-01	2.49E-01	3.16E-03	5.80E-01	3.86E-01	9.38E-03	7.79E-02	3.86E-02	2.05E+00	2.44E-01
70	1	2.89E-02	1.46E+00	1.65E+00		1.38E-01	2.49E-01	3.16E-03	5.80E-01	4.50E-01	9.83E-03	1.53E-01	4.18E-02	2.17E+00	2.44E-01
80	1	3.19E-02	1.54E+00	2.03E+00		1.47E-01	2.49E-01	3.56E-03	5.80E-01	5.30E-01	9.83E-03	1.53E-01	4.18E-02	2.24E+00	2.44E-01
90	1	3.48E-02	1.62E+00	2.41E+00		1.47E-01	2.49E-01	3.93E-03	5.80E-01	6.13E-01	9.83E-03	1.53E-01	4.18E-02	2.35E+00	3.50E-01
100	1	3.76E-02	1.69E+00	2.76E+00		1.47E-01	2.49E-01	4.27E-03	5.80E-01	6.88E-01	9.83E-03	2.30E-01	4.41E-02	2.42E+00	3.50E-01

TABLE E-28: Cumulative % Leached Against L/S Ratio - L/S 10:1; Initial pH 9

L/S Ratio	Duration of Leaching (Days)	Cumulative % Leached													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
10	1	1.33E-02	7.80E-01	1.02E-01		1.08E-01	2.10E-01	1.02E-03		4.64E-02	2.13E-03	6.34E-02	1.73E-02	9.54E-01	
20	1	1.68E-02	1.10E+00	2.22E-01		1.24E-01	2.10E-01	1.47E-03		8.34E-02	3.04E-03	6.34E-02	1.73E-02	9.54E-01	
30	1	2.16E-02	1.30E+00	4.05E-01		1.31E-01	2.10E-01	1.47E-03		1.38E-01	3.04E-03	6.34E-02	2.23E-02	1.07E+00	
40	1	2.40E-02	1.45E+00	6.18E-01		1.36E-01	2.10E-01	1.47E-03	2.21E+00	1.88E-01	3.67E-03	1.41E-01	2.77E-02	1.18E+00	
50	1	2.75E-02	1.58E+00	8.23E-01	2.49E+00	1.43E-01	2.41E-01	1.72E-03	2.85E+00	2.42E-01	4.17E-03	1.57E-01	3.18E-02	1.27E+00	7.60E-02
60	1	2.96E-02	1.70E+00	1.03E+00	2.49E+00	1.43E-01	3.72E-01	2.09E-03	2.85E+00	2.89E-01	4.80E-03	1.57E-01	3.91E-02	1.35E+00	2.12E-01
70	1	3.20E-02	1.80E+00	1.24E+00	2.49E+00	1.43E-01	5.09E-01	2.09E-03	2.85E+00	3.37E-01	5.37E-03	2.77E-01	3.91E-02	1.35E+00	4.55E-01
80	1	3.49E-02	1.88E+00	1.53E+00	2.49E+00	1.58E-01	6.50E-01	2.42E-03	2.85E+00	4.00E-01	6.11E-03	2.77E-01	3.91E-02	1.40E+00	4.55E-01
90	1	3.78E-02	1.95E+00	1.82E+00	2.49E+00	1.58E-01	6.50E-01	3.31E-03	2.85E+00	4.68E-01	6.11E-03	2.77E-01	4.09E-02	1.47E+00	1.50E+00
100	1	4.13E-02	2.03E+00	2.09E+00	2.49E+00	1.58E-01	6.50E-01	3.31E-03	2.85E+00	5.36E-01	6.11E-03	2.77E-01	4.09E-02	1.52E+00	1.50E+00

TABLE E-29: Eh, pH and Conductivity Data for Oxidation Test L/S 10:1; Initial pH 4

Sample Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJOX1	1	1	4.04	8.25	190	196	-12	160
PJOX2	1	2	4.04	8.54	190	193	-12	45
PJOX3	1	3	4.02	8.48	185	189	-13	22
PJOX4	1	4	3.99	8.5	190	192	-7	12
PJOX5	1	5	3.99	8.41	191	176	-14	16
PJOX6	1	6	4.01	8.44	203	180	-6	14
PJOX7	1	7	3.99	8.53	193	180	-13	15
PJOX8	1	8	4.00	8.62	185	186	-7	10
PJOX9	1	9	4.00	9.12	NM	190	NM	-100
PJOX10	1	10	4.02	8.91	215	NM	-51	NM
PJOX11	5	15	3.99	8.42	NM	178	NM	55
PJOX12	3	18	3.97	8.57	192	175	20	45
PJOX13	3	21	4.03	8.7	182	164	21	46
PJOX14	3	24	4.03	8.22	204	193	20	46
PJOX15	4	28	4.00	8.52	202	187	18	43
PJOX16	4	32	3.99	8.3	192	192	17	47
PJOX17	3	35	4.02	8.21	195	190	18	48
PJOX18	4	39	4.03	8.22	195	200	17	47
PJOX19	3	42	3.97	8.28	197	199	17	48
PJOX20	4	46	3.99	8.46	198	207	20	47
PJOX21	4	50	3.99	8.4	202	197	17	40
PJOX22	6	56	3.99	7.74	200	257	17	62
PJOX23	9	65	4.03	7.74	248	272	15	77
PJOX24	7	72	3.97	8.01	254	260	13	68
PJOX25	7	79	3.99	7.87	238	236	21	73

NM - Not Measured

TABLE E-30: Leachate Concentrations for Oxidised Test - L/S 10:1; Initial pH 4

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJOX1	40.0	170	1.13	7461		6.61			10.62	742	1.47		0.44	7.16	15.48
PJOX2	41.0	255	1.27	5709	8.04					456	0.98			1.86	5.87
PJOX3	40.0	229	1.22	5547						390				0.92	
PJOX4	40.0	199	0.99	5714			16.16		7.81	360	1.27	14.93	6.52	1.1	
PJOX5	40.5	179		5318						309			1.03	0.51	
PJOX6	41.0	186	0.84	5426					8.58	313	0.55	1.65	0.77	0.48	
PJOX7	40.5	164	0.8	5341					8.99	283			0.41	0.4	
PJOX8	40.0	157	0.73	5348					18.72	266	0.19		0.37	0.36	
PJOX9	40.5	179	0.71	5186						248	0.27			0.47	
PJOX10	41.0	148	0.55	7361						354	0.35		0.87	0.51	
PJOX11	40.5	123	0.36	8825				26		456	0.41			0.68	
PJOX12	40.0	115	0.38	7683						397	0.43		0.08	0.6	
PJOX13	39.5	174	0.3	7350						372	0.63		0.12	0.5	
PJOX14	40.0	117	0.2	7304						386	0.49			0.44	1.98
PJOX15	40.5	122	0.23	7266						380				0.45	
PJOX16	40.0	144	0.2	7887						423				0.42	
PJOX17	40.0	218	0.16	8451						480	0.87			0.5	
PJOX18	41.0	127		8214						482				0.42	
PJOX19	40.5	146		8571						521	0.7			0.42	
PJOX20	40.5	125		9439				15		626	0.91		0.05	0.47	2.72
PJOX21	40.5	176		8984				17		596	1.02			0.41	3.7
PJOX22	40.0	109		10675				10		834	1.84			0.51	8.29
PJOX23	40.0	90		13044			3.61			1242	3.28			0.79	7.39
PJOX24	40.5	89		12017						1161	2.11				8.58
PJOX25	41.0	105		12817					3.8	1284	2.99			0.51	10.73

TABLE E-31: Leach Rates for Oxidation Leach Tests L/S 10:1; Initial pH 4

Leachate Ident.	Duration of Leach (Days)	Total Leaching Time (Days)	Leach Rates (g/sq. m per day)													
			Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJOX1	1	1	3.38E-06	2.24E-08	1.48E-04		1.31E-07			2.11E-07	1.47E-05	2.92E-08		8.74E-09	1.42E-07	3.07E-07
PJOX2	1	2	5.19E-06	2.58E-08	1.16E-04	1.64E-07					9.28E-06	1.99E-08			3.79E-08	1.19E-07
PJOX3	1	3	4.55E-06	2.42E-08	1.10E-04						7.74E-06				1.83E-08	
PJOX4	1	4	3.95E-06	1.97E-08	1.13E-04			3.21E-07		1.55E-07	7.15E-06	2.52E-08	2.96E-07	1.29E-07	2.18E-08	
PJOX5	1	5	3.60E-06		1.07E-04						6.21E-06			2.07E-08	1.03E-08	
PJOX6	1	6	3.79E-06	1.71E-08	1.10E-04					1.75E-07	6.37E-06	1.12E-08	3.36E-08	1.57E-08	9.77E-09	
PJOX7	1	7	3.30E-06	1.61E-08	1.07E-04					1.81E-07	5.69E-06			8.24E-09	8.04E-09	
PJOX8	1	8	3.12E-06	1.45E-08	1.06E-04					3.72E-07	5.28E-06	3.77E-09		7.35E-09	7.15E-09	
PJOX9	1	9	3.60E-06	1.43E-08	1.04E-04						4.99E-06	5.43E-09			9.45E-09	
PJOX10	1	10	3.01E-06	1.12E-08	1.50E-04						7.20E-06	7.12E-09		1.77E-08	1.04E-08	
PJOX11	5	15	4.95E-07	1.45E-09	3.55E-05				1.05E-07		1.83E-06	1.65E-09			2.73E-09	
PJOX12	3	18	7.61E-07	2.51E-09	5.08E-05						2.63E-06	2.85E-09		5.29E-10	3.97E-09	
PJOX13	3	21	1.14E-06	1.96E-09	4.80E-05						2.43E-06	4.12E-09		7.84E-10	3.27E-09	
PJOX14	3	24	7.74E-07	1.32E-09	4.83E-05						2.55E-06	3.24E-09			2.91E-09	1.31E-08
PJOX15	4	28	6.13E-07	1.16E-09	3.65E-05						1.91E-06				2.26E-09	
PJOX16	4	32	7.15E-07	9.93E-10	3.91E-05						2.10E-06				2.08E-09	
PJOX17	3	35	1.44E-06	1.06E-09	5.59E-05						3.18E-06	5.76E-09			3.31E-09	
PJOX18	4	39	6.46E-07		4.18E-05						2.45E-06				2.14E-09	
PJOX19	3	42	9.78E-07		5.74E-05						3.49E-06	4.69E-09			2.81E-09	
PJOX20	4	46	6.28E-07		4.74E-05				7.54E-08		3.15E-06	4.57E-09		2.51E-10	2.36E-09	1.37E-08
PJOX21	4	50	8.84E-07		4.51E-05				8.54E-08		3.00E-06	5.13E-09			2.06E-09	1.86E-08
PJOX22	6	56	3.61E-07		3.53E-05				3.31E-08		2.76E-06	6.09E-09			1.69E-09	2.74E-08
PJOX23	9	65	1.99E-07		2.88E-05			7.96E-09			2.74E-06	7.24E-09			1.74E-09	1.63E-08
PJOX24	7	72	2.56E-07		3.45E-05						3.33E-06	6.06E-09				2.46E-08
PJOX25	7	79.0	3.05E-07		3.73E-05					1.10E-08	3.73E-06	8.69E-09			1.48E-09	3.12E-08

TABLE E-32: Eh, pH and Conductivity Data for 32 Hour Test - L/S 10:1; Initial pH 4

Sample Ident.	Duration of Leach (Days)	pH (Prior to Leaching)	pH (After Leaching)	Eh - Prior to Leaching (mV)	Eh - After Leaching (mV)	Conductivity - Prior to Leaching (uS)	Conductivity - After Leaching (uS)
PJ5MIN	0.083	4.00	9.27	199	166	-12	115
PJ15MIN	0.25	4.04	9.35	190	159	-12	97
PJ30MIN	0.5	4.04	9.37	190	173	-12	98
PJ1HR	1	4.04	9.41	190	170	-12	100
PJ2HR	2	4.04	9.3	190	163	-12	98
PJ4HR	4	4.00	9.21	199	173	-12	110
PJ8HR	8	3.99	9.12	191	181	-14	109
PJ16HR	16	4.00	9.16	199	170	-12	120
PJ24HR	24	4.04	9.14	190	170	-12	112
PJ32HR	32	4.02	9.04	185	184	-13	124

TABLE E-33: Leachate Concentrations for 32 Hour Test L/S 10:1; Initial pH 4

Leachate Ident.	Leachate Volume (mL)	Elemental Concentration (ug/L)													
		Al	As	Ca	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Pb	Th	U	Zn
PJ5MIN	40.0	294	2.38	1260	9.36	2.44			13.73	115	2			4.51	8.35
PJ15MIN	41.0	298	2.51	1432		2.57			11.27	126	1.72	0.96	0.46	4.36	10.15
PJ30MIN	40.5	276	2.79	1409		2.6			13.1	138	1.72	1.00		4.69	12.96
PJ1HR	41.0	287	2.64	1487		2.63	6.82			136	1.76			4.56	11.64
PJ2HR	41.0	313	3.09	1502		2.66			10.71	135	1.61	0.76		4.51	11.51
PJ4HR	40.5	303	3.49	1774		3.21			14.45	169	1.31			4.83	8.42
PJ8HR	40.0	308	3.5	1805		3.95	13.62		17.03	181	2.55	7.04	14.41	5.53	
PJ16HR	40.0	265	4.1	2010		3.92	6.19			193	1.27	1.22		5.7	11.86
PJ24HR	40.0	286	4.11	1830		4.18	9.48		14.81	191	1.89	1.31	0.68	5.11	49.08
PJ32HR	40.5	264	3.9	2063		4.4	6.5	72	12.67	205	1.52			5.58	