SOLUTE TRANSPORT MODELLING OF LATROBE VALLEY ASH DISPOSAL SITES

By

Gavin M. Mudd

B. Env. Eng. (Hons) *RMIT University*

AUGUST 2000

Thesis submitted in fulfillment of the requirements for admission to the degree of Doctor of Philosophy.

School of the Built Environment
Faculty of Engineering & Science
VICTORIA UNIVERSITY

DEDICATION

To my Nanna, my family and all those who work the land

May their knowledge and that in this thesis help to
continually improve the environment and human happiness

DECLARATION

To the best of my knowledge this thesis contains no material that has been submitted for the award of any other degree or diploma at this or any other University and contains no material previously published or written by any other person except where due reference has been made in the text.

Gavin M. Mudd

ACKNOWLEDGEMENTS

"If I have seen far, it is because I have stood on the shoulders of giants."
(or because I try to work hard !)

First and foremost, I would sincerely like to thank my parents for all of their support and encouragement during my many years of schooling. No thesis can do justice to the love and hope of the truly dedicated parents I am blessed with.

Secondly, I would like to thank my principal supervisor Dr Jayantha Kodikara. His commitment to academic excellence and genuine support and guidance is greatly appreciated. The help of Jason Beard and Dr Domenic Caridi, Dept. of Chemistry at Victoria University, with the batch tests and chemical aspects of this thesis is appreciated. Additional academic support was gratefully provided by Dr Tamie Weaver (School of Earth Sciences, Uni. of Melbourne) and Dr Sam Yuen (Dept. of Civil & Environmental Eng., Uni. of Melbourne). Their combined knowledge and insights were most helpful at critical parts of this thesis.

The two industry partners, Geo-Eng Australia Pty Ltd and Loy Yang Power Ltd, deserve much praise and thanks for providing me with the freedom and resources to undertake the research work presented in this thesis. In particular, I would like to acknowledge Terry McKinley, Russell Pentland, Robin Dunn, Ian Soutar, John Bradley, Chris Daniels, Wayne Gibson, Frank Kappl, Jurgen Schaeffer and Frank Vanooeselaar. Several other staff from Loy Yang Power and Geo-Eng Australia also deserve credit for help at various times. I hope that this thesis is a worthy contribution to continuing environmental and engineering efforts in the Latrobe Valley.

And finally, to my family dog, Pepsi, many thanks for keeping me company during the (many) late nights as I worked towards the completion of this thesis. Such genuine love and devotion is inspirational to all who remain open to it.

ABSTRACT

The successful management of solid wastes arising from the combustion of low-rank coal for electricity generation presents significant engineering and environmental challenges. The power stations in the Latrobe Valley region of Victoria, Australia, have long recognised the need for improved long term understanding of ash disposal. This thesis presents the work undertaken in evaluating the mechanisms which lead to the transport of solutes from ash disposal and develops a methodology to quantify their potential long term impacts on groundwaters beneath a disposal site. The Loy Yang power station is used as a case study.

A detailed literature review is presented on the mechanisms involved in the leaching of solutes from ash disposal. In general, the release of solutes is well understood and is related to the dissolution of more soluble minerals in the ash and advective transport through pore waters as leachate, although the exact controls for trace elements is less well documented. The proportions of particular solutes and/or trace elements is site specific. For the Latrobe Valley, however, there remains little research undertaken on the behaviour of Loy Yang ash, especially aged or leached ash excavated from a disposal pond after a period of some 6 to 12 months.

The principal environmental concerns relating to the disposal of ash are the potential for groundwater contamination from salt fluxes and the transport of trace elements. Thus long term disposal requires a thorough understanding of both the solute fluxes from the ash as well as the controls on the transport of these solutes through groundwater. Predicting the behaviour of ash and the leached solutes under field conditions is difficult and common laboratory tests have been found to be inadequate.

The transport of sulfate in seepage was investigated through back analysis of monitoring data, field monitoring, bacterial analysis and modelling. Sulfate was shown to be undergoing strong biogeochemical reactions which attenuate its rate of migration in shallow groundwaters at the Loy Yang power station. The application of a kinetic solute transport model was able to model the monitoring data obtained to date.

The chemical quality of the ash, and its source from the power station, is a critical aspect of disposal since this primarily determines the leachability and potential fluxes. After slurrying and disposal in a saturated pond, the amount of soluble minerals is lower and therefore the ash presents a lower potential for groundwater impacts.

For ash excavated from a disposal pond and placed within a low moisture environment, such as an Overburden Dump, the potential for leaching and solute transport must be considered differently to that in a saturated disposal pond. Two field trial cells were operated for about 14 months to investigate such behaviour, one artificially irrigated (Wet) and a second open to rainfall only (Dry). Both cells showed the importance of unsaturated flow mechanisms in controlling the water balance and leachate generation, due mainly to the potential of ash to retain moisture in its pores. The irrigated cell showed a marked reduction in leachate salinity as irrigation continued, although some trace elements demonstrated complex leaching patterns.

To further quantify ash leaching rates, a series of laboratory leaching columns were constructed and operated, with electronic logging of soil moisture using Time Domain Reflectometry (TDR). The use of TDR, although able to detect relative changes in soil moisture, was less than successful. The leachate results from the columns were encouraging and provided additional confirmation of leaching curves for particular solutes and trace elements. The soil water characteristic curve (SWCC) was established for the ash through a Tempe Cell test. This quantified more accurately the water retention properties highlighted through the field and laboratory research. Importantly, analysis of the SWCC for the ash shows that it appears to maintain high hydraulic conductivity over typical ranges of matric suctions.

The geochemical controls on solutes in the various ash leachates generated in the field and laboratory were investigated through geochemical speciation modelling and plotting. The major solutes in leachate appeared to be controlled by dissolution from more soluble minerals, such as gypsum and halite, while for other species the controls were more complex. Most trace elements appeared to be controlled by a mix of mineral dissolution, co-precipitation and adsorption mechanisms.

A solute transport and leaching model was developed and applied to the various data sets obtained for this thesis. The model, describing the leaching and transport of solute in one-dimensional steady state flow, gave reasonable calibration to the different column experiments. Extension of this approach to unsaturated flow and solute transport is discussed in light of the experience from the field trials. The conversion of this model to non-dimensional form was then examined and provided a useful approach for assessing the scale effects from different sized column leaching experiments and field trials. The use of batch leaching tests, although not generally representative of field conditions, can be incorporated into this approach and used to estimate the initial concentration of a solute in leachate. The use of these models provides the methodology to quantify leaching over time and at various scales, important in the engineering design of ash disposal sites.

In summary, this thesis presents a detailed qualitative study of ash leaching and solute transport mechanisms, and develops a quantitative methodology for the design and assessment of ash disposal sites.

Table of Contents - Overview

Table of Contents - Detailed

11 Appendices

Figures

Tables

Acronyms

1-D	One Dimensional
2-D	Two Dimensional
ADE	Advection-Dispersion Equation
AI	Acid Insoluble
AP	Ash Pond
CO_2	Carbon Dioxide
DO	Dissolved Oxygen
DOC	Dissolved Organic Carbon
EME	Edison Mission Energy Ltd
EPAV	Environment Protection Authority of Victoria
EPRI	Electric Power Research Institute
FOWL-GH	Fossil Fuel Combustion Waste Leaching Code - GMIN & HELP
HELP	Hydrologic Evaluation of Landfill Performance (model)
HHF	Haunted Hill Formation
LOI	Loss On Ignition
LYAP	Loy Yang Ash Pond
LYP	Loy Yang Power Ltd
MFAS	Morwell Formation Aquifer System
RWP	Relief Well Pit
pCO_2	Partial Pressure of Carbon Dioxide
SAS	Shallow Aquifer System (see HHF)
SECV	State Electricity Commission of Victoria
SO_4	Sulphate
SWCC	Soil Water Characteristic Curve
TCLP	Toxicity Characteristic Leaching Procedure
TDR	Time Domain Reflectometry
TDS	Total Dissolved Solids
TFAS	Traralgon Formation Aquifer System
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
USG	Unsaturated Soils Group (Uni. Of Saskatchewan)
VU	Victoria University
VUT	Victoria University of Technology (now VU)
YF	Yallourn Formation

Publications Arising from this Thesis

Journal Papers

1. Kodikara, J. & Mudd, G. M., 2001, *Scale-Up Modelling of Ash Leaching*. ASCE Journal of Environmental Engineering, (In Preparation).

2. Mudd, G. M., T. R. Weaver & J. Kodikara, 2001, *Environmental Geochemistry of Aged Brown Coal Ash*. Journal of Environmental Quality, (Under Review).

3. Mudd, G. M. & J. Kodikara, 2000, *Field Studies of the Leachability of Aged Brown Coal Ash*. Journal of Hazardous Materials, 76 (2-3), pp 159-192.

Conference Papers

1. Mudd, G. M. & J. Kodikara, 1999b, *Environmental Management Of Coal Ash Disposal : Unsatuarted Flow Modelling Of Field Studies*. Prepared for “Civil and Environmental Engineering Conf. - New Frontiers and Challenges”, Thailand, November 1999, 10 p. (Not published).

2. Mudd, G. M., T. R. Weaver, J. Kodikara & T. McKinley, 1999a, *Studies on the Attenuation of Sulphate in Latrobe Valley Groundwaters*. Proc. “Contaminated Sites Remediation Conf.”, CSIRO Centre for Groundwater Studies, Perth, WA, March 1999, pp 399-405.

3. Mudd, G. M. & J. Kodikara, 1998c, *Coal Ash Leachability : Detailed Field Studies*. Proc. "Australian Institute of Energy (AIE) - 8TH Australian Coal Science Conf.", Sydney, NSW, December 1998, pp 357-362.

4. Mudd, G. M., J. Kodikara & T. McKinley, 1998b, *Groundwater Chemistry of the Latrobe Valley Influenced by Coal Ash Disposal - 2 : Preliminary Kinetic Modelling*. Proc. “Groundwater : Sustainable Solutions”, International Association of Hydrogeologists (IAH) Conf., Melbourne, VIC, February 1998, pp 521-526.

5. Mudd, G. M., T. R. Weaver, J. Kodikara & T. McKinley, 1998a, *Groundwater Chemistry of the Latrobe Valley Influenced by Coal Ash Disposal - 1 : Dissimilatory Sulphate Reduction and Acid Buffering*. Proc. “Groundwater : Sustainable Solutions”, International Association of Hydrogeologists (IAH) Conf., Melbourne, VIC, February 1998, pp 515-520.

6. Mudd, G. M. & J. *Kodikara,* 1997, *Modelling Coal Ash Leaching*. Proc. “9TH Int'l Conf. of the International Association for Computer Methods & Advances in Geomechanics (IACMAG)”, Wuhan, China, November 1997, pp 1237-1242.

7. Mudd, G. M., J. Kodikara & T. McKinley, 1996, *Assessing the Environmental Performance of Coal Ash Disposal*. Proc. "Australian Institute of Energy (AIE) - 7TH Australian Coal Science Conf.", Churchill, VIC, December 1996, pp 363-370.

Miscellaneous Reports

1. Mudd, G. M., 1998c, *Research Report on Loy Yang Leached Ash Studies and Performance of the Trial Leaching Cells*. Unpublished Research Report to Loy Yang Power Pty Ltd, School of the Built Environment, Victoria University of Technology, December 1998, 115 p.

2. Mudd, G. M., 1998b, *Loy Yang Leached Ash Research - Appendix B of Works Approval Application by Loy Yang Power Pty Ltd for the Construction of Leached Ash Dumps at Loy Yang*. School of the Built Environment, Victoria University of Technology, October 1998, 17 p.

3. Mudd, G. M., 1998a, *SoilCover Modelling of Loy Yang - Appendix C of Works Approval Application by Loy Yang Power Pty Ltd for the Construction of Leached Ash Dumps at Loy Yang*. School of the Built Environment, Victoria University of Technology, October 1998, 17 p.

4. Mudd, G. M., 1997b, *Loy Yang Ash Dump Geotechnical Investigation*. Unpublished Research Report, Dept. of Civil & Building Engineering, Victoria University of Technology, 4 p.

5. Mudd, G. M., 1997a, *Predictive Hydrologic Modelling of the Loy Yang Aged Ash Landfill Trial Cells*. Unpublished Research Report, Dept. of Civil & Building Engineering, Victoria University of Technology, 8 p.

Conference Oral Presentations

1. Mudd, G. M., 1998c, AIE 8TH Australian Coal Science Conference.

2. Mudd, G. M., 1998a, IAH Conference - Groundwater : Sustainable Solutions.

3. Mudd, G. M., 1996, AIE 7TH Australian Coal Science Conference.

Conference Poster Presentations

1. Mudd, G. M., 1999, CSIRO Contaminated Site Remediation Conference.

2. Mudd, G. M., 1998b, IAH Conference - Groundwater : Sustainable Solutions.

Oral Presentations - Professional Societies

1. Mudd, G. M., 1999, *Hydrogeological Issues of Coal Ash Disposal in the Latrobe Valley*. April 27, 1999. International Association of Hydrogeologists (IAH), Victorian Branch.
2. Mudd, G. M., 1997, *Solute Transport Modelling of Latrobe Valley Ash Disposal Sites*. March 12, 1997. Australian Geomechanics Society (AGS), Victorian Branch.

Additional Publications by the Author

(Non-Thesis Related)

Conference Papers

1. Mudd, G. M., 2000d, *Remediation of Uranium Mill Tailings Wastes in Australia : A Critical Review*. Submitted to "2000 Contaminated Sites Remediation Conference", CSIRO, December 2000, Melbourne, VIC, 8 p.
2. Mudd, G. M., 2000c, *Uranium Mill Tailings Wastes in Australia : Past, Present and Future Management*. Proc. "Our Nuclear Responsibilities - Nuclear Issues as They Affect Australia, Looking Backwards … Looking Forwards", National Conference of the Medical Association for Prevention of War (MAPW), August 2000, Canberra, ACT. (www.mapw.au.nu).
3. Mudd, G. M., 2000b, *Acid In Situ Leach Uranium Mining : 2 - Soviet Block and Asia*. Proc. “Tailings & Mine Waste '00”, Fort Collins, Colorado, USA, January 23-26, 2000, pp 527-536. (www.sea-us.org.au/pdfs/tmw00/).
4. Mudd, G. M., 2000a, *Acid In Situ Leach Uranium Mining : 1 - USA and Australia*. Proc. “Tailings & Mine Waste '00”, Fort Collins, Colorado, USA, January 23-26, 2000, pp 517-526. (www.sea-us.org.au/pdfs/tmw00/).
5. Mudd, G. M., 1998c, *Corporate Information on Uranium Companies Across Australia*. Background Paper for “Nuclear Free Australia Strategy Forum”, Friends of the Earth (Fitzroy), Melbourne, VIC, December 5-6, 1998, 22 p.
6. Mudd, G. M., 1998b, *The Sustainability of Mound Springs in South Australia : Implications For Olympic Dam*. Prepared for “IAH Commission on Mineral & Thermal Waters”, Ballarat, VIC, September 21-24, 1998, 13 p.
7. Mudd, G. M., 1998a, *The Long Term Sustainability of Mound Springs in South Australia : Implications For Olympic Dam*. Proc. “Uranium Mining & Hydrogeology II Conf.”, Freiberg, Germany, September 15-17, 1998, pp 575-584.

Journal Papers

1. Mudd, G. M., 2000, *Mound Springs of the Great Artesian Basin in South Australia : A Case Study From Olympic Dam*. Environmental Geology, 39 (5), pp 463-476.

Research Reports

1. Mudd, G. M., 2000, *Uranium Mill Tailings Wastes in Australia : Past, Present and Future Management*. Joint Report for the Medical Association for Prevention of War (MAPW), August 2000, Canberra, ACT, 84 p.
2. Mudd, G. M., 1999, *A Review of Australia's Uranium Mining and the Proposed Jabiluka Uranium Mine : A Scientific Case for Placing Kakadu as WORLD HERITAGE IN DANGER*. Technical Submission by the Anti-Uranium Collective, Friends of the Earth (Fitzroy) to the World Heritage Committee of UNESCO, May 1999, Melbourne, VIC, 88 p. (www.sea-us.org.au/pdfs/jab/).
3. Mudd, G. M., 1998, *An Environmental Critique of In Situ Leach Mining : The Case Against Uranium Solution Mining*. Research Report for Friends of the Earth (Fitzroy) and the Australian Conservation Foundation, July 1998, Melbourne, VIC, 154 p. (www.sea-us.org.au/isl/).

Chapter 1

Introduction - The Need for Research on Ash Disposal

A brief outline of the problem of ash disposal and management in the Latrobe Valley is presented. This forms the basis for the research need and overall aims of this thesis.

1.1 Introduction

The successful management of solid wastes arising from the combustion of low-rank coal for electricity generation presents significant engineering and environmental challenges. The Latrobe Valley region of eastern Victoria, Australia, has been meeting these challenges since the 1920's, and indeed has an admirable record of achievement (Gleeson, 1972; Kenley, 1990; Barton, 1992; Harvey, 1993; Waghorne, 1993).

The Latrobe Valley contains three open cut brown coal mining operations with four adjacent power station complexes, shown in Figure 1.1. Together these generate approximately 85% of Victoria's base load electricity supply, forming the backbone of the State's economic activity. These include the Hazelwood power station (1,600 MW) and open cut mine, Yallourn power station (1,450 MW) and open cut mine, and the Loy Yang Power (2,000 MW) and Edison Mission Energy (1,000 MW) power stations, both adjacent to the Loy Yang open cut mine. There is also the small Morwell power station (170 MW), part of the brown coal briquette manufacturing complex.

All sites were developed and operated by the State Electricity Commission of Victoria (SECV), before privatisation in recent times. The Hazelwood and Yallourn complexes are now owned by consortiums of foreign energy utilities and investment companies. The Loy Yang mine, power station and associated infrastructure are owned by Loy Yang Power Ltd (LYP), a consortium of American and Australian investment enterprises. The adjacent Edison Mission power station at Loy Yang is owned and operated by Edison Mission Energy Ltd (EME), a consortium of American energy utilities.

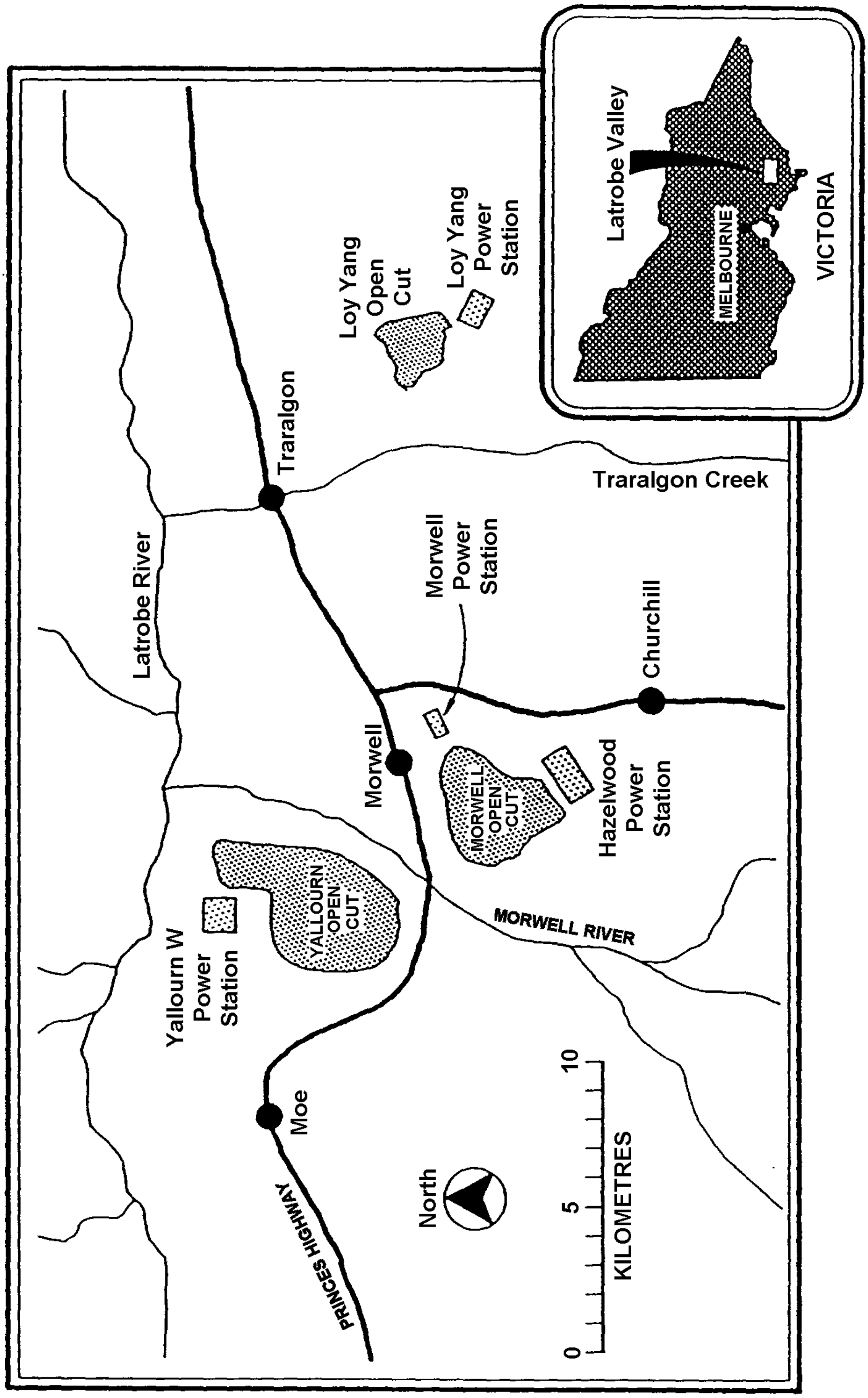


Figure 1.1 - Map of Victoria and Latrobe Valley power stations (Black, 1990a)

There are many aspects to the successful and efficient management of these power stations. These include the operation of large open cut coal mines, depressurisation of deep artesian aquifers to maintain mine stability (and the impact this has on surrounding groundwater resources), the discharge of gaseous effluents to the environment (eg. sulphur and carbon dioxides), treatment and disposal of wastewaters, and the management of solid wastes generated by the power station and the open cut mine. The various solid wastes include mine overburden, inferior coal, interseam materials and solid wastes from the power station consisting mostly of precipitator (fly) ash, partially burnt coal particles (char), bottom (furnace or boiler) ash, salts, sand and clay minerals remaining after the combustion of the coal. It is estimated that the quantity of ash wastes produced alone is of the order of 550,000 tonnes per year (Black *et al.*, 1992). One of the major environmental concerns associated with the operation of these large power utilities is the safe management and disposal of the fly and bottom ash.

Historically, the ash has been hydraulically transported into retaining ponds and allowed to settle. The natural soils at the base of the ponds generally contain a high proportion of clay, giving a low permeability barrier for the pond. The underlying groundwater systems were monitored for possible impacts from the leachate seeping from beneath the ash ponds. Alternative management techniques to this approach have not been extensively researched within the Latrobe Valley or Australia. The methodology currently used is based on overseas research and early research by the SECV.

As part of a broad research initiative in the Latrobe Valley, the Loy Yang complex has been selected for detailed research on quantifying the environmental impacts of current ash disposal techniques, and alternative disposal and management strategies. The research is undertaken with the co-operation and support of Loy Yang Power Ltd, Geo-Eng Australia Pty Ltd and the School of the Built Environment [1], Victoria University. Hence, it should be noted at the outset, that this project is more industry and problem based rather than of a more fundamental nature.

---

[1] - formerly the Department of Civil and Building Engineering.

1.2 Overview of the Loy Yang Complex

The term “Loy Yang” is local Aboriginal language for “big eel” [2]. The Loy Yang complex is the newest and largest of the Latrobe Valley utilities and construction began in 1977. The first excavation of overburden at the open cut mine was undertaken in 1982. The four 500 MW boilers and turbines now owned by Loy Yang Power Ltd (LYP) were commissioned between 1984 and 1988 (previously known as "Loy Yang A"). The second half of Loy Yang ("Loy Yang B"), sold to Edison Mission Energy (EME) before completion, was commissioned between 1994 and 1996. The EME utility contains two 500 MW boilers and turbines. A site plan is shown in Figure 1.2. The open cut coal mine produces approximately 32 million tonnes (Mt; 32×10^9 kg) of low-rank brown coal annually for both the LYP and EME utilities, 3 to 4 million m^3 of overburden and a total of about 300,000 tonnes per year of bottom (boiler) and precipitator ash. The mine has coal reserves of approximately of about 1,500 million tonnes at 1.4% ash. The large reserves gives the Loy Yang site an expected life of up to 50 years, possibly longer.

The Loy Yang Ash Pond (LYAP) was constructed in two seasons from 1979 to 1981 and commissioned in 1982 (Daniels *et al.*, 1993). Several problems over the operational life of the LYAP have developed, including seepage to the west and north. The construction of the pond also saw overexcavation of the natural soils, compromising the integrity of the clayey soil base. Due to higher than expected ash production rates, by 1990 it was realised that the capacity of the LYAP was limited and would not provide sufficient ash storage volume for the intended life of the Loy Yang complex. An aerial photograph is shown in Figure 1.3.

The problem of ash disposal coincided with the onset of excessive boiler fouling due to poorer coal quality, chiefly higher sodium and silica (Waring *et al.*, 1996). The higher sodium and silica in the as-mined coal led to large ash deposits on heat transfer surfaces, and consequently boiler outages were required nearly every four weeks, compared to nearly a full year in the 1980's. This dramatically impacted on station operations.

---

[2] - Loy Yang Power website, 1998, http://www.loyyangpower.com.au/

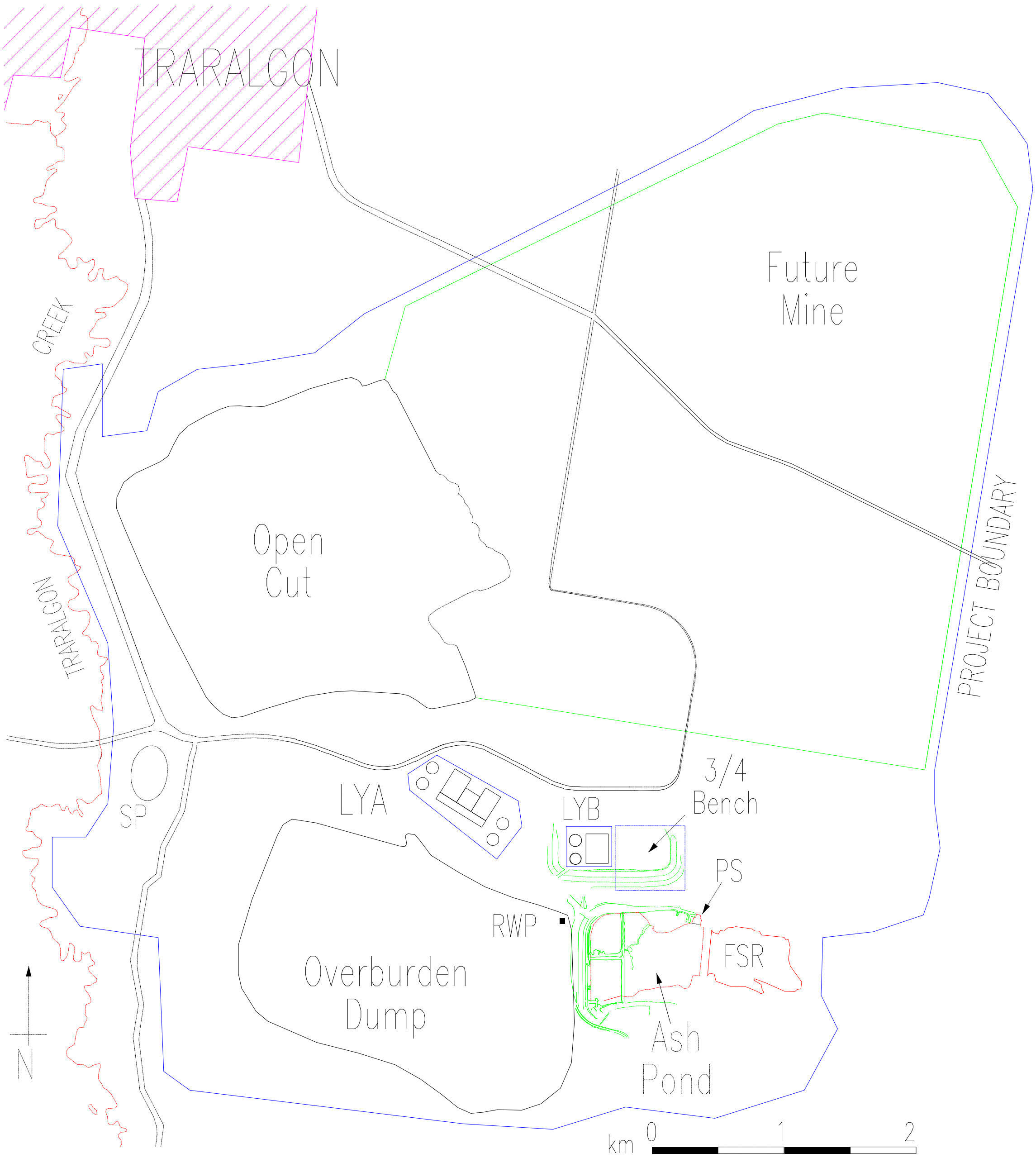


Figure 1.2 - Site plan of the Loy Yang power station complex (approximate scale only)

(adapted from and courtesy of Geo-Eng Australia Pty Ltd)

Notes : LYA is the Loy Yang A power station (2,000 MW, owned by Loy Yang Power Pty Ltd; "LYP"); LYB is the Loy Yang B power station (1,000 MW, owned by Edison Mission Energy Pty Ltd; "EME"); 3/4 Bench is space reserved for future expansion of power production at Loy Yang; RWP is the Relief Well Pit (LYP); FSR is the Fire Services Reservoir (LYP). SP is the Settling Pond (surface water drainage system, discharges to Traralgon Creek; LYP); PS is the Pumping Station for Ash Pond Saline Waste Water (LYP).

Figure 1.3 - Aerial Photograph of the Loy Yang Ash Pond and North-eastern Overburden Dump Region (January 1998) (Courtesy - Loy Yang Power Ltd)

(Note - the field trial cells are located in the bottom left corner of the photo, inside the southern most corner of the dam wall. North direction approximate only. Loy Yang B power station is in the background, owned by Edison Mission Energy.)

Feasibility studies were undertaken by the SECV at Loy Yang on possible options for long term ash management, including a new ash disposal pond, raising the side wall of the LYAP by about 5 m (which itself would still not provide the necessary long term capacity), dry ashing and excavation of deposited ash into the Overburden Dump after a suitable period in the LYAP. The investigation was undertaken in conjunction with studies on alternative ash management strategies and ash utilisation proposals for the Latrobe Valley (eg. Macphee *et al.*, 1994; Black *et al.*, 1992). The capacity of the LYAP was increased in 1995 by raising the dam side walls by 5 m while research on ash disposal outside the LYAP was begun. Two principal issues associated with the continued operation of the LYAP and ash disposal outside this facility were identified :

1. The plume of ash seepage in groundwater beneath and adjacent to the LYAP was gradually increasing, marked by an increase of the salinity of the water. The composition of the saline plume was consistent with the chemistry of ash pond waters, showing significantly elevated sulfate, sodium and chloride compared to normal groundwater chemistry being low concentrations of sodium and chloride. Compared to the ash pond, however, considerably reduced concentrations of sulfate in groundwater monitoring bores were being detected. The exact cause of retardation of sulfate in groundwater was unclear. The geology and hydrogeology of LYAP area is complex, due to the basement structural feature known as Loy Yang Dome and the fluvial nature of the shallow aquifers. Hence there was a demonstrable need to assess the long term solute transport behaviour of the seepage and potential impacts on groundwater at the Loy Yang site, and if there was potential for off-site impacts.

2. The other issue identified was the leachability of Loy Yang ash, and has so far not been studied in detail. This is particularly true for the leaching behaviour of ash under actual field conditions. Earlier research had highlighted the leaching effect of the hydraulic ash transport system and the lower soluble mass after deposition and leaching in an ash pond, although this was based on work at the Hazelwood and Yallourn complexes and not Loy Yang. The leachability of soluble salts and trace elements from ash had not been studied widely at Loy Yang.

These two principal issues, impacts on groundwater quality and leachability in the field, are critical in assessing the long term disposal of ash. The various salts and trace elements leach from the ash stored within the ash pond, which is maintained in a saturated state. At some point, the salts and elements will be leached from the ash and provde minimal ongoing potential for further leachate generation. The ash seepage emanating through the base of the pond provides the source concentrations to groundwater. The migration rates of chemical constituents into and through the groundwater within the Loy Yang site will determine the extent of the potential off-site impact. This is especially poignant given the projected long life of the Loy Yang complex. The concentration of the leachate and migration rates in groundwater are critical to any consideration of alternative methods of disposing of the ash excavated from the ash pond for emplacement within the Overburden Dump or another suitably engineered disposal site.

There is currently no consistent methodology or data for assessing the long term impacts on groundwater resources arising from ash management and disposal within the Latrobe Valley. By investigating the ash disposal systems at Loy Yang, this thesis aims to study this issue more rigourously in order to ash assess disposal and provide guidelines for a more consistent approach, which can be beneficial across the Latrobe Valley and elsewhere.

1.3 Aims of the Thesis

The primary aim of this thesis is to investigate the solute transport of constituents from ash disposal in the Latrobe Valley. In order to achieve this aim, the following specific issues arising from ash disposal and management at the Loy Yang power station were researched :

- a critical review of ash leaching processes based on international and Latrobe Valley literature, especially as this relates to the assessment of long term impacts of ash disposal and solute transport modelling of leachate migration;

- assess seepage migration pathways and historical groundwater monitoring data in order to develop a solute transport model of the relevant hydrogeologic processes, with particular emphasis on sulfate and chloride behaviour;

- analyse the potential for the generation of leachate from ash excavated from the Loy Yang Ash Pond, in particular the salinity and trace element content of any leachate from the ash;

- investigate the geochemical controls on leachate quality, with regard to major solutes and environmentally important trace elements, and the applicability of modelling the solute transport processes for these constituents of leachate; and

- develop solute transport models which represent the major mechanisms and behaviour of ash leaching. This provides a basis for a source function or boundary condition for solute transport modelling of ash disposal sites.

Thus the thesis aims to provide guidelines and a benchmark for future engineering design and environmental management of ash disposal within the Latrobe Valley, thereby contributing to the continuing success of electricity generation from the large resources of low rank brown coal which the region has provided for almost a century.

1.4 Structure of the Thesis

The overall work in this thesis presents an approach to quantify the important aspects of ash disposal. Chapter 2 presents a literature review of ash disposal and leaching research within the Latrobe Valley and internationally, summarising ash leaching processes and impacts on groundwater resources. Chapter 3 presents detailed research on the behaviour of ash leachate seepage which is known to be migrating in shallow groundwater beneath the Loy Yang Ash Pond. On the basis of an analysis of groundwater monitoring data, the reactive geochemistry is identified and a kinetic solute transport model applied to predict the migration rates for sulfate and chloride. The results of a waste classification and laboratory leaching study investigating the leachable mass at various points within the Loy Yang power station complex and ash pond are presented in Chapter 4. The results from a 14 month field trial conducted on the physical and chemical behaviour of excavated leached ash from the Loy Yang Ash Pond are given in Chapter 5. Chapter 6 presents a laboratory investigation of ash leaching, based on the operation of three column tests and associated testing. Chapter 7 presents an analysis of the controls on leachate geochemistry as a basis for assuming solute transport behaviour and modelling parameters. In Chapter 8 an approach is developed for numerical modelling of solute transport arising due to ash leaching and ash disposal. Finally, Chapter 9 concludes the thesis with a review of key findings and makes recommendations for further research.

Chapter 2

Environmental Overview of Coal Ash Disposal

In order to develop a conceptual framework for the current research work being carried out at Loy Yang, a review of the environmental management of coal ash disposal, ash leaching research from international literature and the former SECV is presented. This is then summarised into leaching processes and test procedures as a way to identify controlling processes for solute transport and possible impacts on groundwater.

2.1 Environmental Management of Coal Ash

There are a number of important aspects of coal ash disposal that determine the need for efficient environmental management. Some of the main features that may lead to adverse environmental outcomes include (Libicki, 1978 & 1983) :

- leaching of soluble salts and trace elements from the ash during transport and disposal;
- saline water used to pump ash from the power station to a disposal pond and re-circulation of this water;
- surface water discharge of excess saline water (if any);
- seepage to groundwater from disposal ponds and potential impacts on beneficial uses of the groundwater;
- ash disposed of in landfill or utilisation scenarios; and
- rehabilitation and long term waste containment.

In the Latrobe Valley, excess saline waste water from the ash disposal systems at the three power stations is pumped to an ocean outfall, about 60 km south-east of Loy Yang. The Saline Waste Outfall Pipe and pumping station is located at the north-eastern corner of the Loy Yang Ash Pond (see Figure 1.3). This has regulatory approval and hence only issues relating to seepage, leaching and surface ash disposal will be presented herein.

2.2 Summary of Research by the SECV

The State Electricity Commission of Victoria (SECV) undertook research on many aspects of ash management in the Latrobe Valley. The majority of their research centred on engineering properties, to allow more accurate design and operation of new disposal and dam facilities to meet more stringent environmental and operating demands. A separate focus of research has been on possible beneficial uses of the ash, either as a pozzolan (cementitious material), an additive in building products, fertiliser mix, byproducts or other potential uses. The primary method of ash disposal for all current power stations is through slurrying to a disposal pond, with 7 ash disposal ponds currently in operation (Raisbeck, 1990). The excess saline water from all power station complexes is pumped from Yallourn through Hazelwood to Loy Yang and thence to an ocean outfall pipe for disposal. It is likely that future ash management and disposal will incorporate a mix of utilisation (eg. road or building construction) and other alternatives to the use of slurrying and ash ponds (Macphee *et al.*, 1994).

There have been a number of studies on the leachability of Latrobe Valley coal ash (eg. Deed, 1969, 1973 & 1981; Bone and Schaap, 1980 & 1981; Tang, 1987; Black, 1990a & 1990b). The majority of this work has been centred on the older power station complexes at Yallourn and Hazelwood, and was generally concerned with the hydraulic ash transport system and not the conditions prevailing in an ash pond or at a surface ash disposal site (landfill). The newer Loy Yang complex has only had preliminary sequential batch leaching work performed (Black, 1988), although only major ions were analysed and no trace element analyses were apparently undertaken. No detailed leaching research has been undertaken on Loy Yang ash.

In general, Latrobe Valley ashes are considered to be distinctly different from those reported in the literature, from both a physical and chemical perspective (Beretka & Brown, 1976 & 1977; Raisbeck, 1990; Black, 1990a; Black *et al.*, 1992). It is important to acknolwedge that, due to the variability in coal quality between and within the different open cuts, there is also considerable variation in the quality and properties of the ash at each power station complex (Raisbeck, 1990). A review of the engineering and chemical properties of the ash across the Latrobe Valley is presented below.

2.2.1 Ash Management in Latrobe Valley Power Stations

The management of ash within the various Latrobe Valley power stations is generally the same. The prepared coal is delivered to the boilers where it is combusted to release heat for steam generation for turbines. The majority of the combustion products are fine particles which are carried by the flue gases out of the boiler. The coarser ash particles, principally sand, settle to the bottom of the boiler from where they are collected. This fraction is known as bottom ash, and generally constitutes about 20% of the total ash (Black, 1990a). The flue gases from the boiler are treated with an electrostatic precipitator to remove the fine particles (>99%), and this fraction is thus known as precipitator ash (fly) and comprises about 80% of the total ash (Black, 1990a). The ash contains about 20% char (unburnt coal). The two ash sources are mixed with recycled ash pond water and temporarily held in a large ash pit inside the power station. The ash slurry, with a high liquid-to-solid ratio of about 50:1 for LYP and 10:1 for EME, is then pumped to the ash pond for disposal. A schematic diagram is shown in Figure 2.1.

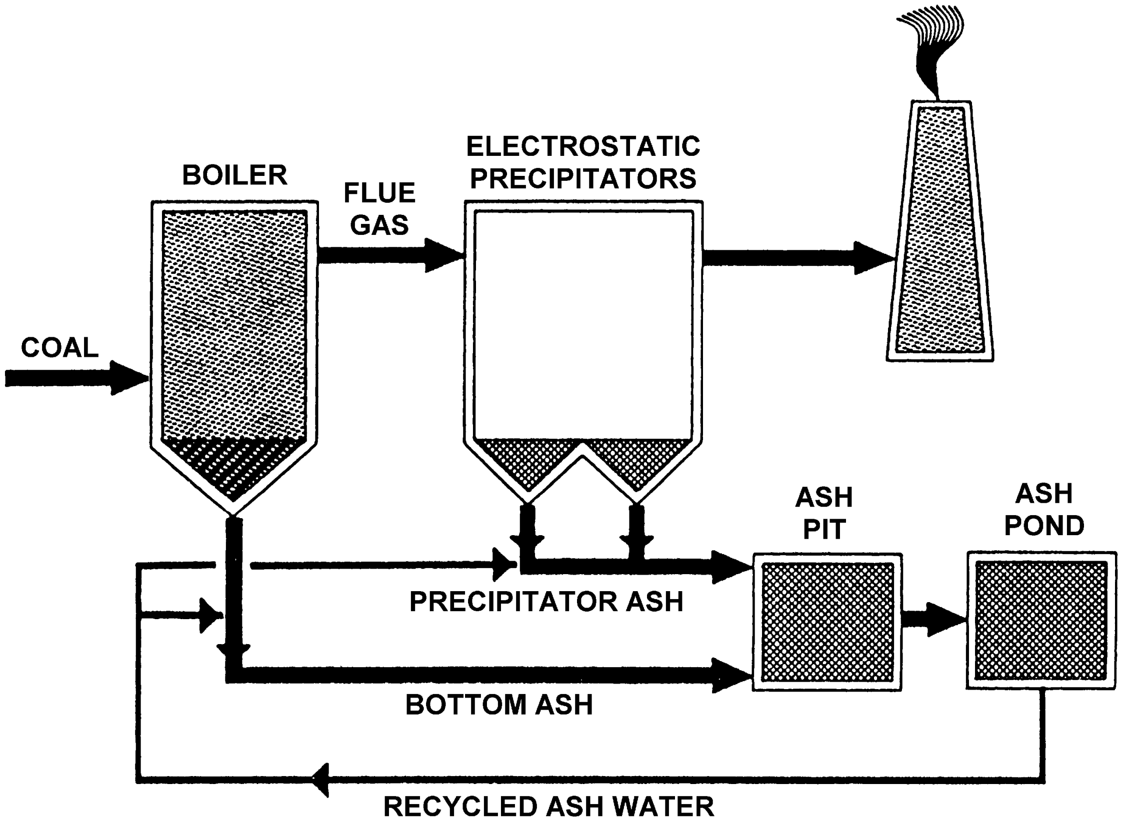


Figure 2.1 - Schematic of the General Ashing System in the Latrobe Valley (Black, 1990a)

2.2.2 Physical Properties

The ash from the Latrobe Valley is typically of very low dry density and high porosity, classified as a sandy silt (Peterson *et al.*, 1982; Raisbeck, 1990). The dry density is generally between 400 to 800 kg/m^3, although values as high as 2,000 kg/m^3 have been measured (Raisbeck, 1990). The average dry density is typically around 720 kg/m^3 (Raisbeck, 1990). The ash particle density or specific gravity (G_s) is dependent on the particle size distribution, which can vary according to the pretreatment applied in the laboratory due to interaction with the soluble salts in the ash (Raisbeck, 1990). The values for G_s can be in excess of 3.00 while for remnant char (unburnt coal) the G_s value is generally as low as 1.50 (Peterson *et al.*, 1982). The average particle density is typically about 2.36 (Raisbeck, 1990).

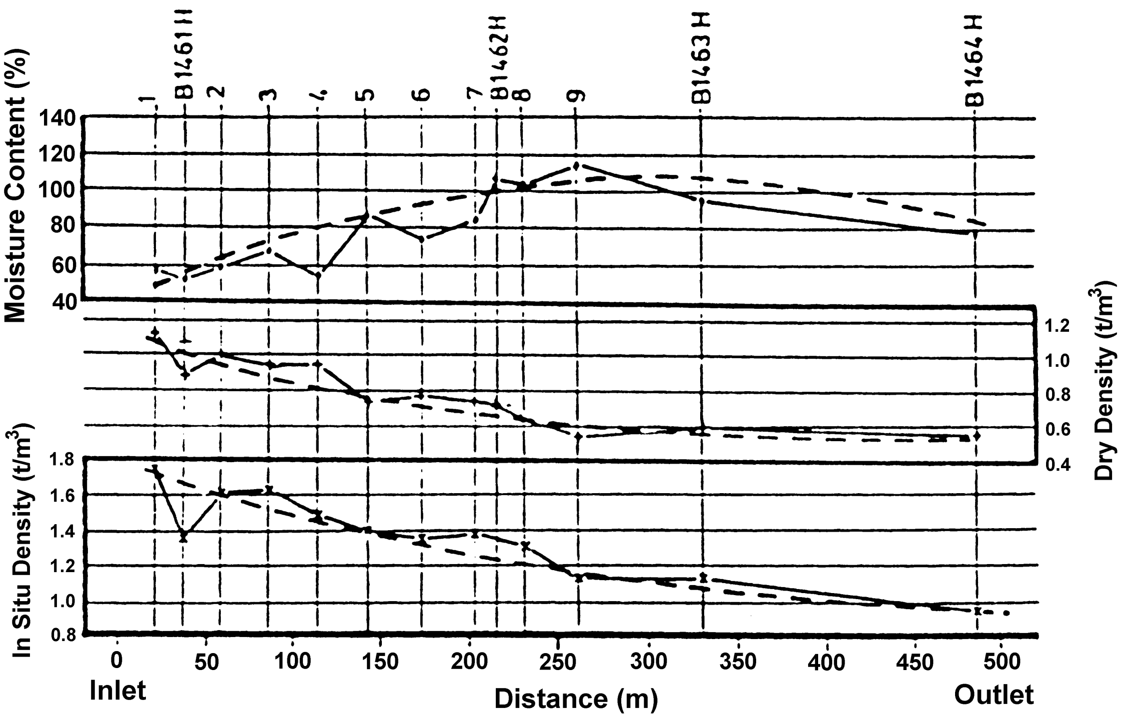


Figure 2.2 - Density and Moisture versus Distance at Hazelwood No. 2 Pond (Raisbeck, 1990)

A positive correlation exists between the in situ and dry density and the moisture content of ash with the distance from the pond discharge point, as shown in Figure 2.2 (Raisbeck, 1990). The highest in situ and dry densities are found closest to the discharge pipe, with densities decreasing with further distance from the pipe. The variation in moisture content with distance from the pipe is related to the decrease in density and the change in particle size distribution (an increase in the percentage of fine particles). This correlation is significant since a higher proportion of char will act to decrease the dry density and particle density characteristics of the ash, due to the lower particle and bulk densities of char (Raisbeck, 1990). A further factor in this process is the proportion of sand in the ash. Sand generally has a particle density of 2.65, and so a higher amount of sand will also affect the characteristics of the deposited ash inside a disposal pond. The sand, as a heavier mineral than other components of the ash, will deposit nearer to the discharge point, as highlighted in Figure 2.2.

The morphology of the ash particles is generally irregular and range from sub-angular through to rounded, sometimes spherical (Beretka & Brown, 1976 & 1977; Raisbeck, 1990). Peterson *et al.* (1982), however, desribes ash particles as generally solid spheres and not cenospherical (hollow). The clay content is generally low and less than 15%, with the remainder comprising fine sand and silt (Peterson *et al.*, 1982; Raisbeck, 1990). The degree of sand and silt in the ash varies with the open cut from which the power station draws its coal and over time. The ash at Loy Yang, Yallourn and Hazelwood can contain up to 75%, 90% and 25% less than 75 μm in size, respectively (Macphee *et al.*, 1994). The Hazelwood ash has about 43% between 75 to 150 μm and 24% between 150 to 212 μm (Macphee *et al.*, 1994).

2.2.3 Mineralogy of Latrobe Valley Ash

The minerals that form the ash in the Latrobe Valley are related to the coal which is utilised at each power station, and will also undergo variation over time (Black, 1990a). Therefore the in situ mineral state of the inorganic components of the coal will have a strong influence on the behaviour and formation of ash within the boilers at the power station (Waring *et al.*, 1996). Because of excessive fouling of the boilers at Loy Yang in the early 1990s the coal is now blended to minimise ash formation (Waring *et al.*, 1996).

One of the main reasons why Latrobe Valley ashes are unique both physically and chemically is the way in which the inorganic constituents are distributed in the coal deposit (Black *et al.*, 1992). The major ash-forming elements found in Latrobe Valley coals occur as cations bound to carboxylic functional groups (Macphee *et al.*, 1994; Black *et al.*, 1992). During combustion, the organically bound cations undergo a series of oxidation and sulfation reactions (Macphee *et al.*, 1994). The low concentrations of inorganic minerals present in the coal (marcasite, pyrite, clay and sand) generally undergo only minor transformations (Macphee *et al.*, 1994; Black *et al.*, 1992). A compilation of the typical chemical composition of Latrobe Valley ashes is given in Table 2.1, where it is compared to black coal ash samples and North Dakota lignite ash.

Table 2.1 - Ash Composition from Latrobe Valley, Australian Black Coal and North Dakota Lignite, USA (%) (Macphee *et al.*, 1994; Nataatmadja & Morgan, 1999)

	Latrobe Valley Brown Coal			Australian Black Coal			North
Oxide	Loy Yang	Yallourn	Hazelwood	Awaba	Tarong	Gladstone	Dakota
SiO_2	60.4$^{\#}$	1.4	6.6	64.5	59.5	50	30.3
Al_2O_3	13.3$^{\#}$	2.1	1.8	26.4	36.0	28	12.5
Fe_2O_3	8.5	24.5	8.7	3.4	1.4	12	4.6
TiO_2	1.7	0.1	0.2	1.1	2.2	1.5	-
K_2O	1.2	0.4	0.4	2.6	0.1	0.7	0.6
MgO	2.2	18.0	18.8	0.6	0.1	1.3	7.9
Na_2O	2.1	11.0	4.5	0.2	0.1	0.3	7.3
CaO	1.0	12.3	28.4	0.5	0.1	3.5	23.6
SO_3	3.4	21.7	15.6	0.4	0.1	0.14	9.6
Cl	<0.1	<0.1	3.4	-	-	-	-
LOI	7.6	8.2	11.7	-	1.5	1.5	1.8

LOI - Loss On Ignition. $^{\#}$ - Highly variable.

The minerals identified in ash to date include thenardite (Na_2SO_4), halite (NaCl), periclase (MgO), haematite (Fe_2O_3), magnetite (Fe_3O_4), lime (CaO), calcite ($CaCO_3$), anhydrite ($CaSO_4$), alpha-quartz (α-SiO_2), alumina (Al_2O_3) and variations of Na-Ca-Mg aluminosilicate species (Drummond, 1988; Black, 1989, 1990a & 1990b; Black *et al.*, 1992; Macphee *et al.*, 1994). Detailed speciation of ash mineralogy is often complicated by the presence of mixed calcium (Ca), magnesium (Mg), iron (Fe) and aluminium (Al) oxide phases, which may include $Ca_2Fe_2O_5$, $MgAl_{2-x}Fe_xO_4$, $MgAl_2O_4$, $MgFe_2O_4$, $MgAl_xFe_{2-x}O_4$ and $Ca_2Al_xFe_{2-x}O_5$ and are difficult to distinguish with current analytical capabilities (Macphee *et al.*, 1994; Cashion & Brown, 1996).

An alternative approach to mineral analysis and speciation is to estimate the mineral composition from oxide analysis of an ash sample. Cashion & Brown (1996) and Macphee *et al.* (1994) have used this approach to estimate the mineral composition of ash, with reasonable accuracy given the difficulties in ash mineral speciation. The calculated mineral composition of Latrobe Valley ashes is given in Table 2.2.

Table 2.2 - Calculated Mineral Composition of Latrobe Valley Ashes (%)
(Macphee *et al.*, 1994)

Mineral	Solubility # Product (K_{sp})	Loy Yang	Yallourn	Hazelwood
Na_2SO_4	$10^{-0.179}$	4.8	25.2	2.0
NaCl	$10^{1.582}$	-	-	5.6
CaO	-	-	7.0	15.0
MgO	-	1.8	14.4	18.4
$CaSO_4$	$10^{-4.36}$	-	12.7	20.4
Fe_2O_3		8.5	11.9	-
$Ca_2Fe_2O_5$	-	-	-	13.7
$MgFe_2O_4$	-	-	15.4	-
SiO_2	$10^{-3.98}$	59.3	1.4	6.0
LOI	-	7.6	8.2	11.7
Other	-	18.0	3.8	7.2
Total	-	100.0	100.0	100.0

- solubility product data from Parkhurst (1995) and Langmuir (1997).

The data in Table 2.2 demonstrates that a large proportion of the minerals present in the ash is in soluble forms (eg. Na_2SO_4, NaCl, $CaSO_4$, CaO, MgO) and therefore readily leachable in an ash pond or to the environment. The ash in the Latrobe Valley generally has very poor pozzolanic (cementitious) characteristics, due to its particle morphology (both shape and distribution), lower lime content and the high proportion of soluble salts present (Peterson *et al.*, 1982; Raisbeck, 1990). Poor pozzolanic properties and high soluble salts is common for many lignite and brown coal ashes around the world (Black *et al.*, 1992). The poor pozzolanic nature of Latrobe Valley ash is also highlighted by the fact that there is no change over time in its permeability or strength.

2.2.4 Leaching Behaviour of Latrobe Valley Ash

Early work on the leachability of Latrobe Valley ashes was specifically designed to look at the problems of pipe scaling in the hydraulic ash transport system (eg. Deed, 1969 & 1973). This work, although not directly relevant to leaching processes in the disposal pond, demonstrated that for Hazelwood ashes 22.8% of the ash mass was water soluble. It showed that the main soluble components of the ash were sodium sulfate (Na_2SO_4) with minor amounts of lime (CaO), magnesium sulfate ($MgSO_4$) and calcium sulfate ($CaSO_4$). The concentration of the major ions found in solution was dependent upon their concentration in the ash and the pH of the leachate.

Bone and Schaap (1980) investigated the solubility of major and trace elements of brown coal ash with sequential batch leaching tests, although their objectives were environmental consideration of the hydraulic ash transport system and not those related to ash disposal. The major conclusions obtained from this study were that the soluble components, principally Ca, Mg, sodium (Na) and potassium (K), were removed in the first batch extraction. Tests on ash sampled from the disposal pond showed minor amounts of soluble components. Their work demonstrated that during hydraulic transport of the ash, the major part of its soluble components were leached before it was deposited into the ash pond. Another important conclusion from their research was that some trace elements, such as selenium, are significant during the leaching process and can be of environmental concern (Bone & Schaap, 1981). The high alkalinity of Latrobe Valley ashes limited the solubility of most trace elements.

Deed (1981) investigated the leaching of mixtures of Morwell ash and overburden, in order to assess different ash disposal options. Both laboratory and field studies were carried out, and the work showed, in both cases, that the major ions leached were Na and SO_4. In the laboratory studies they used columns of 150 mm diameter and 400 mm height, with one column containing Hazelwood precipitator ash and one column with a ratio of 1:1 of ash and overburden. The mixed column demonstrated a reduction in leachate salinity over 22 days, while the ash column remained variable.

The field trials, lasting several months, were carried out on precipitator ash and mixtures of ash to overburden in the ratios of 1:1 and 2:1. The field sites were constructed as crescent shaped mounds 15 m long, 10 m wide and 2.5 m high containing approximately 100 tonnes of ash, with six agricultural drains and a common collection trench draining each site. Spray irrigation systems were used to augment rainfall and ensure that an equivalent of 25 mm of water per day was achieved. The field trials did not show a reduction of leachate concentration over time as the laboratory columns showed. It appears that leachate collection system was poorly designed and did not intercept all leachate. There was a general lack of detailed leachate analyses from both studies, making any consistent interpretation of leaching behaviour difficult.

Tang (1987) investigated the use of dry ash pellets mixed with overburden as a feasible disposal option. Field studies of overburden and ash pellets only, and mixtures of the pellets and overburden were undertaken over a twelve month period. The tests were conducted in specially prepared square cells 3.05 m and 1.83 m deep. The centre of each cell was graded with a coarse gravel drainage layer with a leachate collection pipe which drained into a 500 litre drum. Each cell was loaded with about 18.7 tonnes and compacted to a bulk density of about 1,000 to 1,100 kg/m^3. The presence of ash pellets led to excessively high salinity concentrations, giving difficulties in environmental compliance. Despite the rainfall and leachate volumes being recorded over a twelve month period, leachate samples were only taken for chemical analysis over a period of two months. Hence a long term prediction of leachate behaviour was not possible.

The leachability of Hazelwood/Morwell and Yallourn ash was investigated by Black (1990a & 1990b), respectively. Both investigations used batch and column leaching tests. Sequential batch leaching tests were used for Morwell ash and the Elutriation Test, developed by the Environment Protection Authority of Victoria (EPAV, 1986), was used for Yallourn ash. Samples were collected from both the electrostatic precipitators (fly ash) and the respective ash disposal ponds. The Yallourn work (Black, 1990b) also included some modelling of the migration of the leachate in the groundwater system beneath the Yallourn ash disposal site. The solute transport model used was MYGRT (EPRI, 1986), a semi-analytical model, applied in one-dimension.

There were minor differences in the chemical composition of the two ashes, but the major ions leached were mostly Na, SO_4 and chloride (Cl) with low concentrations of K, Ca and Mg and minor leaching of trace elements. Both ashes showed strong alkaline buffering capacities, that is, a tendency to maintain a strong, alkaline pH in the leachate. The precipitator ash and ash pond sediment showed a marked concentration of leachable elements as a coating of the ash particles, shown in Figures 2.3 and 2.4. This property is critical in the leaching process, as it means that the more soluble components are attached to the surface of particles and are thus more readily leached.

A general trend that could be observed in the behaviour of most major and trace elements for both ashes was a significant initial release followed by a rapid decrease in the rate of leaching towards a steady state concentration. There were, however, a couple of minor deviations from this trend (see data in Table 2.3). The concentration of Ca was relatively stable over the leaching test, while concentrations of fluoride (F), mercury (Hg; Morwell only), selenium (Se) and strontium (Sr) were relatively high and exhibited no distinct pattern in their leaching profile. The majority of trace elements, such as beryllium (Be), chromium (Cr), manganese (Mn), cobalt (Co), copper (Cu) and zinc (Zn), were generally insoluble in the leachates, due to the high alkalinity of the solution. Some results from Black (1990a) and (1990b) are presented in Tables 2.3 to 2.4 and illustrated in Figure 2.5 (Hazelwood Ash Pond Sediment).

To date, only limited laboratory leaching work has been performed on Loy Yang ash. Bone & Schaap (1980) did some sequential batch leaching work on coal from the Loy Yang Open Cut mine and combusted in the experimental furnace at the former SECV research laboratory (Herman Research Laboratories, now HRL Technology). Their work, however, does not reflect the behaviour of ash from Loy Yang Power Station itself, which therefore limits the value of the findings. Black (1988) performed sequential batch leaching work on samples of Loy Yang precipitator ash.

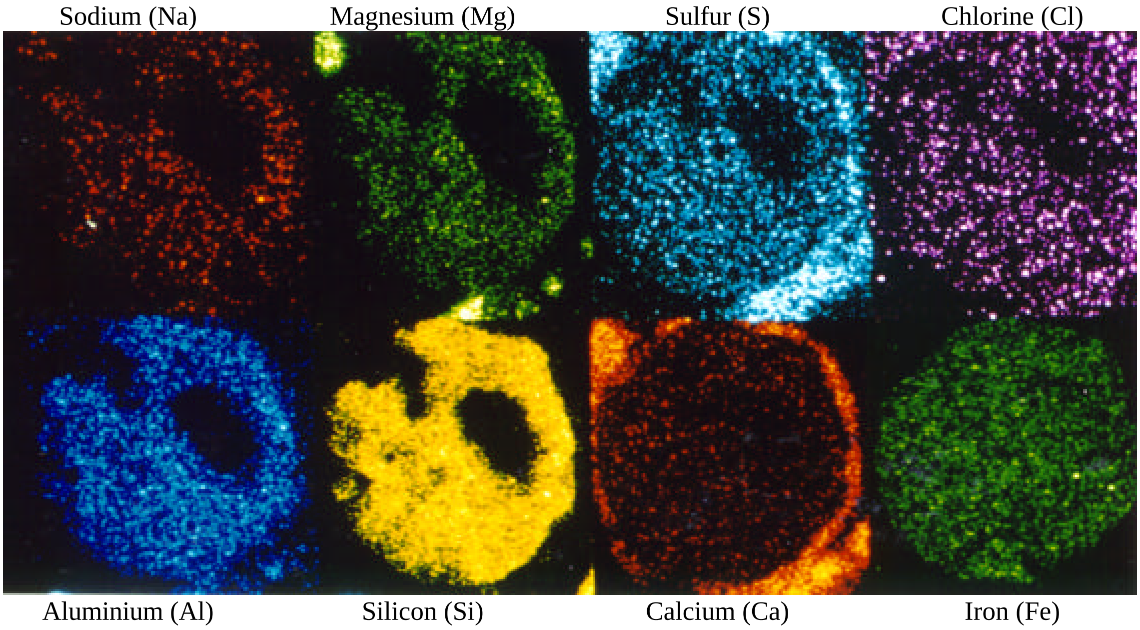

Sodium (Na) Magnesium (Mg) Sulfur (S) Chlorine (Cl)
Aluminium (Al) Silicon (Si) Calcium (Ca) Iron (Fe)

Figure 2.3 - Cross Section X-Ray Maps of Hazelwood Precipitator Ash (Black, 1990a)

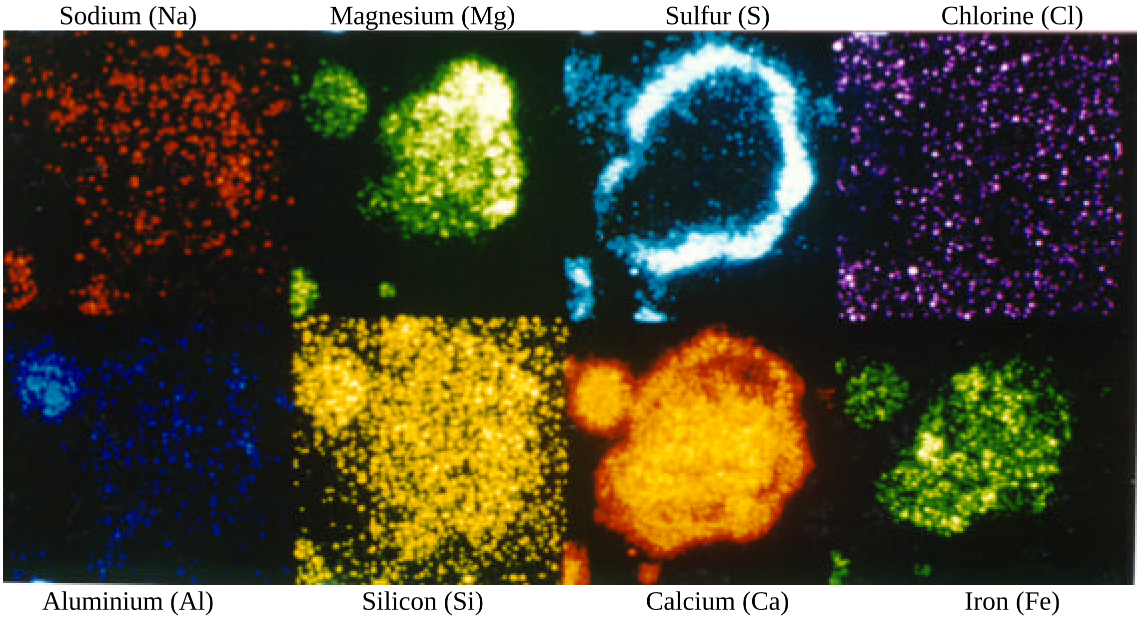

Sodium (Na) Magnesium (Mg) Sulfur (S) Chlorine (Cl)
Aluminium (Al) Silicon (Si) Calcium (Ca) Iron (Fe)

Figure 2.4 - Cross Section X-Ray Maps of Hazelwood Ash Pond Sediment (Black 1990a)

Table 2.3 - Column Leaching Results : Hazelwood Ash Pond Sediment (Black 1990a)

Vol.[#]	0.1	0.35	0.6	1.10	1.35	1.85	2.1	2.6	2.85	3.1	3.6
PV	0.37	1.30	2.24	4.10	5.03	6.89	7.83	9.69	10.63	11.56	13.42
pH	11.8	11.4	9.9	9.7	8.8	11.3	11	10.4	9.1	8.9	11.4
Cl	<1	740	415	100	51	<1	<1	<1	<1	<1	<1
SO_4	31,690	1,340	665	710	695	720	665	640	660	630	410
Na	27,440	1,590	385	230	195	175	160	130	120	105	94
K	2,709	237	67	40	34	31	29	24	22	17	15
Ca	480	520	595	480	490	485	480	505	495	380	325
Alk.	664	124	46	26	33	143	31	22	33	35	78
SiO_2	53	19	15	15	15	16	16	16	17	16	16
B[*]	1.6	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
F	320	310	210	1,930	2,230	190	80	1,530	2,030	1,930	350
V	0.2	0.2	0.2	0.2	0.2	0.3	0.3	0.3	0.3	0.3	0.2
Cr	0.4	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Se	14.9	1.6	0.9	0.2	<0.1	0.1	0.7	0.1	0.1	-	-
Sr	16	14	17	16	16	16	16	14	14	11	-
Ba	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	<0.1
Hg	3.43	0.20	<0.1	<0.1	<0.1	<0.1	0.44	<0.1	1.41	1.68	0.17
Pb	0.2	0.3	0.3	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.3

[#] - Volume in litres and concentration in mg/L. Data for 0.85, 1.6, 2.35, 3.35 L omitted.

[*] - B, F, V, Cr, Se, Sr, Ba, Hg & Pb in µg/L. PV - Column Pore Volumes.

Fe <0.5 mg/L; Mg <0.1 mg/L; Be, Mn, Co, Ni, Cu, Zn, Mo & Cd below detection limits (<0.1 µg/L).

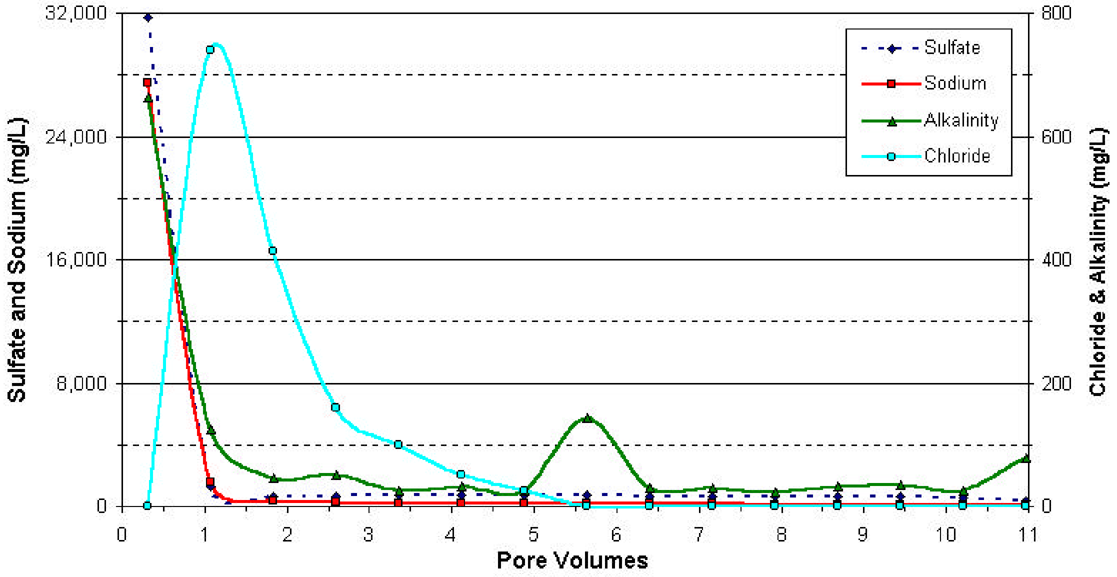


Figure 2.5 - Column Leachate for Hazelwood Ash Pond Sediment (adapted from Black, 1990a)

Table 2.4 - Limited Results[1] of Column Leaching of Yallourn W Stage 1 Precipitator Ash (mg/L) (Black, 1990b)

Vol.	0.1	0.35	0.6	0.85	1.10	1.6	1.85	2.1	2.35	2.85	3.1	3.6
pH	-	-	11.9	11.5	11.4	11.4	11.5	11.8	11.8	11.7	11.8	12.0
SO_4	110,000	76,065	29,660	1,555	1,380	1,265	795	95	34	34	36	86
Na	58,255	43,295	17,240	255	130	83	82	66	55	43	39	32

Vol. - litres; some data omitted (1.35, 2.6, 3.1, 3.35 L).

The work of Bone and Schaap (1980) on Loy Yang experimental ash demonstrated that the leachate would be strongly alkaline and the major components leached would be Na, SO_4 and Ca. A liquid-to-solid ratio of 70:1 was used, with both neutral and acidic conditions tested. The tests did not show any significant difference in major element concentrations, although trace element concentrations were considerably higher in the acidified test. It was estimated that the average leachable mass of major elements of the Loy Yang experimental ash was 36%, and 8.6 % for trace elements. In comparison, the work of Black (1990b) on Yallourn ash samples showed that most trace elements analysed were not leached, except for minor quantities of boron (B), F, Se and Sr. Similar testing on Hazelwood and Morwell ash samples leached minor amounts of B, F, vanadium (V), Se, Sr, Hg and barium (Ba) (Black, 1990a).

The sequential batch leaching work by Black (1988) on Loy Yang precipitator ash showed that the major constituents to be leached were SO_4, Na, Cl, Ca and minor amounts of Mg and K. The results are presented in Table 2.5. No analysis of trace elements was apparently performed. The tests were on 20 g of precipitator ash in 400 ml (a liquid-to-solid ratio of 20:1), conducted using both acidified (nitric acid, pH of 4) and neutral water, although there appeared to be no significant differences between the two tests (the water test concentrations were actually slightly higher).

---

[1] - there is no Cl analyses presented in Black (1990b).

Table 2.5 - Results of Sequential Batch Leaching of Loy Yang Precipitator Ash (mg/L) (Black, 1988)

Batch	pH	TDS	Alk.	Na	K	Ca	Mg	SO_4	Cl
A1	9.6	6,440	41.0	1,895	60.9	330.4	7.3	3,680	690
A2	10.4	610	46.0	112	3.7	45.2	0.9	196.7	40.3
A3	10.5	140	37.4	12.6	0.8	22.2	0.7	62.3	<5
A4	11.2	128	121.4	5.2	1.2	83.5	0.1	118.0	<5
A5	10.0	<10	30.0	5.6	0.4	13.0	1.0	13.1	<5
Initial Mass[#]		(mg)	-	1,160	72	500	960	1,344	280
Leached		(mg)	-	1,015	33.5	247	5	2,035	365
Leached		(%)	-	87.5	46.5	49.4	0.5	151	130

Batch	pH	TDS	Alk.	Na	K	Ca	Mg	SO_4	Cl
W1	9.9	6,020	41.0	1,980	61.9	68.3	6.1	3,800	720
W2	10.3	478	73.0	140	4.7	4.8	0.9	273	52
W3	10.3	124	40.6	17	1.0	0.6	0.7	62.3	5.8
W4	11.1	230	122.4	7.2	1.5	0.3	<0.1	141.0	<5
W5	10.1	78	33.6	6.0	0.4	0.2	0.8	13.1	<5
Initial Mass		(mg)	-	1,160	72	500	960	1,344	280
Leached		(mg)	-	1,075	34.8	37.1	4.3	2,144	389
Leached		(%)	-	92.7	48.3	7.4	0.4	160	139

Notes : A - Acid Batch test; W - Water (neutral) Batch test. [#] - Based on ash analysis.

The results for both batch tests indicated that approximately 19.2% of the ash mass was readily leachable, as can be seen from Table 2.5. The elements showing a percentage leached greater than 100% are likely to include some experimental error, related to analysis of the leachate and ash concentration. Similar inconsistencies are apparent with other batch leaching tests conducted on Latrobe Valley ashes (eg. Bone & Schapp, 1980; Black, 1990a & 1990b).

2.2.5 Research on Leached Ash Pond Sediments

It has been noted in the previous section that the leachable mass within ash sediments from an ash pond was generally lower than that in precipitator ash within the power station. Limited investigation has been undertaken of the in situ leaching within an ash pond, or if ash pond sediments were excavated and disposed of at an external site, for example within an overburden dump. As noted earlier, there is increasing pressure on existing ash ponds and restricted opportunity for the construction of new ponds in the future. Therefore the excavation of ash from a pond and disposed of elsewhere will become an increasingly attractive option, if the leachability of the ash is sufficiently low to meet environmental requirements.

There have been some limited investigations undertaken of ash deposited in the Loy Yang Ash Pond. The ash excavated from the pond, after a suitable period of deposition and leaching of up to 12 months or longer, is referred to as leached ash, to highlight that it has a lower soluble mass than precipitator ash when first taken from a power station (that is, a dry state directly from the electrostatic precipitator prior to slurrying). A review of some preliminary work on this aspect at Loy Yang is presented.

Drummond (1991) conducted elutriation tests and chemical analyses on samples of leached ash obtained from the Loy Yang Ash Pond. Black & Wright (1992) investigated the chemical variability of leached ash across the ash pond delta, but no leaching tests were performed. Their combined work showed a high degree of variability, as summarised in Table 2.6. Kacavenda (1994) undertook a preliminary investigation of the geotechnical properties of field leached ash, including percent fines less than 75 µm, moisture content and in-situ wet and dry densities. The samples were concentrated on the south-western and southern parts of the ash delta at the time. The results are presented in Table 2.7.

Table 2.6 - Chemical Variability of the Loy Yang Ash Pond (Black & Wright, 1992)

Constituent (%)	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	TiO_2	LOI
Average	44.1	1.8	5.5	13.5	4.9	1.1	25.4
Minimum	22.6	1	1.8	5.3	2.8	0.7	3.8
Maximum	73.4	2.9	11.6	30.4	9.4	1.8	45
Std. Deviation	14.6	0.5	2.5	5.7	1.4	0.3	10.5

LOI - Loss on Ignition.

Table 2.7 - Some Basic Geotechnical Properties of Loy Yang Ash (Kacavenda, 1994)

	Range	Average
Percent Fines (<75 μm)	26 to 91	66
In-situ Moisture Content (%)	55.3 to 204.9	112.3
In-situ Wet Density (kg/m^3)	870 to 1,540	1,270
In-situ Dry Density (kg/m^3)	450 to 990	600

Kacavenda & McKinley (1994) investigated further the geotechnical issues associated with ash disposal within the Loy Yang Overburden Dump and the environmental aspects of ash management. The geotechnical characteristics of the ash studied include compaction behaviour, shear strength, Atterberg Limits and field permeability. A total of four samples were studied, three of which displayed no plasticity. One sample (with 100% < 75 μm) had a Liquid Limit of 64% and a Plastic Limit of 10%. The hydraulic conductivity showed some anisotropy, but the difference between the vertical and horizontal hydraulic conductivity was small and the ash could be considered to behave in an approximately isotropic manner. The average hydraulic conductivity was estimated to be $3.5\text{x}10^{-6}$ m/s. The fines were observed to be washed from the near surface ash resulting in a locally higher permeability. Kacavenda & McKinley (1994) considered that the vertical hydraulic conductivity was approximately equal to the infiltration rate, due to the field permeability tests being conducted in vertical boreholes (which were sealed along the walls).

At the time of Kacavenda & McKinley (1994), leached ash excavated from the delta of the Ash Pond was still considered to be contaminated soil according to the criteria of the Environment Protection Authority of Victoria (EPAV, 1993). Any ash excavated from the pond could thus only be disposed of at a landfill licensed to accept such material. The trace element content of leached ash was variable, although generally appeared to be below the EPAV criteria on average. Given the lower soluble mass, the potential leachability under the likely field conditions in overburden was not studied. Kacavenda & McKinley (1994) considered that leached ash may be classified as fill material (uncontaminated soil), due to the low average trace element content and lower soluble mass. McKinley (1995) highlighted the fact that all early SECV chemical testing on ash was on a total concentration basis and were not tested according to EPAV's guidelines (EPAV, 1993), which only required consideration of the acid digestible fraction within soils. Thus the leachable fraction of elements would be significantly overestimated in the early SECV testing compared to current EPAV methodology. To examine this claim, a total of thirteen leached ash samples were collected from the Loy Yang Ash Pond delta in April 1995 and chemically tested according to the EPAV methodology, the results are presented in Table 2.8. Sample locations shown are in Figure 2.6.

Table 2.8 - Leached Ash Quality of the Loy Yang Ash Pond (mg/kg) (McKinley, 1995)

Sample	Ba	Cd	Cr	Co	Mo	Ni	Sn	Hg
1	220	<0.5	16	6	<4	12	<4	0.31
2	230	<0.5	26	5	<4	11	<4	0.67
3	200	<0.5	31	8	<5	20	<4	0.65
4	200	<0.5	51	13	<4	15	<4	1.5
5	150	<0.5	10	3	<4	6	<4	<0.5
6	390	<0.5	42	9	<4	14	<4	1.2
7	18	<0.5	7	<1	<4	2	<4	0.18
8	100	<0.5	71	7	<4	18	<4	1.5
9	420[1]	<0.5	18	18	<4	17	<4	1.1
10	64	<0.5	28	3	<4	9	<4	0.35
11	85	<0.5	20	2	<4	1	<4	0.2
12	390	<0.5	41	12	<4	14	<4	1.5
13a[2]	140	<0.5	46	9	<4	-	-	2.1
13b[2]	90	<0.5	110	11	<10	-	-	1.6
Average	140	<0.5	30	7.3	<4	11.5	<4	0.81
SECV	-	0.4	150	80	25	94	44	0.21
EPAV (1993)	400	5	250	50	40	100	50	2

[1] - Elutriation Procedure gave a value of 0.16 mg/L - the EPAV criteria for this test is 0.5 mg/L.

[2] - Duplicate sample analysed by alternate laboratory.

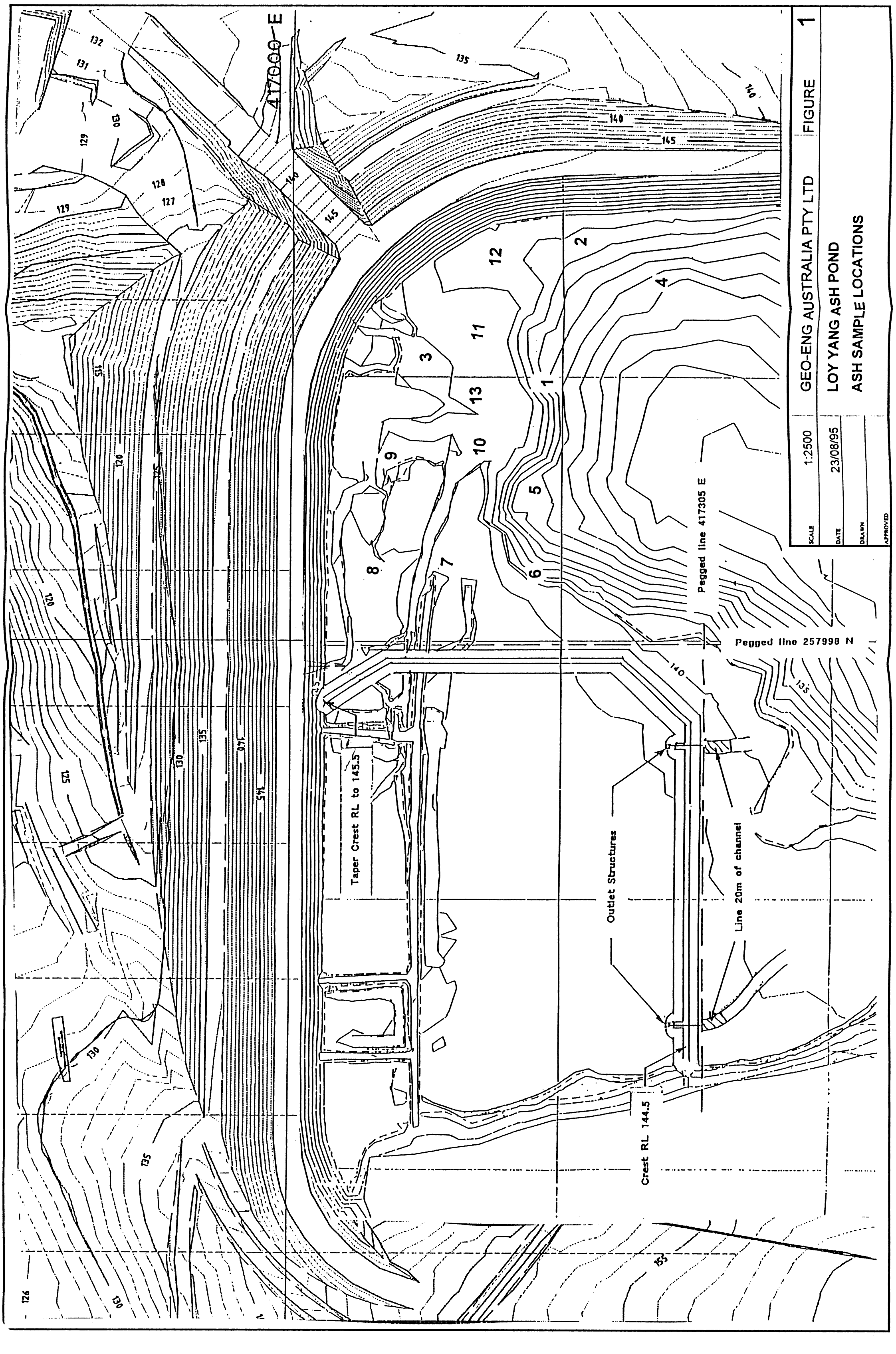


Figure 2.6 - Location Plan of Leached Ash Samples (McKinley, 1995)

The results of McKinley (1995) demonstrated that the overall average of selected elements within leached ash did conform to EPAV criteria for consideration as fill material. The results also showed that earlier SECV testing generally overestimated the leachable concentration significantly. The classification of coal ash as uncontaminated soil has been argued in Australia (Creagh, 1992) and overseas (Dusing *et al.*, 1992; Usmen *et al.*, 1992; Hasselriis, 1994), due to the low leachability of elements. The leached ash excavated from the Loy Yang Ash Pond is now classified as fill material by the EPAV (McKinley, 1998), and can be utilised as a normal soil or construction material. The new classification was subject to verification from further field-based research and the performance of the first ash disposal sites. The Loy Yang complex now operates a twin pond system in the Ash Pond (see Figures 1.2 and 1.3). After one pond has reached capacity, the discharge of ash slurry switches to the second pond and the material from the full pond is excavated for select placement within suitably engineered disposal sites in the Loy Yang Overburden Dump.

The research has continued on possible leachate behaviour under the conditions expected in overburden disposal sites. Given the limited data on the leachability of leached ash compared to precipitator ash, a more intensive study was required to quantify the leaching processes as an input to possible seepage (leachate) entering the groundwater system underneath the ash pond and future ash disposal sites within the overburden dump. Studies undertaken for these two purposes form the basis of Chapters 4 and 5 of this thesis. A review of international literature will now be presented as a basis for the goals and design of the research on ash leaching.

2.3 Literature Review of Ash Leaching and Ash Disposal

2.3.1 Characterisation of Ash Morphology and Mineralogy

Many investigators have found that the properties of coal ash and ash leachate are highly variable, depending upon factors such as the geology of the coal source (black, brown, geologic basin, etc.), combustion method, and the disposal method used (eg. Gray & Lin, 1972; Libicki, 1978 & 1983; Milligan & Ruane, 1980; Bahour *et al.*, 1981; Golden, 1983; Summers *et al.*, 1983; EPRI, 1993; Hasselriis, 1994; Nataatmadja & Morgan, 1999). The following general physical and chemical characteristics can be summarised.

The major constituents of coal ash are generally oxides and/or salts of Si, Al, Fe, Ca, Mg, S, Na, K, titanium (Ti) and Cl (Brown & Ray, 1983; Mattigod *et al.*, 1990). These constituents are predominantly derived from the inorganic material and rock detritus in the coal (Gray & Lin, 1972; Summers *et al.*, 1983; Golden, 1983; Black, 1990b). The different proportions of these elements will generally determine the bulk physical and chemical characteristics of a given coal ash (US-EPA, 1979; Eighmy *et al.*, 1995). For example, Nataatmadja & Morgan (1999) present the chemical composition of coal ashes derived from two black coal-fired power stations in Queensland, Australia. At the Gladstone utility the ash has a high proportion of lime (CaO) and thus the ash leachate is strongly alkaline with a pH of about 12.5. In comparison, the Tarong utility produces ash with a very low amount of lime and the ash leachate is mildly acidic at pH 4. Typical ranges of the major elements in coal ash are given in Table 2.9.

Table 2.9 - Typical Concentrations of Major Ash Constituents (%)
(Mattigod *et al.*, 1990)

	Fly Ash	Bottom Ash
Al	0.1-20.85	3.05-18.5
Ca	0.11-22.30	0.22-24.10
Fe	1-27.56	0.4-20.10
Mg	0.04-7.72	0.2-4.8

	Fly Ash	Bottom Ash
K	0.17-6.72	0.26-3.3
Si	1.02-31.78	5.10-31.20
Na	0.01-7.10	0.08-4.13
S	0.04-6.44	<0.04-7.40

Trace elements that can be present at elevated concentrations in coal ash could include Mn, phosphorous (P), Sr, Ba, Be, B, F, V, Cr, Co, nickel (Ni), Cu, Zn, arsenic (As), Se, molybdenum (Mo), cadmium (Cd), uranium (U), thorium (Th), Hg, tungsten (W) and lead (Pb) (Bone & Schaap, 1980; Dudas, 1981; Summers *et al.*, 1983; Libicki, 1983; Roy *et al.*, 1984; Black, 1990a; Eary *et al.*, 1990; Creagh, 1992; Chander *et al.*, 1994; Chichester & Landsberger, 1996). The presence and concentration of trace elements in coal ash is related to the properties of the coal and the geological basin in which the coal was formed (Golden, 1983). Indeed, if the appropriate analytical equipment were available, virtually all of the known elements could be detected in coal ash, varying in concentration by up to several orders of magnitude (Goetz, 1983). Typical concentrations of trace elements found in coal ash is given in Table 2.10.

Table 2.10 - Typical Ranges of Trace Elements in Coal Ash (mg/kg) (Eary *et al.*, 1990)

	Fly	Bottom
As	2 - 440	0.02 - 168
Ba	1 - 13,800	110 - 9,360
B	10 - 5,000	2 - 513
Cd	0.1 - 130	0.1 - 4.7
Cr	4 - 900	0.2 - 5,820
Cu	33 - 2,200	4 - 930
Pb	3 - 2,100	0.4 - 1,100
Mn	25 - 3,000	60 - 1,900

	Fly	Bottom
Hg	0.01 - 12	0.01 - 4
Mo	1 - 140	1 - 440
Ni	2 - 4,300	<10 - 2,900
Se	0.2 - 130	0.1 - 10
Sr	30 - 7,600	170 - 6,400
V	12 - 1,180	12 - 540
Zn	14 - 3,500	4 - 1,800

It is generally recognised that the many trace elements enriched in coal ash are sorbed on the surfaces of the ash particles (Shannon & Fine, 1974; Theis & Wirth, 1977; Elseewi *et al.*, 1980; Warren & Dudas, 1986; Le Seur Spencer & Drake, 1987; Hasselriis, 1994). Coal ash contains little amounts of organic matter, and so trace elements are thought to sorb onto the surfaces provided by Al, Fe and Mn oxides (Theis & Wirth, 1977). The geochemical behaviour of many trace elements, such as Ba and Sr for example, is further complicated by co-precipitation reactions (Eary *et al.*, 1990; Felmy *et al.*, 1993; Eighmy *et al.*, 1995). There has been research that shows a positive correlation between ash particle size and enrichment of the ash surface with trace elements (Davison *et al.*, 1974; Hansen & Fischer, 1980; Mattigod *et al.*, 1990). The surface-bound nature and correlation with fine particle size for trace elements in coal ash has created cause for environmental concern since such a physical distribution enhances accessibility for leaching.

The ash itself consists of irregularly shaped particles and spheres of complex silicates of these minerals, including minor portions of partially combusted carbon (“soot” or char) and magnetic particles or glass (Golden, 1983; Summers *et al.*, 1983; Mattigod *et al.*, 1990). Coal ash can also contain hollow particles, known as "cenospheres", which helps give ash a low bulk density and high porosity (Mattigod *et al.*, 1990; Creagh, 1992) (although Latrobe Valley ash generally has very few cenospherical particles; Peterson *et al.*, 1982).

The engineering properties of coal ash are highly variable (Gray & Lin, 1972). Bahour *et al.* (1981) reviewed the available data and concluded that properties such as shear strength, compressibility and permeability are, to a certain degree, dependent upon the chemical behaviour and composition of the ash. The presence of lime and water can cause the ash to cement in a similar way to Portland cement (ie. pozzolanic ability), thereby increasing the shear strength with time and decreasing the compressibility and permeability (Bahour *et al.*, 1981). Ash is generally of low bulk density and medium to high porosity (Summers *et al.*, 1983; Mattigod *et al.*, 1990; Usmen *et al.*, 1992; Chichester & Landsberger, 1996). In general, most ashes are weak materials without active pre-treatment prior to or during use or disposal (Nataatmadja & Morgan, 1999). For example, unstabilised ash disposal sites have been known to collapse under heavy rainfall (Nataatmadja & Morgan, 1999).

2.3.2 Characterisation of Ash Leachate

The generation of coal ash leachate is through the contact of water with the ash (Brannon & Myers, 1994). The water soluble salts on the surface of the ash particles are mobilised into solution, creating a potentially high salinity leachate (US-EPA, 1979; Dudas, 1981; Summers *et al.*, 1983). The chemistry of the leachate varies quite considerably, with pH ranging from low (acidic) to high (alkaline), and medium to high total dissolved solids (Bahour *et al.*, 1981; Summers *et al.*, 1983; Roy *et al.*, 1984; Roy & Griffin, 1984). The majority of ash leachates tend to be alkaline due to the lime present (Theis & Wirth, 1977; Mattigod *et al.*, 1990), although high Fe in an ash can lead to an acidic ash through oxidation and the release of hydrogen ions. Indeed, the alkaline nature of many ashes has seen an increasing number of applications, with examples including the neutralisation and/or prevention of acid mine drainage (eg. Ritcey, 1989; Misra *et al.*, 1996), soil cover material for tailings or landfills (eg. Marcus & Sangrey, 1981; Mamane & Gottlieb, 1992), structural fill for road bases or underground mine backfill (eg. Maher *et al.*, 1992; Ahmed & Lovell, 1992; Balsamo, 1998), and substitute fertilizer or soil amendment (eg. Aitken *et al.*, 1984; Aitken & Bell, 1985; Havukainen & Viitasalo, 1992; Balsamo, 1998). The chemistry of leachate, controlled by the varying proportions of soluble minerals within the ash, is often dominated by high concentrations of Na, SO_4 and Ca, and to a lesser extent Cl.

The solubility and extent of leaching of a particular trace element will depend on the pH and redox conditions of the leachate over time, sorption characteristics of the ash and major element chemistry (Eary *et al.*, 1990; Dusing *et al.*, 1992; Eighmy *et al.*, 1995). For example, Dusing *et al.* (1992) presented data that showed Cr is more soluble and thus readily leachable under highly oxidising conditions, while As, V and Fe were more strongly leached under reducing conditions. The solubility of trace elements, therefore, needs to be determined on a site specific basis due to the significant variability between ash mineralogy, geochemical conditions and disposal environments. On the basis of difficulties highlighted earlier in characterising trace element speciation in coal ash, it is similarly difficult to quantify trace element behaviour in leachate.

2.4 Overview of Leaching Processes

There are a number of competing physical and chemical processes occurring during the active leaching of ash during utilisation or disposal. These include dissolution, advection, diffusion, adsorption and mineral precipitation, depicted in Figure 2.7. As highlighted in previous sections, the extent of many of these processes are site specific to a particular power station or coal source. Leaching of ash takes place through dissolution of constituents inside or on the surface of the ash and and transport through the pore structure to the surrounding pore waters (Côté *et al.*, 1986). These processes can be categorised as chemical or physical (transport) phenomena (Côté *et al.*, 1986).

The most common progression for leaching many different waste materials is a large initial leachate plug, known as "initial washoff", which decreases rapidly to a much lower steady state value, controlled by a diffusive leaching flux (Côté, 1986). This "plug flow" behaviour is demonstrated by the column leaching tests of Black (1990a), shown earlier in Figure 2.5. An important distinction to make when comparing the results of different column leaching tests is whether the leachate concentrations are plotted versus time or versus pore volume of the ash in the column. Farquhar (1989) represented this declining rate of leaching as shown in Figure 2.8. As time progresses, the leachate concentration approaches a steady state value and the leached mass approaches a maximum.

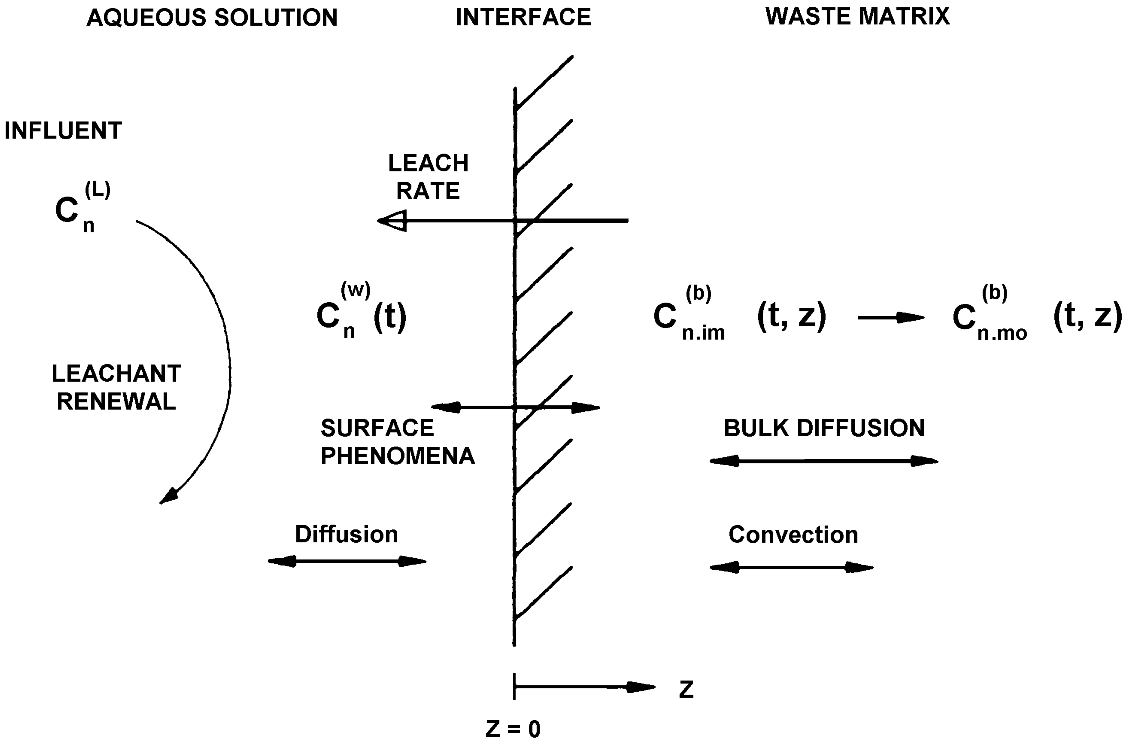


Figure 2.7 - Schematic of Conceptual Leaching Processes in Solid Wastes (Côté, 1986)

where z - distance from the ash particle surface; t - time;

C - concentration of specific solute or constituent (subscript n);

L - leachant concentration subscript (influent water) [$C_n^{(L)}$ (t)];

w - leachate concentration near the surface of the ash matrix [$C_n^{(w)}$ (t)];

b - ash matrix concentration (ie. bulk waste concentration) [$C_{n/im}^{(b)}$ (t) / $C_{n/mo}^{(b)}$ (t)];

im / mo - immobile / mobile concentration within the ash matrix.

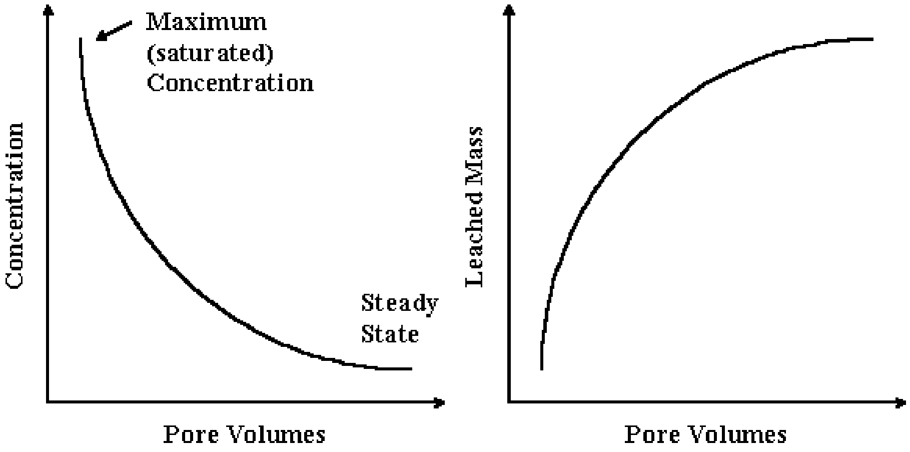


Figure 2.8 - Progressive Leaching versus Pore Volume (adapted from Farquhar, 1989)

A constituent inside the ash matrix may be in an immobile form ($C^{(b)}_{n/im}$), such as precipitated or sorbed, or a dissolved and therefore mobile form ($C^{(b)}_{n/mo}$). The proportion of a constituent in the mobile and immobile phase may be described by equilibrium chemistry or kinetic (rate limited) chemistry (Côté *et al.*, 1986). The position of this equilibrium may be disturbed by diffusion of the mobile phase outside of the ash matrix or advective flow, surface transfer phenomena (sorption) or diffusion of external species (such as acid, H^+, or chemical complexing agents) into the ash matrix (Côté *et al.*, 1986). The chemical concentration at the interface of the ash matrix and the pore space ($C^{(w)}_n$) provides the driving force for exchange between the ash matrix and leachant inflows (Côté *et al.*, 1986).

On the basis of the above discussion and these distinctions proposed by Côté *et al.* (1986), the exponential decline in leachate concentration for major elements such as SO_4, Na and Cl, is controlled by rapid dissolution of available minerals and advective flow of leachate removing these constituents from the pore volume of the ash. The overall driving force for leaching is the concentration difference between $C^{(w)}_n$ and $C^{(b)}_{n/mo}$. The influent solution (at concentration $C^{(L)}_n$) mixes with the aqueous solution at the ash-water interface (at $C^{(w)}_n$) and transports the mass of the constituent away, altering the local equilibrium for the ash matrix and forcing more constituent into solution.

As reviewed earlier, a significant proportion of ash contains more readily soluble minerals, such as halite (NaCl), thenardite (Na_2SO_4) and gypsum ($CaSO_4.2H_2O$), which are predominantly controlled by equilibrium dissolution - an instantaneous process. The migration of fresh leachant into and out of the ash, therefore, leads to a rapid decline in the presence of these minerals as further leachant flows through the ash. This process leads to the exponential decline in leachate concentration described by Farquhar (1989) and typical column leaching tests. For trace and other elements such as Al, Ca and Fe, the controls on leaching would also include the pH of the interface and influent water, sorption ("surface") phenomena and redox state and their behaviour would therefore be different to the "initial washoff" observed for major elements.

An important distinction in the approach described above is the use of pore volumes, or the volume of porosity in a given ash or waste material. By calculating the volume of leachate flow through an ash disposal site or column test and dividing this by the pore volume of the ash material, a standardised curve can be adopted and leachate concentrations plotted versus pore volumes. The pore volumes essentially gives an indication of the liquid-to-solid ratio passed through an ash or waste material. The principal advantage is that this is a non-dimensional approach, facilitating comparison of different ashes and tests.

An alternative approach to leaching processes was presented by Kosson *et al.* (1996). They described leaching phenomena according to three fundamentals (factors) : (i) availability, (ii) solubility and (iii) mass transfer controlled release. The availability is defined as the maximum quantity or soluble fraction of a constituent that can be released into solution under aggressive leaching conditions. Such conditions, in theory, should provide worst case environmental release scenarios for 1,000 to 10,000 years, particularly for trace elements although the more soluble salts may reach this point in a matter of years. The second factor, the solubility of different minerals and trace elements, is also critical to leaching phenomenon, as the low liquid-to-solid ratios generally found in field disposal sites can often lead to a geochemically saturated leachate concentration with respect to particular constituents, minerals and trace elements. As noted previously, the solubility of most trace elements is strongly correlated with leachate pH, and can also be influenced by the presence of chemical complexing agents and redox conditions. The third factor, mass transfer-controlled release, occurs through the slow release of a constituent from the solid matrix into solution. Geochemical saturation or equilibrium with the leachate is often not achieved. This is typically due to control by diffusion, a slow process inside ash grains, although chemical sorption (retardation) and precipitation processes can also be important.

Based on the approach of Kosson *et al.* (1996), major constituents such as SO_4, Na and Cl, are both soluble and available, whereas species such as Fe or Pb are available but not readily soluble. For example, the total percentage of thenardite and gypsum in ash sample would represent the available SO_4 for leaching, but the solubility of SO_4 would be controlled by leachate chemistry and site specific conditions. Trace elements, controlled by complex chemical reactions and sorption phenomena, are therefore limited in leachate by their lower mass-transfer rates.

In summary, by considering the fundamental physical and chemical processes occurring inside ash, leaching phenomena can be described and quantified. To assess these processes, a variety of leaching tests have been developed. These will now be reviewed.

2.5 Overview of Leaching Tests

In order to examine the generation and decay of leachate from a particular ash, a significant amount of research effort has been directed at developing laboratory and field tests which can quickly and economically allow the environmental assessment of ash leachate generation and behaviour. The various leaching tests developed to date have benefits and disadvantages, and can be broadly divided into two main categories of tests : batch and column tests (Black, 1990a). A further type of test is a field or pilot scale test. Batch tests are often referred to as "static" tests since they are effectively independent of time (given that most dissolution reactions approach equilibrium rapidly for the soluble minerals in ash). Column tests are time continuous and can therefore be directly related to the field scale behaviour of ash disposal sites.

The general objectives of batch and column leaching tests are to quantify the availability, solubility and/or mass-transfer controlled behaviour of a particular species or solutes released in ash leachate (Eighmy *et al.*, 1995; Kosson *et al.*, 1996). According to Jackson *et al.* (1984), an ideal leaching method should :

- use a leaching solution likely to be encountered in the disposal environment;
- minimise particle size alteration, leachate dilution and experimental error; and
- allow the estimation of leachate concentrations as a function of time.

2.5.1 Batch Leaching Tests

A batch test involves the mechanical mixing of a specified mass of waste material with a known volume (or mass) of solution for a period of time, after which the chemistry of the resulting leachate is determined (Black, 1990a & 1990b). The main experimental factors that can be altered in batch tests include the ratio of leachant solution to ash mass (or liquid-to-solid ratio), the type of leachant solution (distilled water, sea water or acid-buffered solutions, for example), the mixing method and the period of time for mixing. A summary of these variables is given below in Table 2.11.

Table 2.11 - Summary of Variables in Batch Tests (adapted from Black, 1990a)

	Liquid to Solid Ratio	Leaching Solution	Temp. ^{0}C	Mixing Time	Mixing Method
Range	1:3, 1:4, 1:5, 1:10, 1:20 and 1:100	Distilled, Deionised, Acid buffered, Artificial leachate, Sea water	Room 4 to 25	30 min., 24 to 48 hrs, 7 days	Shaking Orbital Rotation
Average	1:20	Deionised water	Room	24 hrs	Shaking

A variety of standard batch tests with statutory significance have been developed by environmental regulators to minimise the variability between the experimental conditions used and to ensure the compatibility of results. The Environmental Protection Agency of the United States (US-EPA) has developed the "Toxicity Characteristic Leaching Procedure" or TCLP (US-EPA, 1990) while the Environment Protection Authority of Victoria (EPAV) has developed a slightly different batch method called the Elutriation Procedure (EP) (EPAV, 1986). Both tests have standards which allow or require the use of acid buffered solutions or distilled water, specified mixing times or other parameters which can be varied to suit the purpose and waste being studied. The regulators have set concentration limits for different contaminants determined from a TCLP or EP test as the basis for classifying a waste as hazardous or non-hazardous. In principle, both the TCLP and EP tests are intended to provide an indication of the available leachable fraction of a particular contaminant that may become available to the environment.

In order to ascertain the effects of more aggressive solutions (an acidic groundwater, for example) on ash leachability, some researchers recommend the use of both acidic leaching solutions combined with tests using distilled or deionised water in order to ensure accurate worst case leachability scenarios (eg. Black, 1988). Two important considerations in the use of acid-buffered leaching solutions is the type of acid to use, such as acetic, nitric or sulfuric acid, and whether the pH is required to be held constant during the test (de Groot *et al.*, 1989). The TCLP test, for example, requires a constant pH of 5, whereas the EP test requires an initial pH to be established and so the final pH of the leachate will be set by the mineral reactions and leaching characteristics of the ash or waste material.

Batch tests are relatively quick, inexpensive and can be repeated on a large number of samples simultaneously. They provide a "worst case scenario" of leaching by condensing several years of leaching into a short period of time, provided the small sample is representative. Batch testing will determine the available leachable mass within an ash or waste (due primarily to the agitation or mixing), and to a certain extent a constituent's solubility from the ash (depending on the leaching solution and conditions used). Several authors argue that the mixing in batch tests often overestimates ash leachability compared to field conditions (Hasselriis, 1994; Chichester & Landsberger, 1996; Kosson *et al.*, 1996). The contraction of time is a major limitation to batch tests since this may preclude the simulation of long-term leachate release at a disposal site, and can also neglect the kinetic and time-dependent processes which occur in an ash disposal site and are controlled by slower mass-transfer or diffusion processes (Black, 1990a; Mattigod *et al.*, 1990; Kosson *et al.*, 1996). Hence, the test conditions used for TCLP and similar batch tests are not considered to be a good representation of variable field conditions over time in a disposal site or for a potential beneficial use (Hasselriis, 1994).

One approach used to overcome the problem of time contraction is the use of "Sequential Batch Leaching Tests", whereby the same ash (or waste) sample is subjected to several episodes of mixing and chemical analysis (Black, 1988, 1990a & 1990b; Brannon & Myers, 1994). This test allows some interpretation of the effect of time on leaching behaviour, although caution is required before extrapolation to field conditions.

2.5.2 Column Leaching Tests

Another common laboratory test is a Column Leaching Test. This test uses a perspex or glass column of varying dimensions and compacting a sample of ash inside it. A leaching solution is added to the top of the column and the solution of leachate at the bottom of the column is collected for chemical analysis. The flow rates used are generally very low and tend to simulate the average rainfall of the area under study (Black, 1990a). A summary of the variables used is given in Table 2.12. Some example columns are shown in Figures 2.9 and 2.10.

Table 2.12 - Summary of Variables in Column Tests (adapted from Black, 1990a)

	Diameter	Height	Influent Solution	Time
Range	2.5 cm, 5 cm, 6.9 cm, 14.5 cm to 150 cm	20 cm, 30 cm, 80 cm, 250 cm to 2,500 cm	Distilled, Deionised, Acid buffered, Artificial leachate, Sea water	1 month to >2 years
Average	5 cm	60 cm	Deionised water	~ 6 months

The maximum particle size recommended for column tests is no higher than 3 mm or the diameter should be about 10 to 20 times the maximum particle diameter (van der Sloot *et al.*, 1984). The compacting of the ash samples into the column is generally performed to simulate the expected density in disposal sites (Black, 1990a). It is important to ensure uniform packing within the column and to prevent possible preferrential pathways during leaching (such as side wall leakage).

It has been found that by presenting the results in column pore volumes, the results of different column tests can be readily compared (Brown *et al.*, 1976; Black, 1990a). The principal problem with column tests is that they take a significant amount of time to complete, up to several months or years in some cases. The additional equipment and long time periods required often discourages the use of several column tests run simultaneously. The time-bound nature of column tests makes them more representative of the conditions that are likely to occur in a field ash disposal site (Brown *et al.*, 1976; Milligan & Ruane, 1980; Brannon & Myers, 1994; Chichester & Landsberger, 1996).

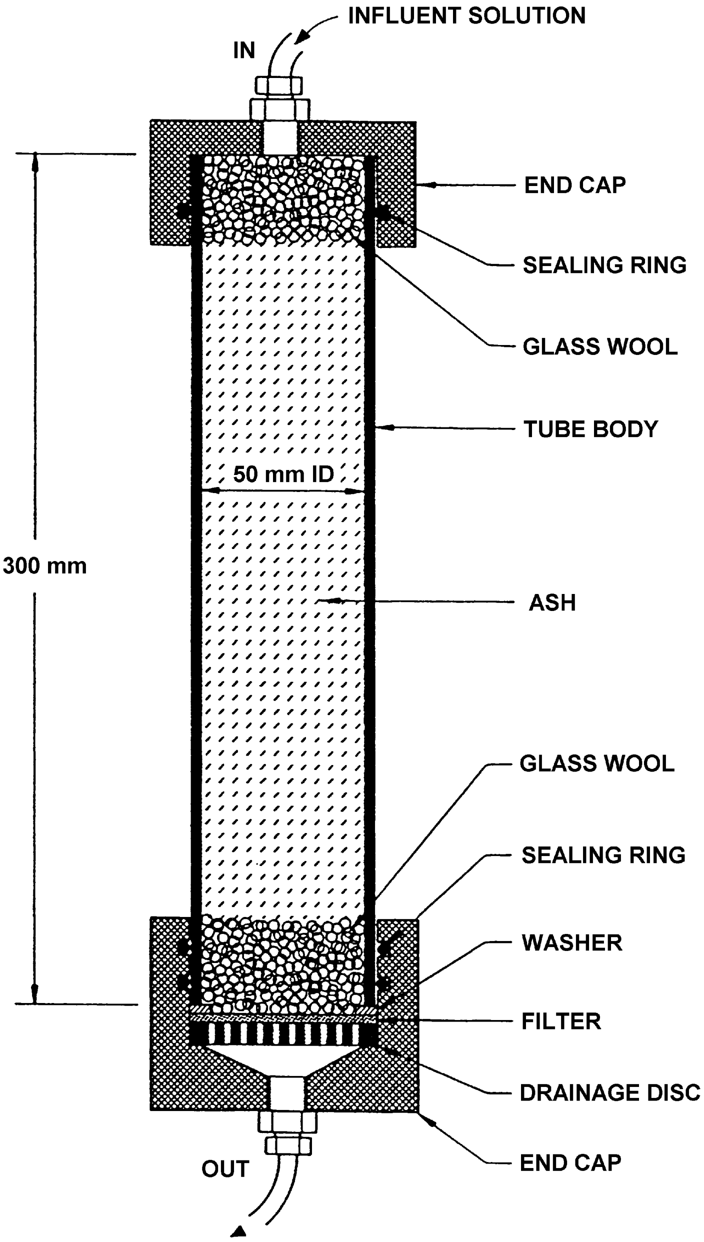


Figure 2.9 - Typical Design of a Column Leaching Test (Black, 1990a)

Figure 2.10 - Examples of Column Leaching Test Equipment (Black, 1990a)

2.5.3 Field Leaching Tests

A less common leaching test is a Field Leaching Test. This involves the construction and operation of small scale disposal sites, based on the expected design of an operational site. There are only a small number of published field studies available in the literature, due principally to their expense to construct and lengthy period of operation. The thickness, width, leachate drainage and collection system, method of inflow application (eg. artificial irrigation or rainfall), period of sampling, internal moisture and chemistry monitoring and so on are variables which depend on the objectives to be achieved.

Fruchter *et al.* (1990) presented the results of 3 years of monitoring and geochemical analysis at an alkaline fly ash field lysimeter at a power station in Pennsylvania, USA. The above-ground lysimeter was 3 m in height, and built as a truncated pyramid with a 30.5x30.5m base and 18.3x18.3 m top. A 50 cm layer of coarse bottom was placed at the base to facilitate drainage. The only inflow was rainfall, leaving the lysimeter with unsaturated conditions for most of the year. The leachate was generally only produced in the winter months from October to May, after heavier rainfall events. The cumulative leachate over the 3 years amounted to 0.3 pore volumes. The monitoring data and geochemical analysis showed that the major solutes leached from the ash were Ca and SO_4, controlled by dissolution of gypsum. Low concentrations of Fe and Al were detected, and were considered to be controlled by their respective amorphous hydroxides. The presence of silica (SiO_2) in the leachate was observed, although its mineral source could not be identified with certainty. There were several trace elements detected in leachate at varying concentrations, namely As, Ba, B, Cd, Cr, Cu, Mo, Sr and Se. Most trace elements appeared to be controlled by solubility and complex co-precipitation processes, although for As, B, Cd, Mo and Se geochemical controls could not be identified.

Hasselriis (1994) presented the results of a field study of an 18 m high (about 60 ft) ash stockpile subjected to natural rainfall for between 4 to 7 years. The ash was derived from a municipal solid waste incineration facility in the USA. The annual rainfall was approximately 100 inches or 2,540 mm. A series of TCLP tests were conducted on core samples of ash obtained from the stockpile. Only the data for lead and cadmium is presented in this paper, and hence comments are limited to these elements. The leachability of Cd was generally very low, at less than 20% of the regulatory criteria. For Pb, the leachability data appeared to indicate substantial migration due to the infiltration of rainwater through the ash profile, leading to redistribution and concentration in the profile. Hasselriis (1994) concluded that ash leachability was low.

Igarashi & Shimogaki (1996) reported on a similar 2 year lysimeter study undertaken in Japan to investigate the reclamation of alkaline coal ash disposal sites. Their primary focus was on modelling of leachate production and migration. The lysimeter used a steel container 5 m in length, 1.5 m in width and up to 2 m in height. An 80 cm layer of sand was placed in the base of the lysimeter for drainage purposes and a 40 cm of loam soil was used to cap the lysimeter. A vertically installed sheet pile was used to control leachate flow during operation. Seawater was then irrigated on the surface until a flow rate of about 83 litres per day was achieved. No fresh water was added to simulate rainfall. The evapotranspiration rate was much lower than the flow rate and this was therefore ignored in the water budget. The monitoring data showed leaching of Ca and Cr from the ash layer into the sand layer, which discharged to the sea. The modelling of the lysimeter was based on unsaturated flow theory using the FEMWATER numerical model. The leaching of ash was represented by a two-fraction approach, with the leaching governed by a first-order kinetic reaction with respect to the solid phase concentration for each fraction, shown below. The two-fraction leaching model was able to represent the overall flow and solute leaching behaviour in the lysimeter, correlating with the transport of chromium through the drainage layer to the sea.

$$\frac{\partial S_1}{\partial t} = k_1.S_1 \qquad \frac{\partial S_2}{\partial t} = k_2.S_2 \qquad \text{and} \qquad S_1 + S_2 = S_0 \qquad 2\text{-}1$$

where S_1 - rapidly-leaching fraction of solid phase concentration;
S_2 - slowly-leaching fraction of solid phase concentration;
S_0 - total solid phase concentration;
k_1 - first-order rate constant for the rapidly-leaching fraction;
k_2 - first-order rate constant for the slowly-leaching fraction.

Johnson *et al.* (1998) reported an extensive field study of an operational landfill in Lostorf, Switzerland, accepting bottom ash from a municipal solid waste incinerator. Their study was conducted over a period of 22 months and examined rainfall, leachate discharge, dye tracer tests and oxygen stable isotopes ($^{18}O/^{16}O$). Their work showed strong evidence of preferrential pathways for water migration in the landfill, leaving little time for interaction with and leaching of the contained soluble salts in the bottom ash. They did not discuss or assess what these preferrential pathways could be. On the basis of chemical and isotopic analyses, they calculated that about 9 to 40% of summer discharge was derived from ash leaching, showing a high proportion of rapid preferrential flow due to the higher intensity rainfall in summer (that is, 60 to 91% of discharge being rainfall). About 20 to 80% of the incident rainfall passed through the landfill in summer. In winter, about 90 to 100% of the discharge was leachate, with only about 10% of the rainfall passing through the landfill. They described this effect as "piston flow", and was critical in examining the time for geochemical reactions in the ash and whether equilibrium could be assumed in hydrological modelling. Their data suggested that a "quasi-equilibrium" situation existed at Lostorf, allowing realistic geochemical modelling of leachate generation and solute transport within the landfill.

The authors did not discuss the hydraulic mechanisms controlling the flow of moisture within the ash landfill and the respective proportions of leachate over the two years studied. The data they present suggests strong control due to unsaturated conditions prevailing within the ash profile, related to the intensity of inflow. This behaviour is important and will be examined further in later chapters of this thesis.

2.5.4 Summary of Leaching Tests

The scale up from batch, column to field studies is generally achieved through the conversion of column and field data to pore volumes. A critical issue in scaling-up various experimental data is that of time versus pore volumes. For example, if two identical columns were packed with the same ash and leached for a period of 6 months but with significantly different flow rates, there would be a similar difference in the pore volumes reached for each column. The leaching curve versus pore volumes would ideally be the same, with the higher flow rate column further along this curve, but the leachate concentration versus time would be significantly different for each column. There appears to be no consistent approach in the literature to accommodate this fundamental issue of scale-up, time and non-dimensional analysis. The ability to relate one methodology to the other is important since water flow models (under saturated or unsaturated conditions) and solute transport models are generally based on time and do not incorporate non-dimensional leaching curves. The various approaches for modelling solute transport and leaching will be analysed and further developed in Chapter 8.

With appropriate care, the combination of batch, column and field leaching tests can assist in understanding fundamental leaching processes and leachate chemistry for a given ash and expected disposal conditions. This enables the description of potential leachate characteristics, which can then be utilised to assess potential environmental impacts on groundwater resources at a given ash disposal site.

2.6 Hydrogeological Impacts of Coal Ash Disposal

There have been relatively few case studies published in the literature concerning the impacts on groundwater resources from ash disposal. A summary will now be presented, as a basis for the analysis of environmental impacts from ash disposal and leaching and potential solute transport rates.

Andrews & Anderson (1978) investigated the combined impact of the 200 hectare cooling lake and 28 hectare ash disposal pit of a Wisconsin (USA) power plant. Their research, based on 6 years of monitoring data, showed that the local surface and subsurface hydrology had been radically altered by both the cooling lake and the ash disposal pit, including thermal heating, changes in groundwater levels and the impact of solutes leaching from the ash pit into groundwater. Solute transport of Ca and SO_4 down-gradient from the ash pit was being detected.

Theis *et al.* (1978) examined the behaviour of trace elements in groundwater derived from the leaching of an ash disposal site in Michigan, USA. The trace elements were shown to be released into groundwater from the disposal pond, although the loading rates of the pond did appear to affect the groundwater concentrations to some degree. They showed a general decrease in concentration of most major and trace elements with further distance from the ash pond. The geochemical controls were thought to be Fe and Mn oxides. The sharp initial peaks observed for many elements, however, suggested that there was either insufficient time or unfavourable conditions (eg. pH) to allow the oxides to exert control relative to the rapid changes in the disposal pond.

Rogers & Kean (1980) investigated the extent of groundwater contamination at a Wisconsin (USA) ash disposal site, located in a disused sand and gravel pit situated in undifferentiated glacial sands, clays and silty clays above dolomite ($CaMg(CO_3)_2$). The pit was not lined before operations commenced. They employed the use of geophysical resistivity techniques to assess the location and migration of subsurface contamination, showing this as a viable technique when combined with laboratory data and testing.

Cherkauer (1980), in a companion paper to Rogers & Kean (1980), addressed the impacts due to leaching and solute transport from the ash disposal site. The ash was deposited in a dry state in the pit, with the leachate being midly acidic at a pH around 4.5 and consisting mostly of SO_4, Ca and Mg with minor Fe and Mn present. The transport of these leachate constituents was detected downgradient from the disposal site, with additional Ca and Mg derived from the dissolution of the dolomite by the acidic leachate. The leachate plume was locally discharging to a nearby wetland. There appeared to be no transport of trace elements from the disposal site, due to sorption on clays in the aquifer.

Milligan & Ruane (1980) undertook a broad study of 2 power plants in the USA to characterise the ash leachate and the varying hydrogeological environments in which leachate could occur. The chemistry of pore waters within the ash disposal site was generally different to that in groundwater, with pore waters showing different pH and higher concentrations of major and minor elements. Importantly, they documented attenuation processes in groundwater that acted to limit and reduce the impact of the ash leachate from a disposal site. The attenuation of constituents in the leachate was primarily due to clays contained within the natural soils. Milligan & Ruane (1980) stated that further research was required to more fully ascertain the impact on groundwater quality from the ash disposal sites.

Libicki (1983) presented the results of a joint Polish-USA study over five years investigating the impacts on groundwater from coal ash disposal in an abandoned sand pit. The study documented direct contamination of groundwater, principally due to the direct contact between the ash in the pit and the underlying aquifer. The extent of migration of the ash leachate was dependent on local hydrogeological conditions and especially hydraulic gradients in the aquifer. The contamination generally consisted of increased salinity from SO_4, Na, Cl with minor K and Ca. There appeared to be marginal inceases in Al, As, B and Pb. The extent of groundwater contamination was dependent on the leachability of the ash, amount of rainfall entering the disposal site and potential self-sealing due to migration and accumulation of the finer particles leading to lower permeability.

A further series of important observations were made by Libicki (1983). Firstly, erratic but detectable impacts on groundwater were noticeable within 12 months of disposal, and was clearly identifiable by 2 years after commencement of the site. Secondly, the extent of groundwater impacts began to decrease after 2 ½ years. The mechanism behind this was unclear, but could be due to recelamation of 30-40% of the surface area of the disposal site, or decreased permeability of the base of the site due to migration and accumulation of the fine particle fraction of the ash. A series of batch tests helped to identify which constituents in the ash would likely lead to impacts on groundwater.

Simsiman *et al.* (1987) investigated the effect of alkaline ash disposal ponds on groundwater quality at a Wisconsin coal-fired power station. The pond is divided into three separate areas, for bottom ash and primary and secondary ash settling ponds. The principal contaminants found to be released were from the secondary ash disposal pond and migrating through groundwater. These were Na, SO_4 and B. The bottom ash pond was shown to have a minor influence on groundwater quality. The primary ash pond did not appear to be influencing the quality of groundwater beneath and downgradient from the pond. This lack of impact was considered to be due to some sealing and reduction in permeability of the primary ash pond, leading to reduced seepage. There appeared to be no attenuation of Na, SO_4 and B in the groundwater, although B was lower in groundwater than the secondary ash pond.

Le Seur Spencer & Drake (1987) reported on the hydrogeology of an alkaline fly ash disposal site and associated impacts. The ash was sluiced into an ash pond at the power station site and dewatered and excavated every summer for disposal at a nearby landfill, the site under study. The disposal site consists of a sequence of loess over clay-rich glacial till, underlain by sandstone bedrock. The ash landfill operated from 1964 to 1973. The groundwater was shown to be impacted with higher salinity (Total Dissolved Solids; TDS), Ca and SO_4, derived principally from gypsum leached from the ash. The high lime and periclase content of the ash provided a substantial alkaline buffer to maintain a high pH. There was some preliminary evidence of low concentrations of As and Se leaching from the landfill, based on the limited data analysis available, although they appeared to be retarded during aquifer transport.

In summary, the of studies investigating contamination of groundwater arising from ash disposal have highlighted the inherent complexity in assessing such impacts. In general, the transport of trace elements appears to be limited or retarded in most cases due to varying site specific factors, such as the presence of dolomite or clays in the host sediments. The major elements, such as SO_4, Ca, Na and Cl, are more commonly transported in groundwater from seepage arising from ash disposal. The impact generally decreases with distance from the disposal site, but can vary depending on preferrential pathways, hydraulic gradients and remedial works to the surface of the facility. Thus, a study of possible rates of solute transport would need to be undertaken to ascertain the particular conditions applicable for the Latrobe Valley.

2.7 Summary of Ash Leaching and Disposal

The engineering and environmental management of the ash produced from coal-fired power stations has been reviewed. Coal ash, including both the bottom ash from boilers and the fly ash collected from electrostatic precipitators, is generally of low bulk density, high porosity and contains a moderate percentage of soluble salts, principally Ca, SO_4 and Na. The nature and properties of coal ash are highly variable and dependent factors such as the geology of the coal and the design and operating conditions of the power station. The extent of trace elements within a particular ash are related to the geological formation of the coal and combustion and collection processes within the power station. Most trace elements tend to be sorbed onto the surfaces of ash particles and may be available for leaching.

The leaching of ash occurs through contact with water either through wet slurrying in the power station for pumping and disposal of the ash to a contained pond or dam, or through infiltration of rainfall at dry ash disposal sites. The chemical nature and concentration strength of the leachate will depend primarily on the mineralogy of the ash, such as the lime, gypsum and Fe and Al oxide content. The pH of most ash leachates tend to be mildly alkaline, although acidic leachates are also known.

The common solutes present in the leachate are SO_4, Ca, Na, Cl, and to a lesser extent, K, Fe and Al. The solubility of the trace elements will depend to a large extent on the chemistry of the major elements present, and whether the leachate is alkaline or acidic. Common trace elements include As, B, Ba, Cu, Mo, Se, Sr and Zn. Complex geochemical processes, including solubility controls, co-precipitation and sorption, are known to control most of the trace elements in ash leachate. The demonstration of geochemical controls and processes involving trace elements can be difficult.

The impacts on groundwater quality arise from the leaching of ash and migration of the seepage to shallow groundwater systems. Very few case studies exist on the impacts on groundwater from ash disposal. The studies published to date have shown migration of major elements Ca, SO_4 and Na; trace elements appeared not to be undergoing transport.

Chapter 3

Hydrogeology, Ash Pond Seepage and Aquifer Biogeochemistry

The regional hydrogeology of the Latrobe Valley, the specific aquifer systems at the Loy Yang Ash Pond and a detailed analysis of the history of the impacts of ash leachate seepage on groundwater is presented. The research undertaken on seepage pathways, groundwater chemistry trends and the behaviour of sulfate and chloride is presented, demonstrating the occurrence of attenuation of sulfate and active biogeochemical processess. A one-dimensional kinetic solute transport model is then applied to model the migration of sulfate and thereby deduce reaction rates.

3.1 Regional Geology and Hydrogeology

The Latrobe Valley is part of a major structural feature known as the Latrobe Valley Depression (LVD) (Hocking *et al.*, 1988; Gloe & Holdgate, 1991). The LVD is the onshore portion of the Gippsland Basin and contains Victoria’s major fossil fuel reserves as low rank brown coal or lignite (Douglas & Ferguson, 1988; Barton *et al.*, 1992). The offshore portion of the Gippsland Basin contains large petroleum reserves.

The LVD has a complex history of depositional and erosional environments from the early Eocene through to the Late Pliocene and consists of various Tertiary sequences of interbedded sands, clays, coal measures and volcanics; principally the Morwell, Traralgon and Yallourn Formations (Brumley *et al.*, 1981; Daniels *et al.*, 1993; Schaeffer, 1996). These are unconformably overlain by up to 30 metres of Late Pliocene Haunted Hill Formation (HHF) sediments (Daniels *et al.*, 1993). The basement underlying the LVD region consists of Mesozoic sandstones and siltstones of the Strzelecki Group (Brumley *et al.*, 1981). A typical east-west regional cross section of the Latrobe Valley is shown in Figure 3.1, with the geological substructure (overburden removed) shown in Figure 3.2.

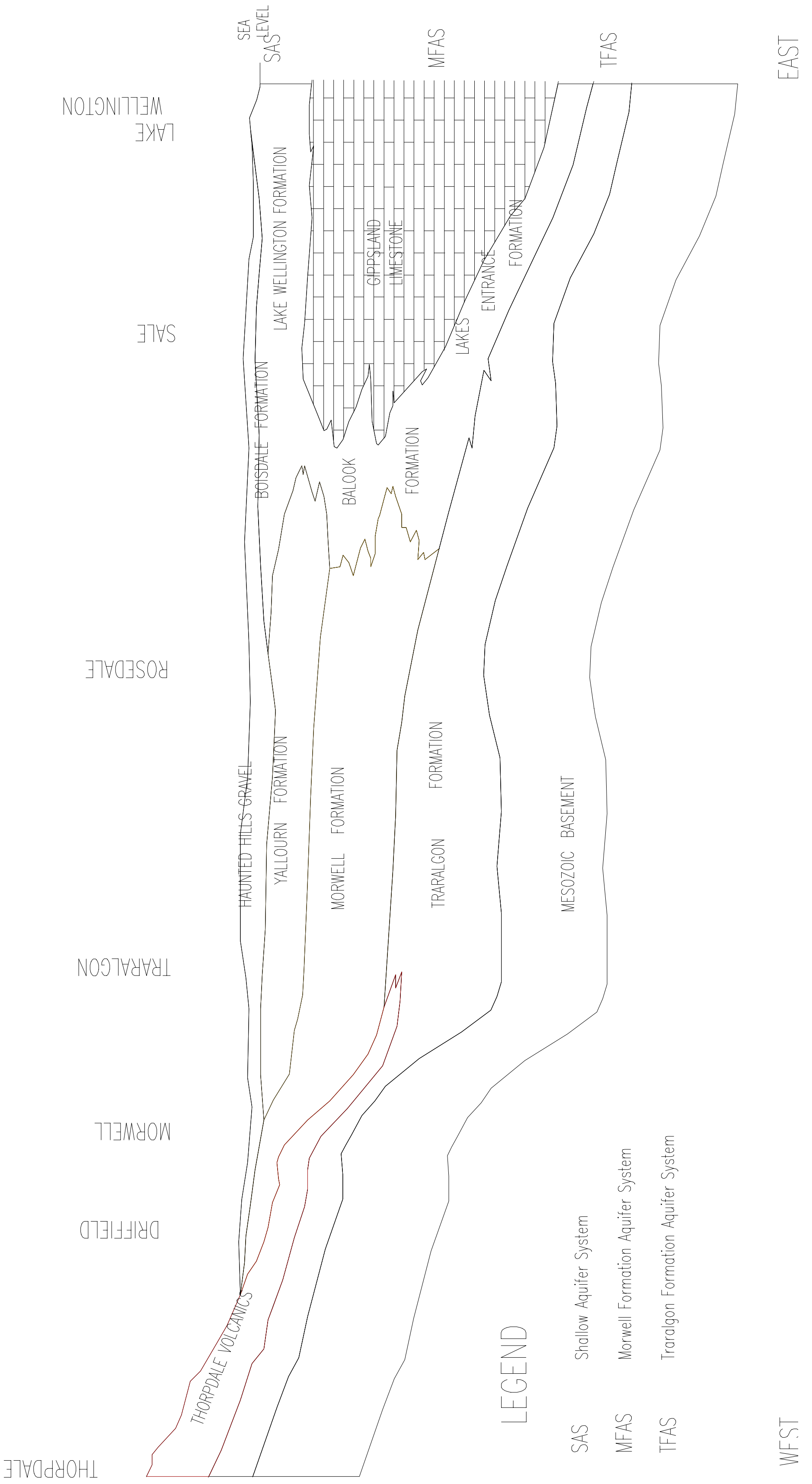


Figure 3.1 - Regional East-West Cross Section of the Latrobe Valley

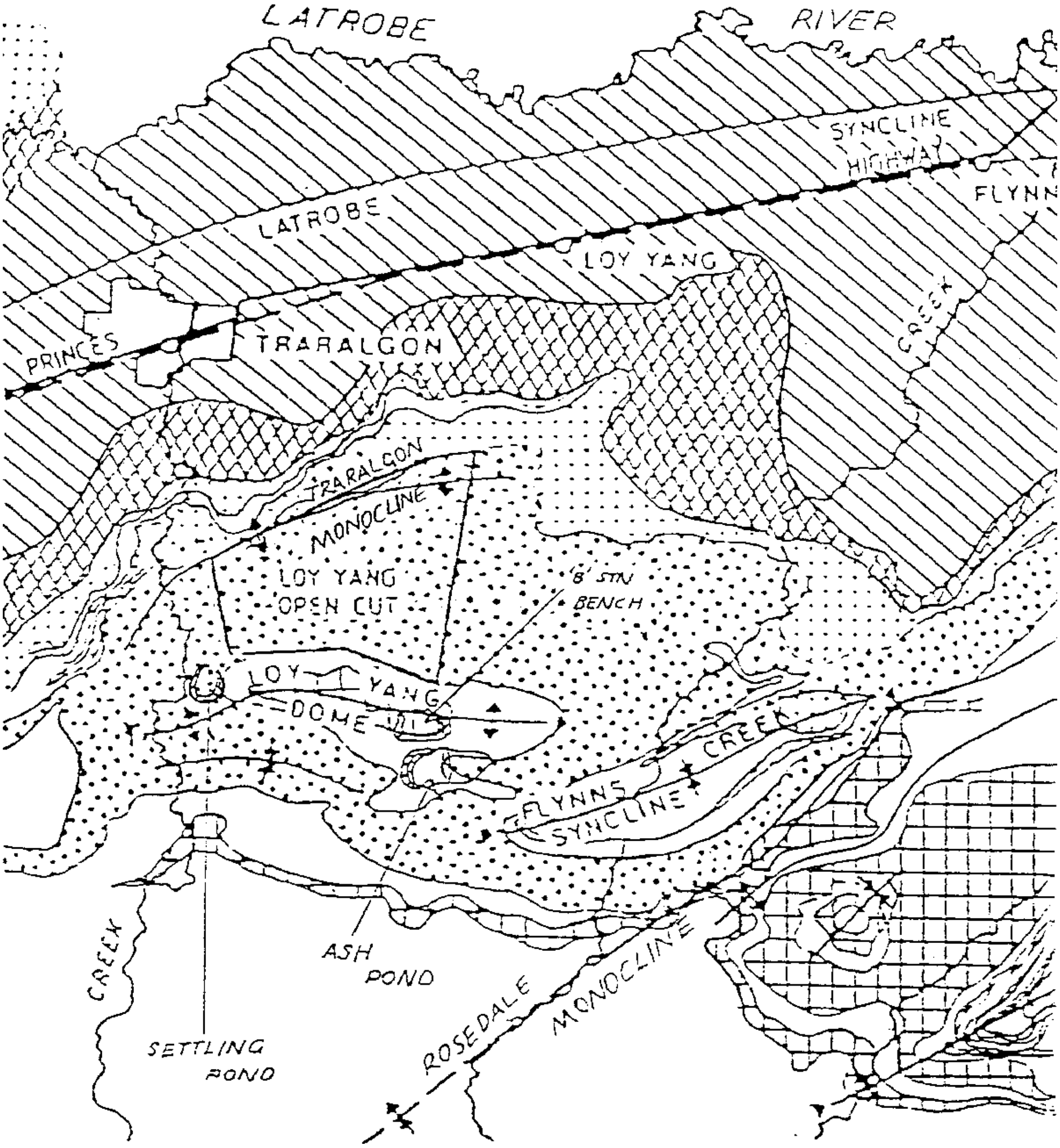


Figure 3.2 - Geological Substructure of the Eastern Latrobe Valley Depression (Overburden Removed) (Daniels *et al.*, 1993)

The hydrogeology correlates with the major geological formations, principally the Morwell Formation and Traralgon Formation Aquifer Systems (MFAS / TFAS), while the deeper Strzelecki Group of sandstones and siltstones forms a fractured rock aquifer system beneath the weathered zone underlying the Tertiary Latrobe Group Strata (Brumley *et al.*, 1981). The word “system” is used with some caution, to emphasise that rarely does one aquifer exist; rather, numerous sand, gravel and basalt aquifers of varying thickness, lateral extent and interconnection occur (Schaeffer, 1996). These are interbedded with coal, clay, silt and weathered basalt units varying in thickness which act as aquitards (Brumley *et al.*, 1981). Furthermore, within individual sand beds, there can be a high degree of heterogeneity and anisotropy (Schaeffer, 1996).

The groundwater systems in the Latrobe Valley are very complex in terms of lithologic variability, hydraulic properties and groundwater flow (Daniels *et al.*, 1993; Daniels, 1994b). Some aquifers extend over large areas and, partly through complex geologic structures, into the offshore part of the Gippsland Basin while other aquifers are only of local extent (Schaeffer, 1996).

For the purposes of classification, three regional aquifer systems are formally classified (Schaeffer, 1996) :

> **Shallow Aquifer System (SAS)** This system consists of unconfined to semi-confined aquifers within the Haunted Hill Formation, recent alluvial sediments and between the Yallourn and M1 coal seams. It occurs throughout most of the Gippsland Basin. It generally occurs close to the surface and in many areas provides low yields for domestic and agricultural purposes. At Hazelwood and Loy Yang mines, the Haunted Hill Formation will be removed during the mining of the underlying coal seams. Towards the east, the Boisdale and Jemmy's Point Formations and the upper part of the Balook Formation are interpreted as belonging to this regional aquifer system.
>
> **Morwell Formation Aquifer System (MFAS)** In the western part of the LVD this confined aquifer system consists of interbedded sands, clays and minor fractured basalts, consisting of the M1, M1A, M1B, M2A, M2B and M2C aquifers. It extends eastward through a barrier sand sequence (Balook Formation) into marls, limestone, mudstone and sandstones of the offshore Gippsland Limestone and Lakes Entrance Formation. Groundwater is extracted from this aquifer system as a result of mining operations at the

Hazelwood and Loy Yang open cut mines and for domestic and agricultural activities towards the east. Aquifers belonging to this system generally occur between 100 and 700 m beneath the present surface, apart from structural highs where they may subcrop at shallower depth beneath the younger aquifer systems. The MFAS is quite permeable, with an average transmissivity of 100 m^2/day and ranging from 5 to 190 m^2/day (Thatcher, 1976; Wood, 1993; Daniels, 1994b).

Traralgon Formation Aquifer System (TFAS) This system extends across the entire Gippsland basin and consists of many thick interbedded sands, clays, coals and basalts onshore (M2, TR Aquifers) and interbedded sandstones, mudstone, coals, and basalts offshore (Latrobe Group Aquifers). Individual sand units can be up to 15 m thick. Apart from structural highs where these sediments may be exposed, aquifers belonging to this system occur between 150 and 1,500 m beneath the present surface. Groundwater is extracted as part of mining in the LVD onshore, and oil and gas production activities offshore. The TFAS is highly permeable with an average transmissivity of 480 m^2/day and ranging from 50 to 1300 m^2/day (Wood, 1993; Daniels, 1994b). The extraction of TFAS groundwater at Loy Yang for mine stability commenced in December 1992, and is expected to reduce hydrostatic pressure levels in the LYAP area in the future.

In the vicinity of the Loy Yang Ash Pond, interpretation of the aquifer stratigraphy is complicated by the presence of several inferred faults and the Loy Yang Dome, an elevated Mesozoic basement structure (Daniels *et al.*, 1993, Daniels, 1994a & 1994b). The geologic and tectonic history of the Loy Yang Dome area has produced a complex reorientation of the structural blocks within the basement, leading to faults and inferred steeply dipping strata (Daniels *et al.*, 1993, Daniels, 1994a & 1994b). The elevated nature of the Loy Yang Dome has led to erosion of the Morwell Formation locally around the LYAP, with coal seams often truncated and aquifers of only limited extent (Daniels *et al.*, 1993, Daniels, 1994a & 1994b).

There is localised increases in hydrostatic pressure in the M2C aquifer at the LYAP, which subcrops beneath the unconformity, attributable to downward leakage of ash pond seepage (Daniels *et al.*, 1993).

The water quality of the major aquifer formations is generally good, with Total Dissolved Solids (TDS) averaging less than 500 mg/L, although some localised areas of higher salinity are known (Brumley *et al.*, 1981). The water is typically of a Na-Cl type, with minor quantities of bicarbonate (HCO_3), SO_4 and Ca (Brumley *et al.*, 1981). The groundwater can contain high concentrations of dissolved carbon dioxide (CO_2) gas, which has been noted for bore corrosion problems in the early years of the SECV (Brumley *et al.*, 1981; Geo-Eng, 1995). Traces of hydrogen sulfide gas can be detected by odour in bores and groundwater samples (Brumley *et al.*, 1981; Geo-Eng, 1995; Daniels, 1994a).

3.2 Geology of the Haunted Hill Formation

The sequence of cover sediments in the LVD were originally known as the Haunted Hill Gravels (cf. Thomas & Baragwanath, 1949), however, they were renamed as the Haunted Hill Formation due to their lithologic variability (Hocking *et al.*, 1988).

The geology and geochemistry of the Haunted Hill Formation (HHF) was studied in detail by Bolger (1984) on a regional scale extending from Yarragon in the Moe Swamp Basin through the Haunted Hills east of Moe to Rosedale on the eastern edge of the Latrobe Valley Depression. In his study, the various depositional environments, mineralogy and boundary relationships of the Haunted Hills Formation are described in reference to the underlying Tertiary coal-bearing sequences. A brief summary of the Loy Yang and nearby areas is given here from Bolger (1984), as well as more recent work by Mulder & Pedler (1990), Hudson (1990), Daniels *et al.* (1993) and Daniels (1994a). Geologic cross sections of the Loy Yang Ash Pond area are given in Figures 3.3 to 3.4.

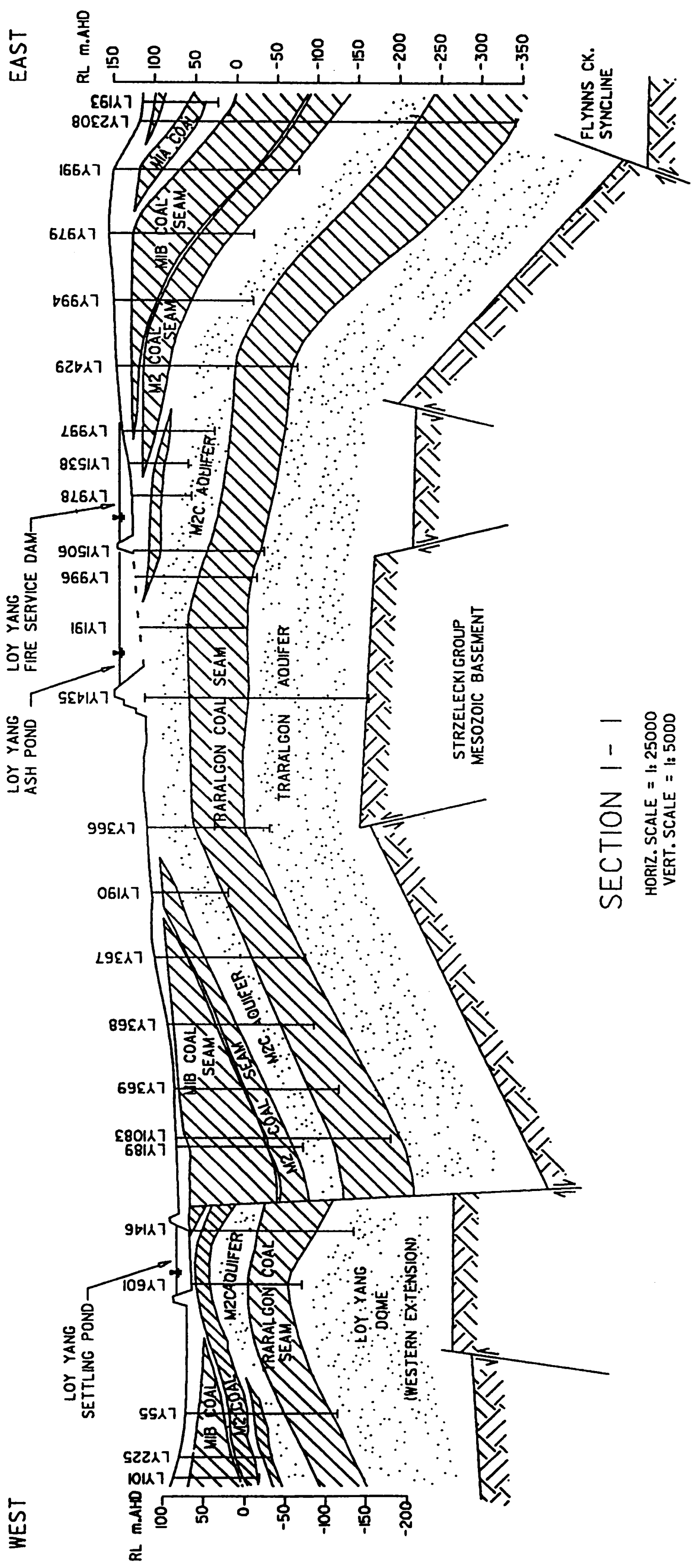


Figure 3.3 - East-West Geologic Cross Section of the LYAP Area (Mulder & Pedler, 1990)

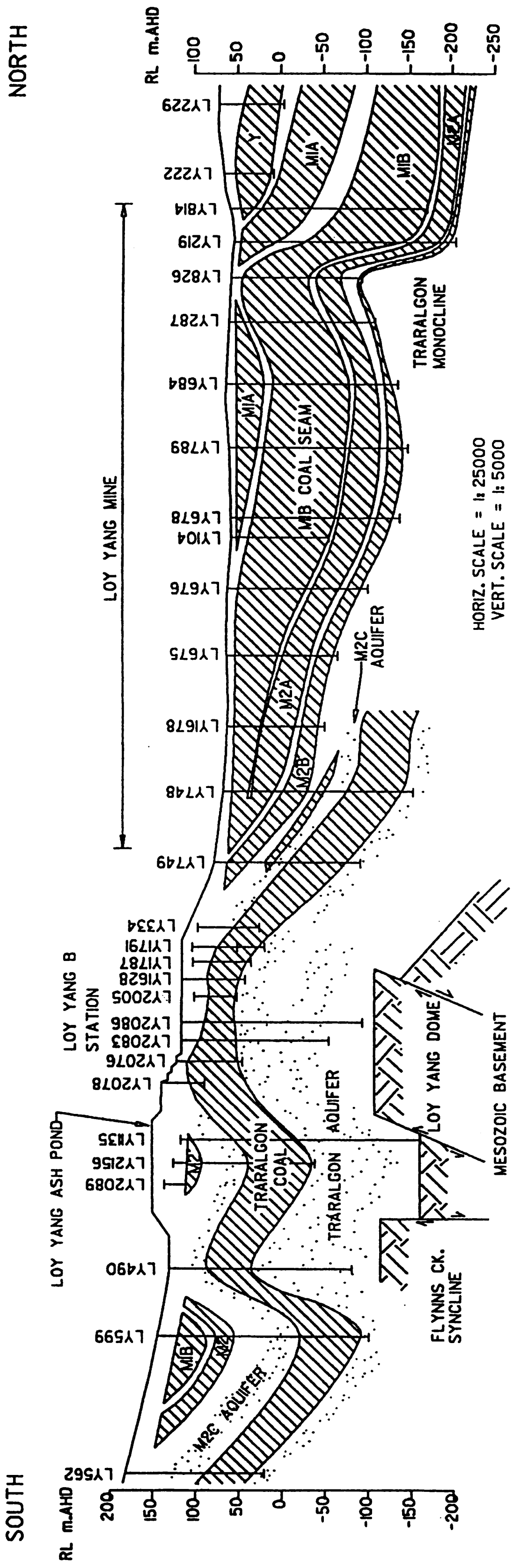


Figure 3.4a - North-South Cross Section of the Loy Yang B Station Bench Area (Mulder & Pedler, 1990)

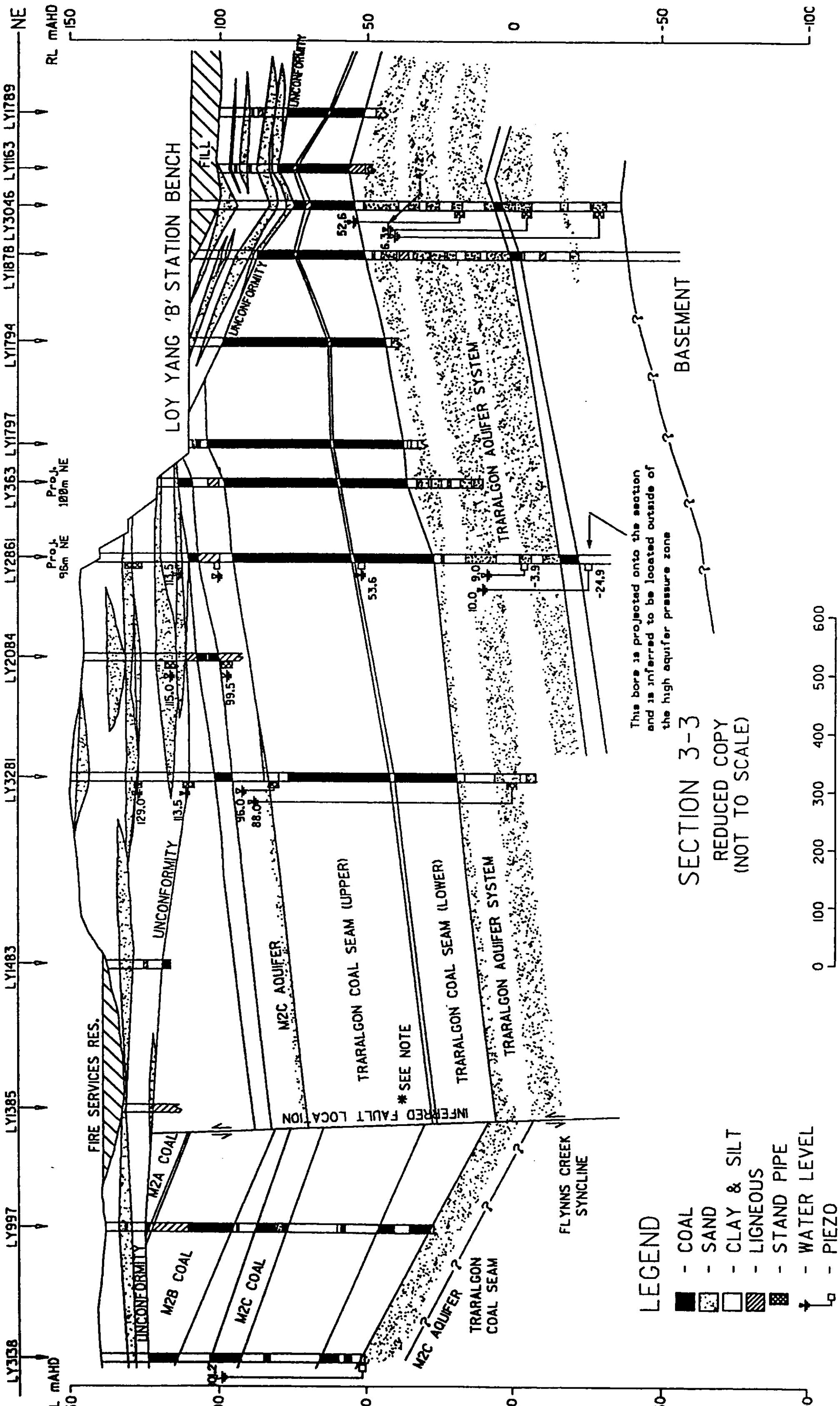


Figure 3.4b - North-South Cross Section of the Loy Yang B Station Bench Area (Daniels *et al.*, 1993)

The HHF sediments were deposited in an oxidising, high energy, multiple channel "braided" river system, in contrast to the reducing, low energy deposition of the underlying coal and sedimentary strata. The HHF consists of ferruginous clays, sandy clays, sands, gravels and clayey sands and gravels. The HHF are dominantly trough cross-bedded and horizontally bedded coarse sands and pebble gravels. The coarse sediments are interpreted to be channel deposits, and individual sand lenses of up to 5m in thickness can be found. There is a high proportion of clay in the sediments at the unconformity between the Haunted Hill Formation and the underlying Morwell Formation sediments. The mineralogy consists of common quartz with minor feldspar, micas, sedimentary and rare volcanic rock fragments, and the heavy minerals zircon and tourmaline. Kaolinite is the major clay mineral, with subordinate illite and mixed layer illite/montmorillonite. There is abundant organic matter within the HHF sediments (Bolger, 1984), including reworked layers of coal, ligneous and peat materials (Mulder & Pedler, 1990).

Due to the oxidising conditions that prevailed during the accumulation of Haunted Hills sediments, indicator minerals such as haematite and limonite cements and ferrugenous palaesols can be used to distinguish the Haunted Hills Formation from the lower sedimentary units where the unconformity is not clearly recognizable. The presence of siderite and pyrite is anomalous, as these are formed under reducing conditions only. The source of the Fe^{3+} from the limonite and haematite in HHF sediments is unclear, although Bolger (1984) thought this to be due to post-depositional diagenetic alteration of Fe-bearing minerals.

The HHF sediments are therefore dominated by channel sands and levee clays, leading to a highly heterogeneous aquifer. Numerous sand and clay lenses can be found, with the interconnection of channel sands shown to form a continuous layer from beneath the Fire Services Reservoir to the Loy Yang B 3/4 bench (see Figure 3.4b). The HHF is also known to contain faults, derived from movements in the underlying Mesozoic basement, which truncates some stratigraphic layers while providing possible hydraulic connections between other layers, as shown in Figure 3.4b. Faulting is also visibly extensive in the Loy Yang Open Cut.

3.3 Hydrogeology of the Haunted Hill Formation

The HHF forms an unconfined to semi-confined aquifer system above the Late Pliocene unconformity (Schaeffer, 1996). Due to the fluvial nature of the HHF, it is difficult to accurately monitor all individual sand lenses and hence present a typical picture of aquifer pressures (Daniels *et al.*, 1993; Daniels, 1994a).

The water quality of the HHF is generally of good quality, although locally higher salinities ranging up to about 7,500 mg/L have been noted within the Latrobe Valley region (Geo-Eng, 1999). The water chemistry is analagous to the deeper aquifers, being of a Na-Cl type water with minor HCO_3. The concentrations of SO_4, Ca, Mg and Fe are generally low, although areas of higher Fe do occur within the HHF at the Loy Yang site.

The background water quality of HHF aquifers was reported by Mulder & Pedler (1990), with further regional data on the HHF aquifers presented by Geo-Eng (1999). This data is summarised in Table 3.1. There appears to be some variation in HHF groundwater quality across the Latrobe Valley, hence this aspect needs to be considered in any interpretation of groundwater quality data. The water chemistry generally tends to be dominated by Na and Cl.

Table 3.1 - Background Water Quality of HHF Groundwater (mg/L)
(adapted from Mulder & Pedler, 1990; Geo-Eng, 1999)

TDS	Na	K	Ca	Mg
240 - 3,000[1]	38 - 210	0.5 - 11	1.3 - 54	0.1 - 19

pH	SO_4	Cl	HCO_3
4.5 - 7.6	<1.0 - 65	43 - 300	2.9 - 500

[1] - A TDS value of 7,365 mg/L was measured by Geo-Eng (1999) about 10 km to the northeast of Loy Yang.

The Ash Pond and Fire Service Reservoir have formed a seepage mound in the HHF and no significant unsaturated zone is likely to exist beneath the pond, based on comparison of natural ground contours before the LYAP and recently measured piezometric head levels. Seepage flows are north to the B-Station 3/4 bench and west to the overburden dump. No seepage has been detected either to the east nor the south, which would require groundwater flow against the natural gradient of the topography and through areas of lower permeability due to a higher clay content.

3.4 Seepage History of the Loy Yang Ash Pond

The Loy Yang Ash Pond was commissioned in 1982. During construction of the dam wall for the LYAP, additional material was excavated from the pond near its centre to use as fill material for the dam wall (Pedler & Raisbeck, 1988; Daniels *et al.*, 1993). This over-excavation exposed the HHF sands near the unconformity, providing a direct conduit for seepage flow into HHF aquifers beneath the LYAP. Within a relatively short period, significant ash pond seepage was observed under the dam embankment. The seepage was creating a small artesian head on the base of the dam wall, and there was concern about the geotechnical stability of the dam wall. The seepage was thought to be occurring through the old borrow pit (Reinsch *et al.*, 1982). A water balance and tracer study by Wood *et al.* (1982) estimated a seepage loss of 1,000 m^3/day.

In 1986 seepage was found to be discharging to the southern batters of Loy Yang B Station (see Figure 1.2). Investigative drilling was carried out on the ridge but failed to intercept seepage; ongoing monitoring of these bores show that they remain dry (Daniels *et al.*, 1993). A cut-off drain was installed to capture seepage flows and lower the water level below the ground surface (Pedler & Raisbeck, 1988), although this was not completely effective at capturing all seepage (Daniels *et al.*, 1993). The existing network of groundwater monitoring bores was further developed to monitor groundwater chemistry. As part of environmental management and EPA licence requirements additional bores were also added to the network, namely 3135, 3281 and 3282 (Mulder & Pedler, 1990; Daniels *et al.*, 1993).

A seepage modelling study by Pedler & Raisbeck (1988) estimated a total seepage loss of 890 m^3/day. The seepage flow at the B Station measured in 1993 was 104 m^3/day, although not all seepage was known to be collected and monitored in flow readings (Daniels *et al.*, 1993).

Mulder & Pedler (1990) undertook a solute transport modelling study of the seepage from the LYAP. The HHF aquifer was assumed to be a uniform 5 m thick sand, with the groundwater velocity (taken as a constant) calculated from the outflow of the Relief Well Pit (RWP) system. Both one- and two-dimensional (1-D / 2-D) solute transport models were used, with the calibration of the 1-D model MYGRT (EPRI, 1986) used to refine model parameters for the 2-D model MOC (Knoikow & Bredehoeft, 1978). The aquifer properties were based on measured values from the Loy Yang mine and previous experience in the Latrobe Valley. The values were considered typical for the sands of the HHF. The influence of groundwater and aquifer chemistry on solute migration was modelled through the use of retardation coefficients for Na and SO_4, while for Cl conservative transport with no reactions were assumed. The retardation coefficients of 1.1 were adopted through the use of the 1-D model and visual calibration to the 8 years of limited monitoring data available at that time. The results predicted that seepage related impacts on the HHF aquifer should remain within the boundaries of the Loy Yang site. The complex geology was recognised as a major uncertainty in this study.

A historical timeline of ash seepage is compiled below in Table 3.2. It is summarised from Reinsch *et al.* (1982), Wood *et al.* (1982), Pedler & Raisbeck (1988), Mantyvirta & Clancy, (1989), Mulder & Pedler (1990), Daniels *et al.* (1993), Daniels (1994a), McKinley (1992; 1993; 1994a & 1994b). The EPAV has permitted existing ponds to continue to operate providing their seepage does not affect the beneficial uses of the aquifers at the project boundaries. The State Environment Protection Policy (Groundwaters of Victoria) (the "SEPP"), issued by the EPAV in December 1997, specifically allows for an attenuation zone for an ash pond operated at a coal-fired power station (EPAV, 1997). The beneficial uses of groundwater within this zone are not required to be met, providing that such uses are met at the boundary of the zone.

Table 3.2 - History of Ash Pond Seepage at Loy Yang

1979-1981	• Loy Yang Ash Pond is constructed in two seasons - the Haunted Hill sands are exposed in an internal burrow pit used for building the dam wall;
1982	• Seepage is observed emanating from the western toe of the ash pond; a water balance study estimates the seepage is approximately 1,000 m^3/day;
1983	• investigation reveals that migration of leachate from the ash pond is occurring and a series of relief wells are installed to capture seepage flows and reduce hydrostatic pressures; sampling shows localised contamination;
1986	• seepage discharge found on the Loy Yang B Bench;
1987	• regular groundwater monitoring program initiated;
1988	• detailed seepage analyses are undertaken, including field investigation and computer modelling in a north-south section (through to Loy Yang B) and in an east-west section (through to the dam toe and relief well pit); estimates of seepage flows were 890 m^3/day;
1989	• a review of ash production rates shows that there is insufficient capacity in the Ash Pond, which would fill by 1995 if no remedial options were undertaken; they recommended that pond capacity be increased;
1990	• a solute transport study is undertaken including both field work and computer modelling of SO_4 and Cl movement through the Haunted Hills aquifer; • the study concludes that pollution is currently localised to the shallow aquifers only (Haunted Hill), and that the pollution will remain within Loy Yang boundaries for the duration of the ash pond's design life;
1992	• a review of groundwater quality monitoring data shows that seepage is now reaching the intermediate aquifers, particularly the M2C aquifer;
1993	• a more detailed investigation of the seepage at Loy Yang B revealed that it did contain ash pond seepage; this report showed : – the possible connection of intermediate and deeper aquifers through the presence of inferred faults in the ash pond and Loy Yang B region, – seepage at the Loy Yang B bench was a combination of natural water, fire service reservoir water and ash pond seepage; • annual review of groundwater quality monitoring shows : – TDS, SO_4 and Cl concentrations have stabilised within the HHF, except bore 3135U, which had rising Cl concentrations and low SO_4, – Hydrogen sulfide can be detected in most groundwater bores, – North-east of the ash pond, high Cl concentrations indicate a higher background salinity, although high SO_4 concentrations are also found, indicating ash pond seepage, – the salinity of the Loy Yang B bench seepage increased markedly between 1992 and 1993; analysis of the field data shows that the seepage pathway is indirect, emanating from the eastern end of the pond and not in a north-south manner as might be expected;
1995	• current PhD research project established.

3.5 Analysis of Seepage Migration

The seepage impacts on groundwater at the Loy Yang Ash Pond up to early 1995 are reviewed. A review of monitoring and earlier work to 1995, including the assumptions used regarding migration pathways and solute migration, are critical in determining a valid approach for long-term projections of seepage migration and possible impacts on the groundwater quality of the HHF (McKinley, 1997).

3.5.1 Water Quality of the Ash Pond

The quality of water in the LYAP will determine the flux or loading of solutes on groundwater systems. The quality of free-standing or supernatant water within the LYAP is of moderate salinity and strongly alkaline. The trace element content is generally low due to the alkaline pH, although low concentrations of As, Ba, B, Se, Mo and Sr can be present. These are common contaminants in Australian and overseas coal ashes, as highlighted in Chapter 2. All groundwater and surface water quality monitoring at Loy Yang has been undertaken by the SECV from 1982 to 1995.

The salinity of the LYAP has gradually increased since commissioning in 1982, with the water quality fluctuating in accordance with the coal quality being mined and utilised within the power stations. The ash pond water is of a Na-SO_4-Cl type chemistry. The concentrations of Na, SO_4, Cl and pH within the LYAP are presented in Figure 3.5. The major solutes of concern with respect to potential impacts on water resources is therefore SO_4, Na and to a lesser extent Cl. This thesis will not examine the behaviour of trace elements in seepage and groundwater (it should also be noted that these elements are generally not found in significant concentration in HHF groundwaters to date).

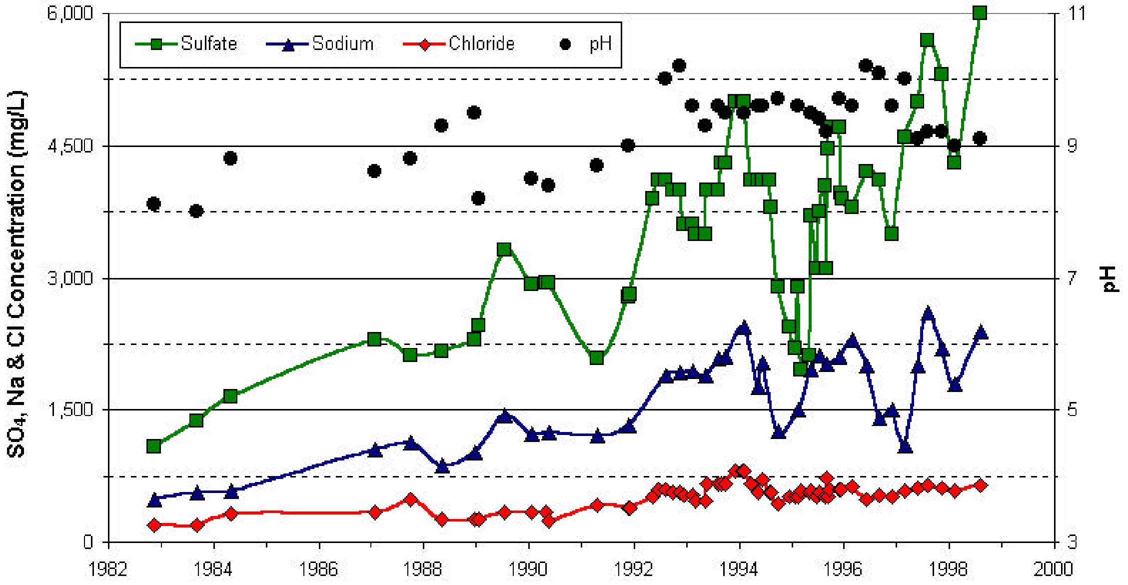


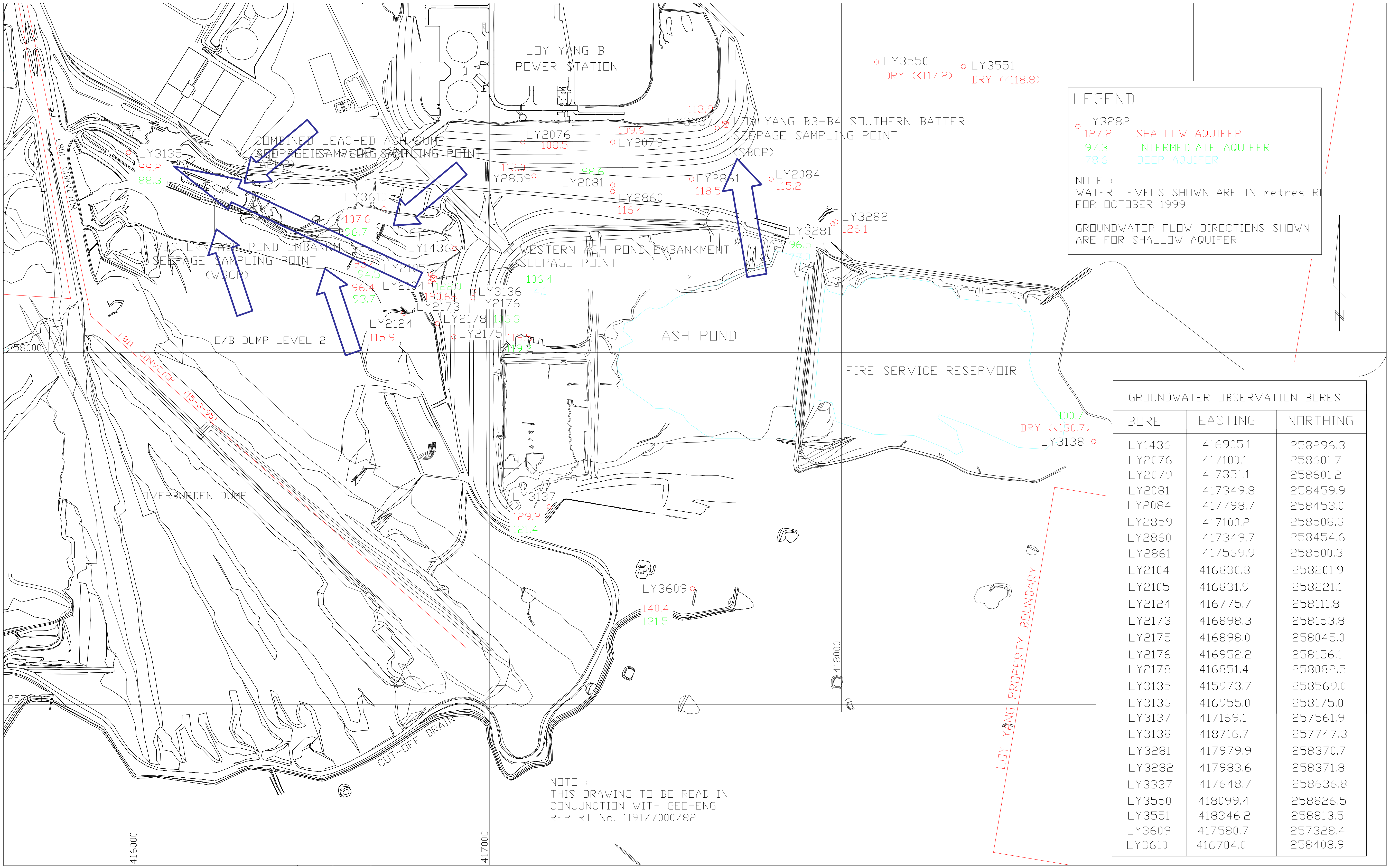
Figure 3.5 - LYAP Chemistry : Sulfate (SO_4), Sodium (Na), Chloride (Cl) & pH

3.5.2 Piezometric Surface and Groundwater Levels

The piezometric surface or water level of all groundwaters in the vicinty of the LYAP are monitored regularly. The aquifers monitored include the Haunted Hill, Morwell and Traralgon Formations.

The deeper Morwell and Traralgon aquifers are showing the influence of large scale extraction for depressurisation purposes within the Loy Yang Open Cut. The piezometric levels are gradually declining, and this is expected to continue for some time before steady state is achieved with mine depressurisation activities. Adjacent to the LYAP, the local M2C aquifer is showing a small increase in piezometric head. This aquifer, due to truncation and erosion across the Loy Yang Dome, is only present beneath the LYAP and is not expected to be hydraulically connected to other aquifers.

The HHF aquifers have shown steady state piezometric heads for some years. This condition is thought to be due to equilibrium being reached between seepage flows and groundwater in the HHF. The increase in storage capacity and operational water level of the LYAP in 1995 has not led to any significant increase in groundwater levels in the HHF aquifers.



NOTE :
WATER LEVELS SHOWN ARE IN metres RL FOR OCTOBER 1999

GROUNDWATER FLOW DIRECTIONS SHOWN ARE FOR SHALLOW AQUIFER

NOTE :
THIS DRAWING TO BE READ IN CONJUNCTION WITH GEO-ENG REPORT No. 1191/7000/82

GROUNDWATER OBSERVATION BORES

BORE	EASTING	NORTHING
LY1436	416905.1	258296.3
LY2076	417100.1	258601.7
LY2079	417351.1	258601.2
LY2081	417349.8	258459.9
LY2084	417798.7	258453.0
LY2859	417100.2	258508.3
LY2860	417349.7	258454.6
LY2861	417569.9	258500.3
LY2104	416830.8	258201.9
LY2105	416831.9	258221.1
LY2124	416775.7	258111.8
LY2173	416898.3	258153.8
LY2175	416898.0	258045.0
LY2176	416952.2	258156.1
LY2178	416851.4	258082.5
LY3135	415973.7	258569.0
LY3136	416955.0	258175.0
LY3137	417169.1	257561.9
LY3138	418716.7	257747.3
LY3281	417979.9	258370.7
LY3282	417983.6	258371.8
LY3337	417648.7	258636.8
LY3550	418099.4	258826.5
LY3551	418346.2	258813.5
LY3609	417580.7	257328.4
LY3610	416704.0	258408.9

Figure 3.6 Piezometric Heads in the HHF, Groundwater Monitoring Bore Locations and Interpreted Seepage Pathways (courtesy of Geo-Eng Australia Pty Ltd; see Geo-Eng, 1999)

The reduced level (RL) of the natural ground surface contours before construction of the LYAP, in the central area where seepage is considered to occur, is approximately 115 to 118 m RL (Mulder & Pedler, 1990). The most recent groundwater level data for bores in the RWP area (western embankment) and near the B-Station bench are between 110 to 125 m RL, indicating a minimal unsaturated zone between the base of the LYAP and the HHF. The head data in Mulder & Pedler (1990) also suggests a minimal unsaturated zone. A compilation of water levels in the HHF is provided in Figure 3.6. This figure includes the location of the groundwater monitoring bores in the vicinity of the LYAP.

3.5.3 Seepage Migration Pathways

The water level data in Figure 3.6 demonstrates that two principal seepage pathways exist - to the west towards the Overburden Dump, and to the north towards the B Station Bench. The estimated flows for the western seepage, based on data collected by Loy Yang staff from the Relief Well Pit system, is about 600 to 750 m^3/day, while for the northern seepage the flow is approximately 115 m^3/day (Daniels *et al.*, 1993). Daniels *et al.* (1993) and Daniels (1994a), through analysis of geological cross sections across the LYAP region, demonstrated that the northern seepage pathway is not in a direct line from the LYAP to the bench, rather it is inferred to meander through a sand channel north-east towards the Fire Services Reservoir, then north-west to the bench. There is no seepage apparent to the east nor to the south, due to thick lower permeability clay lenses in this area and being topographically upgradient from the LYAP.

The solute transport modelling of Mulder & Pedler (1990) assumed a 5 m thick uniform sand aquifer, conservative chemistry and a retardation coefficient of 1.1 for Na and SO_4 to account for chemical reactions and adsorption. Their work predicted a significant and rapid increase in solutes reaching bore 2124U, although this has not yet occurred as predicted. The review of seepage pathways presented above suggests that the use of a uniform and homogenous sand aquifer is not practical, given the complexity of geology and flowpaths demonstrated by recent and ongoing monitoring and analysis. Their assumptions concerning sorption and chemical reactions have not been validated. All of these factors are critical in assessing solute transport rates in groundwater.

The northern seepage pathway is complex and inferred with a minimum of groundwater monitoring bores. This precludes any realistic appraisal of groundwater flow and solute transport which enables an interpretation of the physical and chemical factors affecting migration. The western seepage pathway, on the other hand, has a demonstrable head distribution and several groundwater monitoring bores with historical data available, which align along this pathway. The western flow path shown in Figure 3.6 can accordingly be simplified as a one-dimensional (1-D) pathway, allowing a more rigorous assessment of groundwater flow and solute transport. The following analysis will therefore concentrate on the seepage pathway to the west of the LYAP. This allows the effects of chemical reactions and sorption to be determined, if indeed they are important in controlling solute transport from the LYAP.

3.5.4 Seepage Impacts on Intermediate and Deep Aquifers

The monitoring of Morwell Formation aquifers in the vicinty of the LYAP has shown limited impact on the water quality of the M2B aquifer. The mechanism of seepage reaching this aquifer is uncertain, but may be due to the complex faulting over the Loy Yang Dome around the LYAP (Daniels *et al.*, 1993; Daniels, 1994a). The impact became noticeable around 1989, based on an increase in SO_4 from a background of 30 mg/L to about 700 mg/L by 1991 in some monitoring bores (McKinley, 1992 & 1993). The concentration of SO_4 appears to have stabilised since this time.

The monitoring of Traralgon Formation aquifers in the vicinty of the LYAP has shown no apparent impacts on water quality of these aquifers. The water quality continues to be low salinity and dominated by a Na-Cl chemistry, similar to background.

It is unclear to what extent the faulting around the Loy Yang Dome has created the possibility for seepage to reach the deeper aquifers of the Traralgon and Morwell Formations beneath the LYAP. The faults shown in Figure 3.4b are inferred only, and thus no realistic assessment of seepage impacts can be attempted. Continued monitoring and investigation of these aquifers is recommended.

3.5.5 Seepage Impacts on Haunted Hill Formation Aquifers

Based on the previous sections, the HHF aquifers are the main recipient of seepage from the LYAP, and are thus are of most concern regarding groundwater quality. It was identified in Section 3.4 and Table 3.2 that the salinity (TDS, Na, SO_4 and Cl) in bores in the Relief Well Pit (RWP) area at the western base of the LYAP is rising. The analysis and interpretation of the monitoring data has not always been extensive.

The concentrations of Na and SO_4, key indicators of ash pond seepage identified in Section 3.5.1, have been rising steadily in the Relief Well Pit (RWP) and groundwater monitoring bore 2124U (bore locations are given in Figure 3.6). The distant monitoring bore 3135U, installed in 1990, has yet to show any increase in SO_4, with samples generally below analytical detection limits (1 mg/L). The concentration of Na in bore 3135U is only slightly higher, and thus cannot be attributed to seepage directly, but is more likely to be either natural variability and/or the influence of ash pond seepage (but is still considerably lower than ash pond concentrations). The pH of bore 2124U and the RWP has stabilised at a value of about 5, which indicates a decrease of about 2 units compared to the background levels measured in 1982. The monitoring data collected from 1982 to early 1995 is presented in Figures 3.7 and 3.8.

The concentration of Cl has increased in most bores compared to background, and has stabilised at a concentration only slightly lower than that in the LYAP since about 1988. Bore 3135U had an increasing concentration of Cl, with the 1995 concentration being slightly higher than the average in the LYAP. The reason for this higher Cl is unclear, but may have resulted as a combination of higher background Cl in this region and/or ash pond seepage. Drainage from the overburden dump is also a possibility.

Despite nearly 15 years of alkaline seepage, the pH of HHF groundwater maintains mildly acidic conditions, with an apparent trend of decreasing pH. The geochemical mechanisms behind this acid buffering will be discussed in further detail later in this chapter.

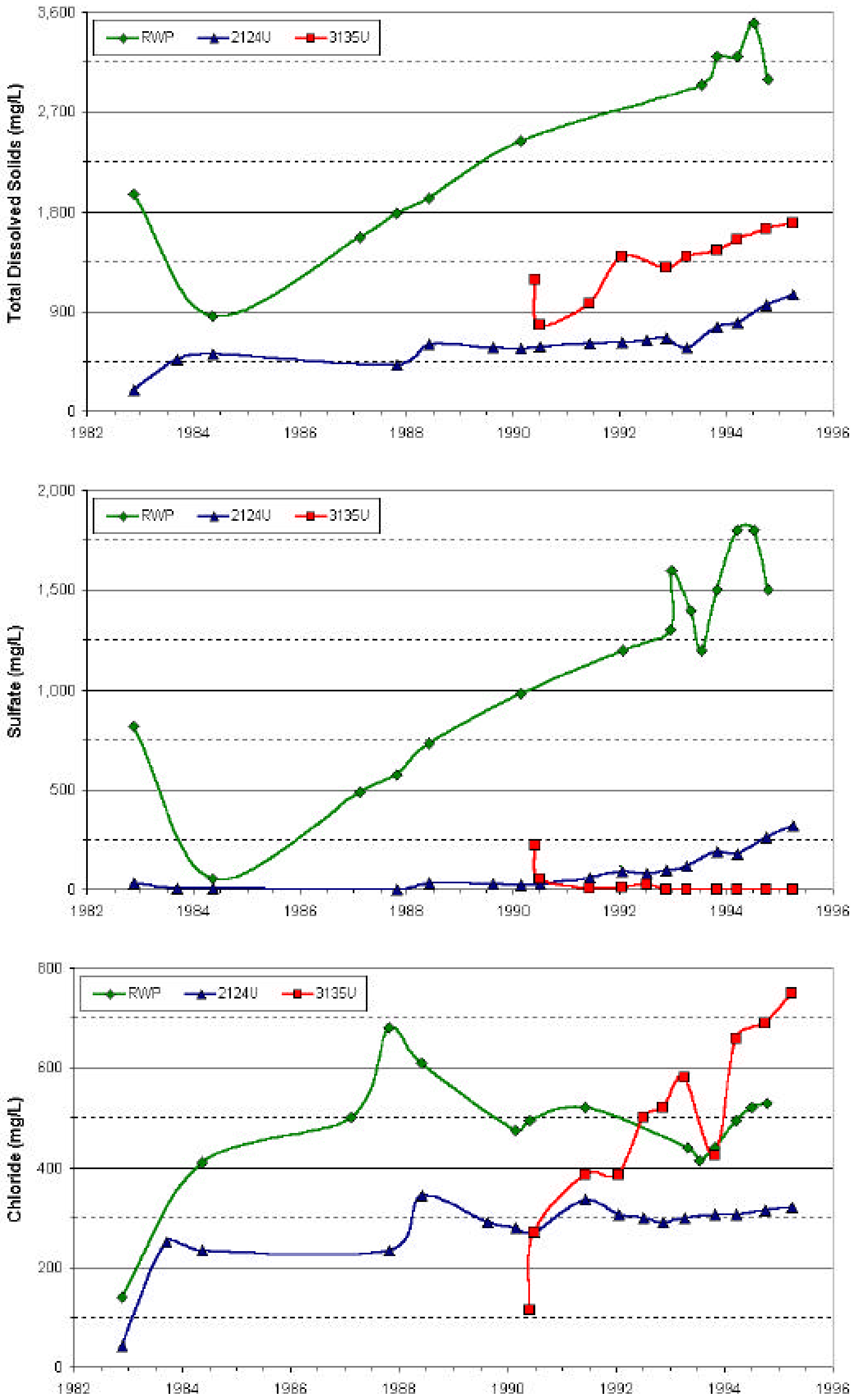


Figure 3.7 - HHF Groundwater Quality West of the LYAP : TDS, SO_4 & Cl

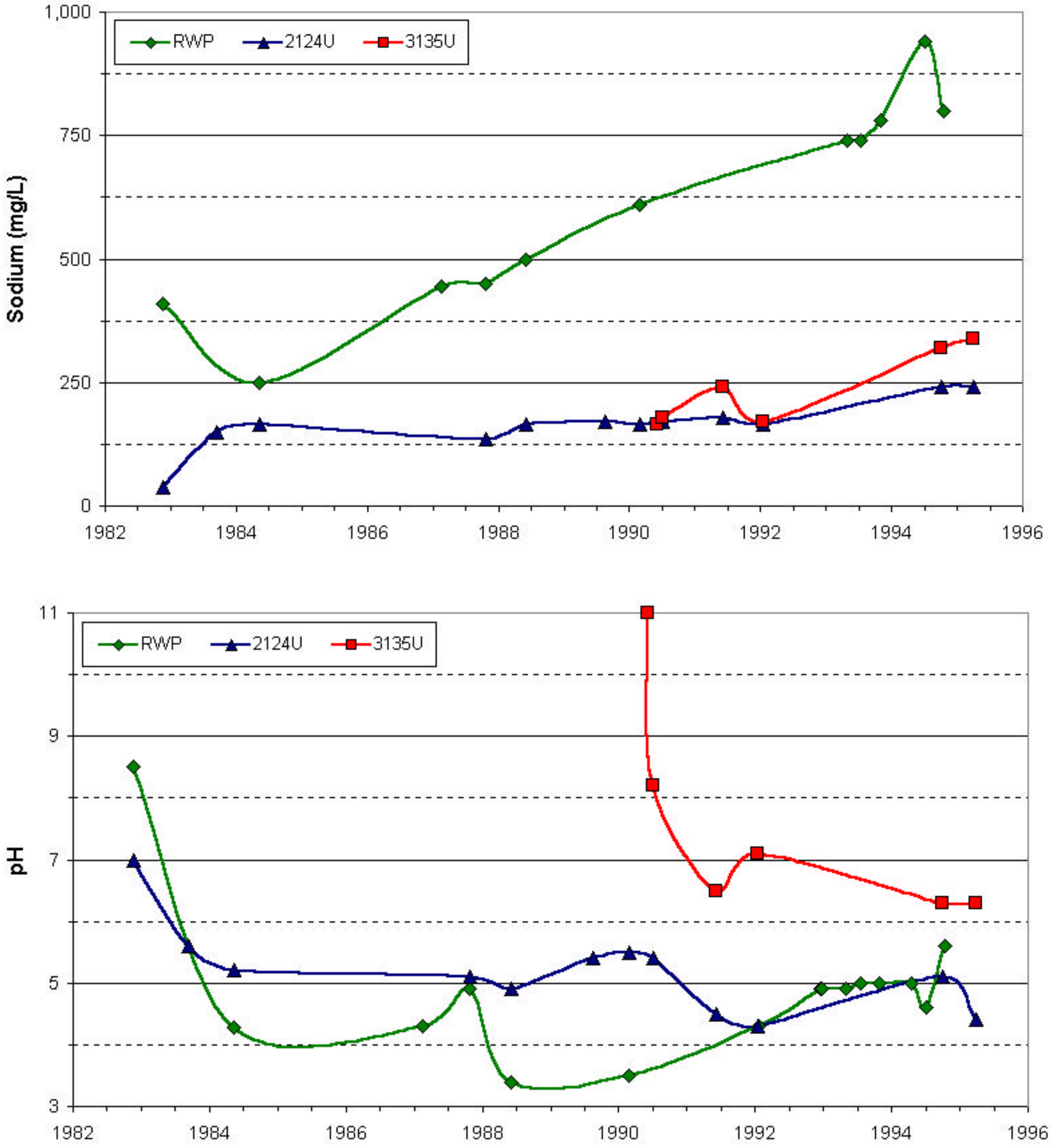


Figure 3.8 - HHF Groundwater Quality West of the LYAP : Na & pH

It is difficult to establish a clear picture of the apparent trends of groundwater quality for monitoring data from the B-Station bench. There has been an increase in salinity since about 1988, which appears to have been stable since late 1993 (McKinley, 1994). A similar pattern can be seen for Na. The concentrations of SO_4 and Mg appear to be increasing steadily with time, suggesting the seepage is derived partly from the LYAP and not entirely from the Fire Service Reservoir (FSR).

The monitoring data for Cl, however, is anomalous. The concentration of Cl at the onset of seepage in 1986 was more than 900 mg/L, almost twice the average Cl concentration of the LYAP to that point in time. The new HHF monitoring bores, 3282L and 3282U, installed between the FSR and the bench in 1992, gave initial Cl concentrations of approximately 1,300 to 1,400 mg/L, still significantly higher than that in the LYAP. The seepage water collected from the bench shows a slow increase in Cl, while bores 3282L and 3282U appear to be in a decreasing trend towards the concentration in the LYAP. The behaviour of Cl demonstrates the compelxity of seepage sources and solute transport to the bench. It appears to include LYAP and FSR water, although the proportion of each cannot been ascertained with current data. The remained of this chapter will examine the western seepage pathway only. It is recommended that monitoring and analysis of B-Station groundwater quality data be continued for the forseeable future.

3.5.6 Analytical Approach to Solute Transport in the HHF

In order to estimate possible solute transport rates through the HHF aquifers from the LYAP, a one-dimensional solute transport analysis was undertaken using an analytical solution to the governing equation. This was applied to the western seepage pathway, as this is the dominant seepage pathway affecting the HHF aquifers identified previously.

The mathematical equation that describes the transport of a solute through a porous medium is well documented. The migration of a dissolved solute in flowing groundwater will depend upon the groundwater velocity, porosity effects due to the tortuous pathway around grains, sorption reactions and chemical reactions (Freeze & Cherry, 1979). The transport of a solute due solely to groundwater flow is known as advective flow. Due to the interference from grains that comprise the aquifer materials, solutes are forced to travel a longer path around each grain, leading to dispersion and spreading of the solute in the groundwater. The process of diffusion, where solutes migrate due to chemical concentration gradients, is important in low velocity systems. The combined effect of dispersion and diffusion is known as hydrodynamic dispersion (Fetter, 1993).

The advection-dispersion equation (ADE) for describing the transport of a solute in groundwater is derived by considering an elemental volume of aquifer material and the fluxes of a solute into and out of this volume. The working assumptions are that the porous medium is homogenous, isotropic, saturated, that Darcy's Law for groundwater flow is valid and there are no chemical reactions affecting the transport of solutes (conservative transport) (Freeze & Cherry, 1979; Fetter, 1993; Zheng & Bennett, 1995). In one dimension, this can be expressed as :

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} \qquad 3\text{-}1$$

$$v_z = \frac{K}{\eta}\frac{\partial h}{\partial z} \quad \text{and} \quad D_z = \alpha_z v_z + D^* \qquad 3\text{-}2 \ \& \ 3\text{-}3$$

where C - solute concentration (mg/L); η - aquifer porosity;
z - linear distance from solute source (m); t - time (day);
α_z - longitudinal dispersivity (m); D^* - effective diffusion (m^2/day);
D_z - Coefficient of hydrodynamic dispersion (m^2/day);
v_z - Linear groundwater velocity (Darcy velocity divided by porosity) (m/day);
K - hydraulic conductivity (m/day); h - hydraulic head (m);
$\partial h/\partial z$ - hydraulic gradient (often as "i" - no units).

The analytical solution to equation 3-1 was first given by Ogata & Banks (1961). Their solution assumes constant velocity and uniform flow conditions with the following initial and boundary conditions :

$$C = \frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{L - v_z t}{2\sqrt{D_L t}}\right) + \exp\left(\frac{v_z L}{D_L}\right)\operatorname{erfc}\left(\frac{L + v_z t}{2\sqrt{D_L t}}\right)\right] \qquad 3\text{-}4$$

Initial Conditions : $C(x,0) = 0 \quad x \geq 0$ 3-5a

Boundary Conditions : $C(0,t) = C_0$ and $C(\infty,t) = 0 \quad t \geq 0$ 3-5b

where C_0 - source concentration; L - length of seepage path;
erfc - complementary error function; exp - exponential function;
D_L - hydrodynamic dispersion for seepage path of length L.

The incorporation of chemical and sorption reactions in the ADE is generally achieved through the use of extra terms to account for the changes in solute concentration over time due to the respective chemical processes (Miller & Weber, 1984) :

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{\rho_D}{\eta} \frac{\partial C^*}{\partial t} + \left(\frac{\partial C}{\partial t}\right)_R \qquad 3\text{-}6$$

where ρ_D - bulk density of the aquifer;

C^* - sorbed concentration of solute on aquifer sediments;

$\left(\frac{\partial C}{\partial t}\right)_R$ - chemical or biological reaction term (solute source or sink).

Assuming SO_4 and Cl do not undergo chemical reactions, it is necessary to describe their sorption behaviour. Cl, a member of the halide group of elements, is generally considered to be chemically non-reactive and does not undergo sorption to any measurable degree (Freeze & Cherry, 1979; Fetter, 1993; McBride, 1994). The following analysis will therefore concentrate on sorption processes as they may control SO_4 transport in comparison to Cl.

There are a variety of ways to model sorption processes, all with different ways to account for the sorbed concentration, C^*, noted in 3-6. This is primarily due to the mechanism controlling the sorption and the amount and nature of the sorption sites in the aquifer sediments. The simplest approach is to assume a linear relationship between the sorbed and dissolved concentrations, with the constant of proportionality called the distribution coefficient, or K_D (Knox *et al.*, 1993; Fetter, 1993). The value for K_D at a particular site is constant for steady state chemical evolution of groundwater, although many groundwater systems undergo dynamic chemical evolution and thus K_D is variable over time and space (Reardon, 1981; Brusseau, 1992). We will assume steady state and constant K_D behaviour for groundwater chemistry, assumimg that sorption is instantaneous and reversible (Manassero *et al.*, 1998). Mathematically this becomes :

$$C^* = K_D C \qquad 3\text{-}7$$

Substituting this into 3-6 gives (Fetter, 1993) :

$$\frac{\partial C}{\partial t}\left(1+\frac{\rho_D}{\eta}K_D\right)=D_z\,\frac{\partial^2 C}{\partial z^2}-v_z\,\frac{\partial C}{\partial z} \qquad 3\text{-}8$$

$$R=1+\frac{\rho_b}{\eta}K_D \qquad \text{(retardation factor)} \qquad 3\text{-}9$$

Alternative sorption models are non-linear and account for factors such as limited sorption sites, kinetic rates of sorption, surface transfer phenomena or other processes (Fetter, 1993; McBride, 1994; Langmuir, 1997). Linear sorption models are often used due to their mathematical simplicity. Mulder & Pedler (1990) provided no geochemical basis for their adoption of a retardation factor of 1.1 for SO_4 (and Na), rather these values being based on visual calibration of 1-D model runs. Thus, for the sake of simplicity and given the weak and reversible nature of sorption of SO_4 (cf. Chao *et al.*, 1962), a linear sorption model will be adopted for this analysis using the value of R as 1.1 for SO_4 and 1.0 for Cl (no sorption). The analytical solution for 3-8, with the following boundary and initial conditions is (Bear, 1972; Bedient *et al.*, 1994) :

$$C=\frac{C_0}{2}\left[\operatorname{erfc}\left(\frac{R\,L-v_z\,t}{2\sqrt{R\,D_L\,t}}\right)+\exp\left(\frac{v_z\,L}{D_L}\right)\operatorname{erfc}\left(\frac{R\,L+v_z\,t}{2\sqrt{R\,D_L\,t}}\right)\right] \qquad 3\text{-}10$$

The values chosen for this analysis are summarised in Table 3.3, including their corresponding reference and brief notes concerning its suitability. Although there is some uncertainty with values such as hydrodynamic dispersion, porosity and hydraulic conductivity, using typical values from available literature for similar aquifer materials should allow an estimate of potential transport rates. Three different values of hydraulic gradient were used to incorporate realistic variations in groundwater velocity at the base of the ash pond embankment (with higher hydraulic gradients) compared to distant bore 3135U (with a lower gradient). An east-west cross-section of the hydraulic heads is shown in Figure 3.9, which also form the boundary and initial conditions. The results are presented in Figure 3.10 for Cl and Figure 3.11 for SO_4. The analysis assumes zero concentration of SO_4 and Cl prior to the influence of ash pond seepage.

Table 3.3 - Solute Transport Parameters

Parameter	Value	Notes
Seepage Length (L)	1,350 m	Distance to bore 3135U west from LYAP
Time (t)	14 years	Time of seepage migrating west
Hydraulic Conductivity (K)	5 m/day	Data from Mulder & Pedler (1990), Daniels *et al.* (1993) & Daniels (1994a)
Hydraulic Gradient (i)	0.05, 0.02 & 0.01	Based on water levels in the LYAP, in adjacent HHF bores and distance between these points
Porosity (η)	0.43	Data from Mulder & Pedler (1990), Daniels *et al.* (1993) & Daniels (1994a)
Longitudinal Dispersivity (α_z)	60 m	Based on Gelhar *et al.* (1985), Gelhar (1986), Gelhar *et al.* (1992) & Fetter (1993)
Effective Diffusion Coefficient (D^*)	4.32×10^{-5} m^2/day	Based on Fetter (1993)
Source : SO_4 - C_0 Source : Cl - C_0	2,500 590	Based on monitoring data around the LYAP to early 1995

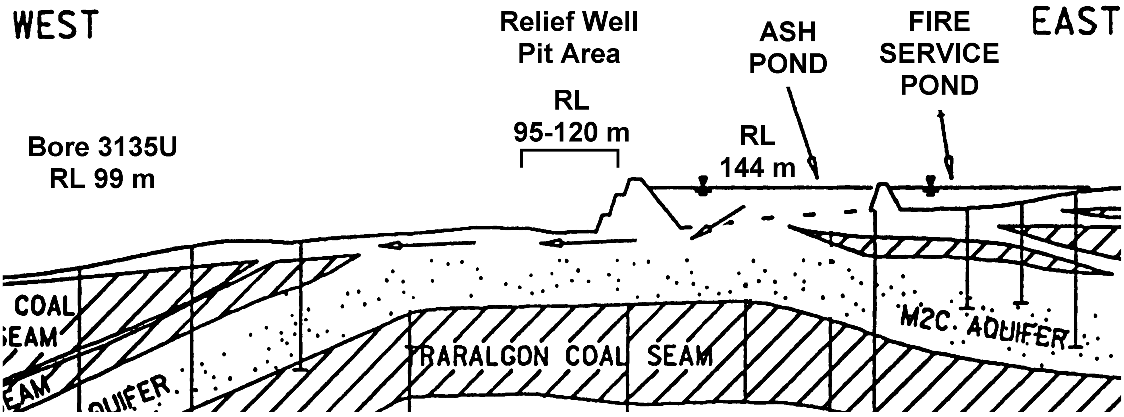


Figure 3.9 - East-West Cross-Section of the LYAP and Hydraulic Heads in the HHF (adapted from Figure 3.3)

The monitoring data for Cl, SO_4 and Na from the RWP and bores 2124U and 3135U do not appear to correlate well with the applied analytical model. There are several factors which may influence this lack of agreement. Firstly, the Cl concentration assumed as the source is only marginally above the background concentration before the influence of seepage (~200 to 400 mg/L). This would improve the visual fit for the early data, though not significantly. The large difference in SO_4 concentration between seepage and background means that incorporation of background in the model would not improve the model fit.

Secondly, the different velocities adopted for the analysis indicate a large variation in the breakthrough of both Cl and SO_4 at distance along the seepage path. For example, the maximum velocity of 0.25 m/day shows SO_4 arriving at bore 3135U by 1996 at about 1,000 mg/L, yet monitoring data does not indicate any change in SO_4. The transport of Cl at this velocity suggests some influence of seepage at 3135U, although the field data is still above the model prediction. The groundwater velocity used in the analytical model is critical in assessing the transport of Cl. Based on the groundwater levels in Figure 3.6, the higher velocity of 0.25 m/day used by Mulder & Pedler (1990) is an overestimate, since the average hydraulic gradient over the length of the seepage path adopted above is lower than that at the base of the ash pond embankment, where their analysis was undertaken. The distant monitoring bore 3135U has a hydraulic head of 99.2 m while most monitoring bores around the RWP range between 95 to 120 m. This shows that over the 2 km flowpath between the RWP and 3135U the average hydraulic gradient is of the order of 20 m per 2 km ($i = 0.01$), compared to the ash pond embankment region with gradients of about 25 m per 0.5 km ($i = 0.05$). Thus the velocities of 0.05 and 0.1 m/day are considered more realistic than the higher value used by Mulder & Pedler (1990).

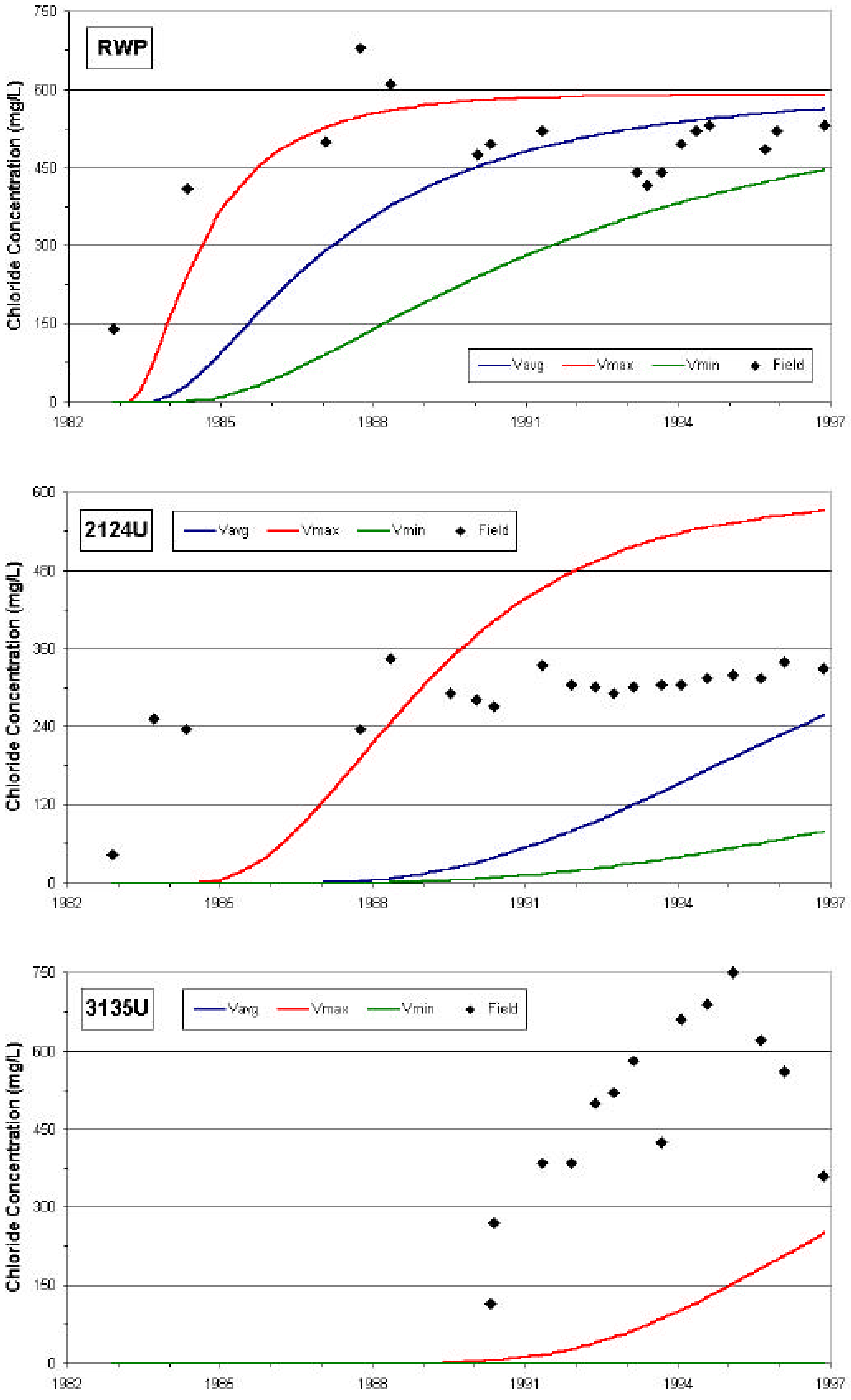


Figure 3.10 - Transport of Chloride from the LYAP

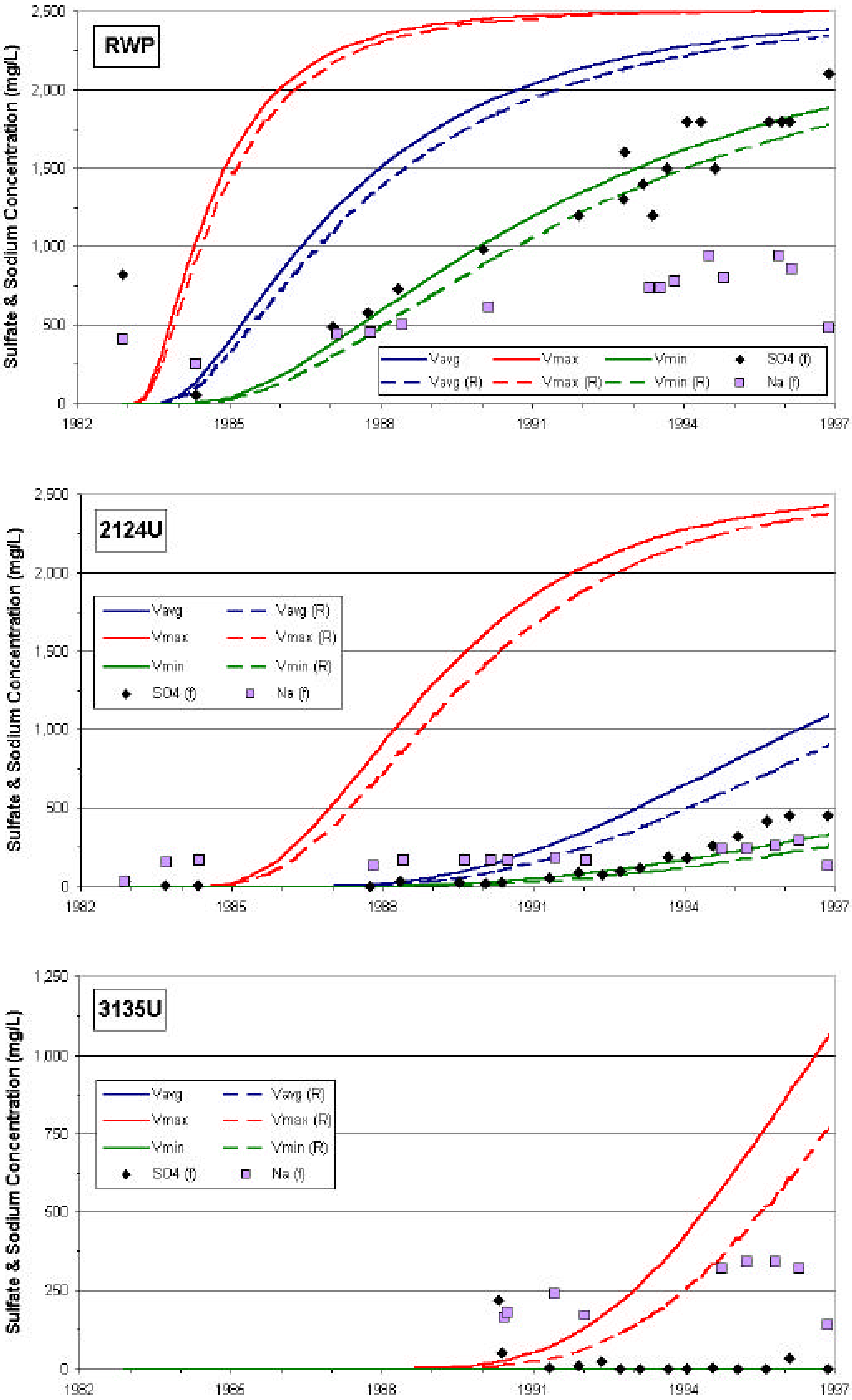


Figure 3.11 - Transport of Sulfate (and Sodium) from the LYAP (R - retardation)

Thirdly, the source concentrations are assumed to be constant over the 14 years of the analytical model. As shown earlier in Figure 3.5, this is not the case. The concentrations of SO_4 and Cl have both increased overall in the ash pond since 1982, with a degree of short term variation evident. If the source concentrations were increased in the model, it would act to further shift the model predictions away from the field data. Fourth, the use of a retardation factor of 1.1 for SO_4 transport does not significantly affect model predictions. Fifth, the field data for Na given in Figure 3.11, and for the same flow and transport parameters as SO_4, shows no correlation to the model. Finally, the model assumes a one-dimensional linear flow path, which simplifies the complex and heterogeneous nature of the HHF aquifers.

The appropriate groundwater velocity, based on Cl data, would appear to be in the range of 0.05 to 0.1 m/day. The model predictions for SO_4 are close to the field data, although given the recently higher source concentrations in the ash pond, the fit is not realistic. A further consideration that is important in the analysis of the graphs in Figures 3.10 and 3.11 is the shape of the breakthrough curve, that is, the gradient and curvature of the concentration versus time. For the RWP, the modelled SO_4 concentration is asymptotically approaching a maximum (source) concentration by 1996, compared to the field data which is still increasing. Thus, if a higher source concentration was assumed, the modelled prediction would have greater initial curvature (or solute breakthrough) and be closer to that for the maximum velocity and the model would correlate less with the observed field data.

The analytical solute transport model applied above has shown that the transport of SO_4 and Cl from the LYAP is complex. By calibrating the model parameters against Cl transport, it can be seen that there is some degree of conjecture in determining the appropriateness of model fit to SO_4 data, irrespective of whether retardation is incorporated or not. The gradual increase over time for SO_4 at both the RWP and bore 2124U suggests further controls on SO_4 transport are apparent than those assumed above. It would appear reasonable, therefore, to further investigate any possible chemical reactions which may be influencing the behaviour of SO_4 in the HHF aquifers.

3.5.7 Mixing Calculations of Seepage and Groundwater

In order to assess the effect of 15 years of ash pond seepage impacts on HHF groundwater quality, the geochemical computer model PHREEQC (Parkhurst, 1995) was used to calculate the groundwater chemistry of different mixing ratios of ash pond seepage and natural HHF groundwater. The PHREEQC program, which stands for "pH REdox and EQuilibrium Chemistry", is designed to calculate the chemical saturation states of a water quality, mixing of different waters and geochemical reactions.

Mulder & Pedler (1990) chose the water quality of bore 2124U from November 1982 as the basis for background quality of HHF groundwater. This data was considered typical for the HHF and prior to ash pond seepage. The water quality of the seepage in Table 3.4 is based on the average of LYAP data obtained to early 1995. On the basis of previous seepage investigations and modelling studies of the LYAP, the ratio of groundwater flow to seepage volumes is estimated to be between 1:2 to 1:4 (Wood *et al.*, 1982; Reinsch *et al.*, 1982; Pedler & Raisbeck, 1988; Mulder & Pedler, 1990; Daniels *et al.*, 1993; Daniels, 1994a). The results are given in Table 3.5.

Table 3.4 - Groundwater Chemistry Data Used in PHREEQC Mixing Calculations

	pH	Na	K	Ca	Mg	SO_4	Cl	Alk.
HHF	7.0	38	2.4	18	3.2	32	43	61
LYAP	9.0	1,400	51	250	50	2,970	425	100

Table 3.5 - PHREEQC Mixing Calculations of Seepage and HHF Groundwater

GW:AP[1]	pH	Na	K	Ca	Mg	SO_4	Cl	Alk.
1:4	8.74	1,133	42	205	41	2,395	350	67
1:2	8.41	928	34	170	34	1,952	293	69
1:1	7.82	723	27	135	27	1,509	235	70
2:1	7.40	517	20	100	20	1,065	178	72
4:1	7.17	312	12	65	13	623	120	73
RWP[2]	5.5	860	-	-	-	1,800	520	-
2124U[3]	4.1	290	1.2	6.2	66	450	340	-

[1] - Ratio of groundwater (GW) to ash pond (AP) seepage; [2] - Monitoring data from February 1996; [3] - April 1996.

As can be seen from Table 3.5, it is not possible to justify the monitoring data on the basis of seepage and groundwater mixing alone. This is particularly true for pH and SO_4, where field values are substantially different to those predicted by non-reactive mixing. A further point to note is that the source concentrations within the LYAP have risen further during the 1990's. If this point is taken into account, the difference between the mixing calculations and the observed monitoring data would be even higher.

The above mixing analysis of groundwater and ash seepage shows that for the estimated ratio of seepage and groundwater flows, the chemistry should be dominated by that of seepage from the ash pond and not natural HHF hydrochemistry. A comparison of the mixing calculations to the monitoring data from bore 2124U and the Relief Well Pit (RWP) shows little apparent correlation to the observed data. It follows then that there appears to be quite reactive geochemical processes occurring in the HHF aquifers, especially for SO_4. This issue needs to be considered in detail for realistic solute transport assessments. The geochemistry of SO_4 in HHF aquifers will now be addressed as a prelude to further solute transport modelling.

3.6 Geochemical Controls on Sulfate Migration

3.6.1 Overview of Sulfur Geochemistry

Sulfur can exist in a number of valence states in groundwater, ranging from S^{2-} to S^{6+} in a variety of partly soluble minerals, and is particularly sensitive to redox conditions (Morse *et al.*, 1987; Langmuir, 1997). The oxidised form of sulfur is generally the most stable and soluble species, as sulfate - SO_4^{2-} (Fetter, 1993). In reducing environments, the reduced form of sulfur is stable as sulfide species - S^{2-}, HS^- or H_2S (aqueous) (Fetter, 1993). The chemical changes of sulfur are thermodynamically favourable at typical environmental conditions, although mostly at very slow kinetic rates (Langmuir, 1997). When the various reactions are catalysed by bacteria or microorganisms, the kinetic rates increase dramatically (Chapelle, 1993; Fetter, 1993; Langmuir, 1997). The geological cycling of sulfur in the environment is therefore controlled by dissolution and/or precipitation of soluble minerals, oxidation/reduction (redox) reactions and biological processes (Morse *et al.*, 1987).

Sulfate can undergo adsorption onto the oxide and hydroxide surfaces of Fe, Al and Mn at low pH (Chao *et al.*, 1962; Rowe *et al.*, 1995). It is possible for SO_4 to weakly adsorb onto organic carbon, although this is dependent on soil chemistry and the speciation of the organic material (Chao *et al.*, 1962). In general, the adsorption of SO_4 is considered to be a geochemically weak and reversible process, and therefore a minor control on natural concentrations of SO_4 in groundwaters (Chao *et al.*, 1962; Bagchi, 1990; Rowe *et al.*, 1995). The value for the distribution coefficient (K_D) for SO_4 is zero, giving a retardation factor unity (1) (Barone, 1990; Rowe *et al.*, 1995). The use of retardation coefficients in solute transport analysis is generally based on adsorption being the major control on solute concentration (Reardon, 1981; Zheng & Bennett, 1995). For sorption to occur in HHF aquifer sediments, a high proportion of Fe or Al oxides or organic carbon would be required for significant SO_4 adsorption, more typical of lateritic soils (Chao *et al.*, 1962). The aquifer sediments of the HHF are coarse sands with much lower proportions of Fe oxides than laterite soils, and thus possess only a small amount of sorption sites. Given the weak and reversible nature of SO_4 adsorption, the degree of attenutation demonstrated for the HHF at the Loy Yang Ash Pond should, therefore, not be solely due to adsorption. It follows therefore that the most plausible geochemical reaction controlling SO_4 in the HHF is SO_4 reduction, or conversion from SO_4 to sulfide (Berner, 1971; Bagchi, 1990; Langmuir, 1997).

3.6.2 Biogeochemistry of Sulfate Reduction

The geochemical process of reducing SO_4 to sulfide generally requires the presence of organic carbon (Berner, 1964; Appelo & Postma, 1994; Langmuir, 1997). This association has been noted since the early-19^{TH} century, although its chemistry and environmental significance were not widely appreciated until the 1960's (Morse *et al.*, 1987). The presence of SO_4 and organic matter thermodynamically favours the formation of sulfide and oxidation of carbon (Morse *et al.*, 1987; Machel, 1989). At ambient environmental temperatures below about 85 ^{0}C, specialised SO_4-reducing bacteria (SRB) are required to ensure rapid reaction rates are maintained, while SO_4 reduction without bacteria (abiological or thermochemical SO_4 reduction) can only proceed appreciably at temperatures in excess of 100 ^{0}C (Machel, 1989). Due to the bacteria involved in the process, the term biogeochemistry is often applied.

All plants, animals and bacteria metabolise sulfur in order to synthesize amino acids and for other cellular functions (Berner, 1982; Postgate, 1984). There are generally two pathways for the SO_4 reduced by biological activity - incorporated into cellular materials or excreted as hydrogen sulfide gas (H_2S) (Berner, 1980; Postgate, 1984). The sulfur may be incorporated directly into organic molecules as SO_4 or it may be reduced to sulfide (Postgate, 1984). The process of direct metabolism and incorporation into cellular materials is termed *assimilatory sulfate reduction* (Goldhaber & Kaplan, 1975; Postgate, 1984). The process of SO_4 reduction and excretion as hydrogen sulfide is termed *dissimilatory sulfate reduction* (Dockins *et al.*, 1980; Postgate, 1984; McLaughlin & Knight, 1989). A minor quantity of the sulfur is incorporated into biomass, but the majority of sulfur is converted to hydrogen sulfide (H_2S) gas (McLaughlin & Knight, 1989). The process is a kinetic reaction and mediated by specialised bacteria and microorganisms (Berner, 1980; Postgate, 1984).

Traditionally, SO_4 reduction was considered to occur in strictly anaerobic and reducing environments (Berner, 1980; Morse *et al.*, 1987; Dvorak *et al.*, 1992; Hard & Babel, 1995). More recently, active reduction of SO_4 has been observed in the microenvironments of decaying fish (Berner, 1971) and in the photosynthetic zone of microbial mats in the presence of dissolved oxygen (Canfield & Des Marais, 1991). The SO_4-reducing bacteria (SRB) can survive in aerated water for several days, suggesting a degree of oxygen tolerance (Hardy & Hamilton, 1981; Cypionka *et al.*, 1985; McLaughlin & Knight, 1989).

The geochemical reaction for SO_4 reduction is represented as (Matthess, 1982) :

$$2CH_2O + SO_4^{2-} + 2H^+ \rightarrow H_2S + 2CO_2 + 2H_2O \qquad \text{3-11}$$

where CH_2O represents organic matter in the aquifer sediments.

This reaction shows that SO_4 reduction is coupled with the oxidation of organic matter, consumption of acidity and the release of alkalinity (carbonate). Sulfate is used as an electron acceptor by SRB during the oxidation of organic matter (Hard & Babel, 1995). Sulfate reduction is therefore expected to increase the pH of water.

Under conditions of high SO_4 and organic matter, SO_4 reduction can be approximated by a zeroth order kinetic process with respect to SO_4 and proceeds at a constant rate, independent of SO_4 and organic matter concentration (Berner, 1964 & 1981; Goldhaber & Kaplan, 1975; Boudreau & Westrich, 1984). When the organic matter is limited, the rate of SO_4 reduction is controlled by the availability and reactivity of organic matter (Goldhaber & Kaplan, 1975; Berner, 1981). Sulfate concentrations less than 3 mM or 300 mg/L (about 10% of the average SO_4 concentration in seawater; cf. Langmuir, 1997), however, may affect the rate of SO_4 reduction (Boudreau & Westrich, 1984).

The chemical form and abundance of the organic matter plays a critical role in determining the rates of dissimilatory sulfate reduction (Goldhaber & Kaplan, 1975; Drever, 1997). A wide range of organic materials can be used by bacteria, including hydrocarbons, fatty acids, carbohydrates and amino acids (Berner, 1971 & 1980; Hard & Babel, 1995). Sulfate reducing bacteria, however, tend to prefer short chain organic acids such as lactic, pyruvic and formic acids and their salts (Berner, 1980; Postgate, 1984; Dvorak *et al.*, 1992; Hard & Babel, 1995; Langmuir, 1997). For example, organic matter derived from marine algae is more readily degraded than terrestrial sources, such as vascular plants (containing resistant lignin, resins and waxes), since algae are more easily metabolised and provide a plentiful supply of the essential biological nutrients, namely nitrogen (N) and phosphorous (P) (Westrich & Berner, 1984; Waples; 1985).

The major group of bacteria that facilitate SO_4 reduction are those of the *Desulfovibrio*, *Desulfotomaculum* or *Desulfomonas* genus (Postgate, 1984; McLaughlin & Knight, 1989; Chapelle, 1993). The SRB, although the only bacteria to thrive on the metabolism of SO_4, are not alone in their processing of organic carbon and nutrients in sediments and are generally part of an active subsurface microbiological community (Goldhaber & Kaplan, 1975; Jørgensen, 1978a; Berner, 1980 & 1981; Postgate, 1984; Berner & Westrich, 1985; Charbeneau & Weaver, 1992). Often, the heavier organics are first degraded by other bacteria to shorter chain molecules, which SRB can then utilise directly (Sorokin, 1962; Goldhaber & Kaplan, 1974 & 1975; Charbeneau & Weaver, 1992; Drever, 1997). Another example of the interrelationships in subsurface communities is the competition between bacterial reducers of ferric iron (Fe^{3+}) and SRB (Chapelle & Lovley, 1992).

Different SRB species are known to have varying tolerances to salinity, temperature and pH (Postgate, 1984; Langmuir, 1997). The salinity range in which active SRB can be found is large, ranging from fresh waters to marine sediments and oil field brines (Hem, 1985; Langmuir, 1997). The tolerance for temperature has been demonstrated to range from as low as 0 ^{0}C to as high as 110 ^{0}C near deep sea hydrothermal vents (Jørgensen *et al.*, 1992; Langmuir, 1997). The pH tolerance of some species can vary from acidic (4.2) to alkaline (9.9) (Zehnder, 1988). A mildly acidic environment ($pH < 4$) appears to inhibit SO_4 reduction (Wakao *et al.*, 1979; Widdel, 1988). Hard *et al.* (1997) state that pH tolerance can be dependent on the strains of SO_4-reducing bacteria present and geochemical conditions. Indeed, the ability of SRB to generate alkalinity gives them a unique buffer against acidic environments (Hammack & Edenborn, 1992). The SRB are thus adaptable to most natural environments except, of course, aerobic environments (Postgate, 1984).

The rates of biological SO_4 reduction can be assessed through analysis of the stable sulfur isotopes of ^{32}S and ^{34}S, since the process tends to concentrate the lighter ^{32}S isotope in the hydrogen sulfide and the heavier ^{34}S isotope in the remaining SO_4 (Goldhaber & Kaplan, 1975; Dockins *et al.*, 1980; Postgate, 1984). The radioactive isotope of sulfur, ^{35}S, can also be used in assessing bacterial rates of SO_4 reduction through the addition of a $^{35}SO_4$ radiotracer (Sorokin, 1962; Jørgensen, 1978b; Westrich, 1983; Jones *et al.*, 1996).

The H_2S gas formed by SO_4 reduction is highly reactive and soluble, which generally reacts with ferrous iron (Fe^{2+}) in aquifer sediments to form highly insoluble sulfide precipitates (ranging from FeS to FeS_2) (Jørgensen, 1978a; Morse *et al.*, 1987; McBride, 1994; Appelo & Postma, 1994). The mineral siderite ($FeCO_3$) may also form and limit Fe solubility, determined by the alkalinity or the partial gas pressure of carbon dioxide (pCO_2) dissolved in the groundwater (McBride, 1994).

3.7 Sulfate Reduction at Loy Yang

The generally low concentrations of SO_4 in the various groundwaters across the Latrobe Valley has long been attributed to the reaction between SO_4 and reworked coal fragments in the aquifer matrices, due to the conversion of SO_4 to and the presence of hydrogen sulfide in bores (cf. Brumley *et al.*, 1981; Daniels *et al.*, 1993; Daniels, 1994a; Geo-Eng, 1995). The distinct odour of H_2S gas can be detected in groundwater samples from many bores tapping deep, intermediate and shallow aquifers.

The HHF aquifer sediments are known to contain pyrite nodules (FeS_2) and siderite ($FeCO_3$) (Bolger, 1984). Their presence was considered anomalous due to the high-energy, oxidising nature of the fluvial deposition of HHF sediments. Bolger (1984) also noted extensive organic matter in the HHF. Although no source was given, it was presumably derived from weathering and reworking of the underlying Morwell coal seams during the Pliocene. This study did not investigate or report on the concentration or chemical form of the organic material noted. The reworking of lignitic organic material was reported by Thorstenson *et al.* (1979) as the source material for driving SO_4 reduction in North and South Dakota. An examination of geologic cross-sections in the LYAP area shows the presence of peat lenses in the HHF aquifer sediments (see Mulder & Pedler, 1990).

The groundwaters of the Latrobe Valley are also known to contain significant quantities of carbon dioxide, which led to corrosion problems of steel-cased bore in the early years of the SECV (Geo-Eng, 1995). The dissolved CO_2 concentration of the M1 and M2 aquifers at the Hazelwood mine ranged from 93 to 170 mg/L (presumably laboratory and not field measurements) (Brumley *et al.*, 1981). Similar values of dissolved CO_2 have more recently been observed in groundwater bores within the Loy Yang Open Cut (Bradley, 1998). The redox state nor the oxygen content of the various formation groundwaters have not been studied or reported widely to date (Brumley *et al.*, 1981). The decreasing trend in pH does not correspond with expected behaviour for SO_4 reduction, which consumes acidity and releases alkalinity. The acid buffering may be due to release of carbon dioxide, or another geochemical process.

The presence of SO_4-reducing bacteria (SRB) within Latrobe Valley groundwaters, and particularly at Loy Yang, has not been investigated to date. The quantity and nature of dissolved organic species in groundwater has also yet to be studied.

Despite the data being incomplete in relation to the redox state of HHF aquifer sediments and its organic content and speciation, these conditions described above suggest that SO_4 reduction could be a likely process that controls the sulfur cycle in Latrobe Valley groundwaters. This is due to the apparent abundance of organic material and the presence of H_2S gas. In order to study this further, a more extensive groundwater sampling and analytical regime was established. This work complemented the existing monitoring of groundwater in the vicinity of the LYAP.

3.8 Groundwater Monitoring at Loy Yang

The current monitoring of groundwater in the vicinity of the LYAP is designed to help assess the localised impacts by ash pond seepage on receiving aquifers. This monitoring is undertaken in accordance with EPA licence requirements for operation of the Loy Yang Ash Pond. The analyses undertaken on all groundwater samples to early 1995 generally included TDS, pH, electrical conductivity (EC), Na, SO_4 and Cl. The regular analysis of groundwater samples for trace element migration has recently been included in the LYAP monitoring program, although this data is not reviewed in detail in this thesis. A location map of LYAP groundwater monitoring bores was given earlier in Figure 3.6.

As part of this doctoral thesis, the water quality analyses for the groundwater monitoring program at the LYAP were expanded from early 1996 to late 1998. This was intended to allow the controlling geochemical processes for SO_4 to be assessed in more detail. The expanded analysis of groundwater quality was applied to most samples, however, only the HHF aquifer data is included in this thesis, due to the complex relationships of the intermediate and deep aquifers to seepage from the LYAP discussed earlier. An analysis of the additional HHF monitoring data and chemical processes will be presented after the data from individual monitoring rounds is presented.

3.8.1 Sampling Methodology

All groundwater samples were obtained through the use of small diameter bailers (less than 50 mm diameter). The samples were stored in plastic bottles, within a chilled esky, and submitted to the laboratory for analysis within six hours from the time they were obtained. Although bailers may introduce oxygen into samples and allow partial degassing of CO_2 and H_2S, experience has shown that with great care and methodical sampling, representative samples of groundwater chemistry can be obtained (Bradley, 1998).

Based on the availability of equipment, different field monitoring devices were used on different sampling rounds. These devices will be listed for each round. At different sampling rounds, additional field equipment was used to obtain specific data, such as field alkalinity and carbon dioxide concentrations. The field pH/Eh meters were calibrated using the standard solutions supplied with each meter used at various times.

All monitoring and sampling of groundwater bores is undertaken in conjunction with Geo-Eng Australia Pty Ltd, under contract to the Infrastructure Services Group (ISG) of Loy Yang Power Ltd (LYP). Sampling of RWP and B Station seepage water was undertaken by EnviroGen Pty Ltd from 1995 to June 1997, and by THIESS Environmental Services Pty Ltd from July 1998 to present. The analysis of groundwater samples was undertaken by EnviroGen Pty Ltd from early 1995 to June 1997. From July 1997, the contract was awarded to WSL Consultants Pty Ltd.

3.8.2 Monitoring Data of April 1996

The analyses of groundwater samples was extended to include all major cations, anions, SiO_2 and alkalinity speciated to HCO_3 and carbonate (CO_3). Field monitoring of pH and redox state was undertaken using a Hanna pH Meter, model HI 9023, while Electrical Conductivity was measured with a Hanna Conductivity Meter, model HI 9033. The analytical results for HHF bores are given in Table 3.6.

Table 3.6 - Analytical Results for HHF Groundwater, April 1996 (mg/L)

Bore	Temp	pH		Eh	TDS	Na	K	Ca
		F	L					
RWP			5.5		3,200	860		
2124U		5.8	4.1	69	1,200	290	1.2	6.2
3135U		5.5	6.5	85	1,300	320	1.5	15
3282L		6.2	4.1	48	2,700	810	4.9	7.6
3282U		6.1	6.0	55	2,300	770	4	8.5
B Stn		6.1	6.2	57	2,300	750	2.3	11

Bore	Mg	Fe	SiO_2	SO_4	Cl	HCO_3
RWP				1,800	520	
2124U	66	3.6	9.2	450	340	
3135U	52	170	3.2	34	560	320
3282L	110	47	12	370	1,300	
3282U	110	33	12	430	850	52
B Stn	84	0.27	14	440	930	54

Notes - Temp. in ^{0}C; Eh in mV; F - Field; L - Laboratory; RWP - sample from Feb. 13, 1996..

The groundwater chemistry demonstrates the mildly acidic character of the water, and that the redox state is only weakly oxidising (indicating low dissolved oxygen concentrations). The Fe concentrations are variable, although elevated at bores 3135U, 3282L and 3282U. Minor variation between field and laboratory determined pH is evident in this round.

3.8.3 Monitoring Data of October 1996

The expanded suite of major cations and anions was continued for all groundwater samples. Further analyses were included to test for the bisulfide (HS^-) and dissolved CO_2 content of groundwaters, with special bottles containing preservative prepared by the laboratory (EnviroGen). The field testing program was expanded to allow for measurement of dissolved oxygen (DO), field alkalinity (as $CaCO_3$). Results are given in Table 3.7.

The field pH/Eh meter failed to calibrate and function properly, and hence this data has been rejected and not included. Importantly, the sulfide analyses are all below the analytical detection limit. There is notable carbon dioxide present in all bores.

Table 3.7 - Analytical Results for HHF Groundwater, October 1996 (mg/L)

Bore	Temp	pH (L)	Eh (L)	TDS	Na	K	Ca
2124U	13.4	4.4	580	1,200	130	0.5	6.5
3135U	11.6	6.4	160	930	140	0.6	9.3
RWP	-	4.8	-	3,800	480	-	-
3282L	13.8	3.8	510	2,400	140	5.3	3.5
3282U	13.7	6.8	300	2,500	150	25	14
B Stn	-	6.5	-	2,600	960	-	-

Bore	Mg	SO_4	HS^-	Cl	Alk.	$CO_{2\,(aq)}$ (L)
2124U	64	450	<0.1	330	<1	32
3135U	41	<1	<0.1	360	350	220
RWP	-	2,100	-	530	-	-
3282L	81	350	<0.1	1,200	<1	200
3282U	100	520	<0.1	1,000	11	26
B Stn	-	660	-	970	-	-

Notes - Temp. in ^{0}C; Eh in mV; F - Field; L - Laboratory; RWP & B Stn from Nov. 13, 1996.

3.8.4 Monitoring Data of April 1997

The analyses of groundwater samples was extended to include all major cations, anions, Al, SiO_2, alkalinity (speciation to HCO_3/CO_3), dissolved hydrogen sulfide (H_2S), nitrate (NO_3^-) and dissolved Total Organic Carbon (TOC). This allows an assessment of organic and nutrient concentrations s within HHF groundwater. Field monitoring of pH and redox state was undertaken using a TPS pH-Eh probe (model number no known). The dissolved carbon dioxide ($CO_{2\,(aq)}$), total alkalinity and dissolved oxygen (DO) were measured in the field. The $CO_{2\,(aq)}$ was determined by titration with 0.1 M NaOH using a phenophthalein indicator, as per the standard method (APHA, 1992). The alkalinity was measured using a Hach Drop Titration kit. The DO was measured using the Hach DO probe (model unknown).

Additional groundwater bores screened in the HHF were also sampled in the vicinity of the LYAP embankment. The bore 3138U, east of the Fire Services Reservoir (FSR; see Figure 3.6), is hydraulically upgradient of possible seepage and is thus considered a better representation of background groundwater quality, although historically it often contains small volumes of water (slow recharge) and is not used for sampling. A small sample volume was retrieved from 3138U. All analytical results are given in Table 3.8.

Table 3.8 - Analytical Results for HHF Groundwater, April 1997 (mg/L)

Bore	Tmp	pH		Eh	DO	TDS	Na	K	Ca	Mg	TOC
		F	L								
2104U	13.8	5.40	6.5	111	-	430	120	0.4	9.6	12	51
2105U	14.4	6.85	7.8	24	-	990	220	-	-	-	-
2124U	13.6	4.71	4.8	170	2.4	1,300	320	0.9	7.6	73	8
2173U	14.7	6.75	7.4	44	-	500	120	2.5	27	15	5
2175U	13.4	6.95	7.5	33	-	170	30	1.6	9.8	6.4	12
2176U	13.6	6.46	7.4	47	-	460	75	2.8	29	2.8	4
3135U	12.7	6.34	6.4	55	-	940	190	1.2	13	43	63
3138U	10.3	6.50	7.5	45	-	550	120	3.1	19	7.2	-
RWP	15.0	-	5.0	-	-	4,100	980	2.7	54	78	-
3282L	12.0	3.63	4.2	212	<0.1	2,800	730	79	6.8	120	8
3282U	11.5	5.77	6.7	89	3.7	2,600	760	3.4	5.6	110	14.2
B Stn	15.0	-	6.3	-	-	2,900	720	1.7	12	110	-

Bore	SiO_2	Fe	Al	Cl	H_2S	SO_4	NO_3	HCO_3	Alk.^{F}	$CO_{2\,(aq)}$	
										F	L
2104U	14	24	11	230	<0.1	22	<0.01	33	-	-	-
2105U	-	140	-	520	-	40	0.97	-	-	-	-
2124U	10	24	2.8	340	0.3	510	0.07	<1	30	158	71
2173U	9.4	28	13	190	-	45	4.6	49	-	-	5
2175U	9.1	2.2	1.5	24	<0.1	45	1.1	32	-	-	4
2176U	2	2.9	10	160	<0.1	23	0.88	82	120	66	5
3135U	3.4	22	1.2	370	<0.1	<1	<0.01	360	270	1,936	190
3138U	-	27	10	210	-	23	0.55	-	-	-	-
RWP	11	24	0.4	790	-	2,900	-	4	-	-	56
3282L	13	40	96	1,400	0.1	500	<0.01	<1	0	481	32
3282U	12	81	15	1,200	<0.1	550	0.68	12	30	76	18
B Stn	18	<0.1	0.4	1,100	-	730	-	60	-	-	8

Notes - Temp. in ^{0}C; Eh in mV; F - Field; L - Laboratory; RWP & B Stn from May 13, 1997.

All samples tested for hydrogen sulfide were below analytical detection limits (0.1 mg/L) except for 2124U with a concentration of 0.3 mg/L. This is expected since H_2S is highly reactive and likely forms iron sulfide precipitates (eg. FeS_2). The concentrations of Al, dissolved oxygen and NO_3 are low, although Fe was measured at moderate concentrations in some bores. The groundwater also gave generally high concentrations of dissolved TOC, with bores 2104U and 3135U giving very high TOC values. It is interesting to note that these bores also register low SO_4 concentrations, with bore 2104U at 22 mg/L and 3135U below detection limits (1 mg/L).

The dissolved carbon dioxide ($CO_{2\ (aq)}$) concentrations are quite high, and it was apparent that the concentrations measured in the field were markedly higher than those in the laboratory. Bore 3135U had a value far in excess of all other bores at 1,936 mg/L, equivalent to a partial CO_2 gas pressure (pCO_2) of about 0.96 atm (calculated from the equilibrium between dissolved and gaseous CO_2; see Section 3.10). This compares to the average pCO_2 in the atmosphere of about $10^{-3.5}$ atm (Langmuir, 1997). The decrease in $CO_{2\ (aq)}$ from the field to the laboratory varies widely, and can range from a factor of 2 to 10 lower. The sample obtained from bore 3135U could be observed actively degassing upon sampling and exposure at the surface. The pH values obtained in the field are generally lower (more acidic) than those obtained in the laboratory by about one unit. This change in pH is most likely due to degassing of carbon dioxide. This change in carbon dioxide and pH is consistent with similar monitoring of groundwater extraction bores located in the Loy Yang open cut (Bradley, 1998).

3.8.5 Monitoring Data of October 1997

The expanded suite of major cations, anions and nutrients was continued for this round of groundwater sampling. Unfortunately, the author became ill during this period and was unable to undertake the additional field measurements for pH, Eh and $CO_{2\ (aq)}$. The sampling period is based on EPAV licence requirements for the Loy Yang facility and thus the field work could not be postponed. All analytical results are given in Table 3.9.

The water quality data continued to indicate the presence of dissolved TOC within HHF groundwater, with bore 3135U again recording a very high concentration of 45 mg/L. The NO_3 and Al concentrations were low, although Fe was also high for bore 3135U. The water quality of new groundwater bore 3551, situated northeast of the LYAP and Fire Servcie Reservoir (see Figure 3.6), indicates a low salinity consisting mostly of Na and Cl with no apparent influence of seepage.

Table 3.9 - Analytical Results for HHF Groundwater, October 1997 (mg/L)

Bore	Temp	pH (L)	Eh (L)	TDS	Na	K	Ca	Mg
2178		6.0	325	1,900	470	3.2	33	63
2124U		3.7	475	1,600	340	<1	8.4	95
3135U		6.5	413	960	220	1.3	13	45
RWP		4.9		4,200	1,000		49	
3282L		4.2	492	2,600	710	3.5	7.2	100
3282U		5.9	323	2,500	730	3.2	8.2	100
3551	17.3	6.5		610	130			
B Stn		6.6		2,700	870		15	

Bore	Al	Fe	SiO$_2$	SO$_4$	Cl	HCO$_3$	NO$_3$	TOC
2178	0.5	3.2	27	1,200	300	40	0.1	23
2124U	3.4	0.4	9.5	860	350	<2	0.4	4
3135U	0.25	110	10	<5	340	370	1.3	45
RWP				2,300	550			
3282L	8.1	64	15	580	580	44	0.15	11
3282U	0.02	0.02	9	860	1,000	28	0.4	6
3551				12	220	<2		
B Stn				780	930			

Notes - Temp. in ^{0}C; Eh in mV; L - Laboratory; RWP & B Stn from Nov. 17, 1997.

3.8.6 Monitoring Data of April 1998

The groundwater quality analysis program was substantially extended to analyse the geochemical speciation of biological nutrients such as N and P, with F also included. The different species of N were analysed, including NO_3^-, nitrite (NO_2^-) and ammonia (NH_3). The species of P were analysed as P and orthophosphate (PO_4^{3-}). This allows an assessment of geochemical pathways from bacterial activity in HHF aquifer sediments (Morse *et al.*, 1987; Knox *et al.*, 1993; Bedient *et al.*, 1994). The absence of sufficient concentrations of nutrients can lead to decreased activity of SRB (Dockins *et al.*, 1980). The dissolved CO_2 concentration was determined in the field, using the previous method of titration with 0.1 M NaOH (APHA, 1992). The field pH/Eh meter used was a Hanna pH Meter, model HI 9023. Analytical results are given in Table 3.10.

Table 3.10 - Analytical Results for HHF Groundwater, April 1998 (mg/L)

Bore	Temp	pH		Eh	DO	TDS	Na	K	Ca
		Fld	Lab						
2104U	19.9	6.85	5.6	78	5.8	1,700	440	6	26
2124U	16.5	4.28	4.8	136	3.5	1,700	330	0.5	8
2173U	17.5	5.95	5.7	25	3.7	490	110	2.5	34
2175U	17.1	5.95	5.0	107	3	3,100	790	9	33
2176U		-	6.5	-	-	730	160	0.5	59
2178	18.5	5.55	6.3	54	3.7	1,900	450	1.3	34
3135U	15.9	4.62	5.8	38	3.4	880	200	1.6	15
RWP	15.4	4.93	4.7	125	2.8	4,600	1,200	32	64
3282L	17.7	4.29	4.2	161	2.9	2,500	600	2.5	5
3282U	20.2	6.21	5.8	58	2.6	1,600	630	3	8
B Stn	-	-	6.8	-	-	2,900	900	-	21

Bore	Mg	Fe	Al	SiO_2	H_2S	SO_4	HCO_3	Cl	TOC
2104U	37	0.38	0.14	39	<0.1	600	64	430	7
2124U	110	18	2.9	8	1.0	810	<2	340	3
2173U	15	7	0.11	7.5	<0.1	29	76	190	2
2175U	87	14	0.7	8.5	<0.1	1,800	10	440	3
2176U	25	0.6	0.13	12	-	52	180	330	2
2178	65	3.4	0.07	18	0.2	840	90	280	24
3135U	50	130	0.05	3.5	<0.1	<5	310	380	47
RWP	75	23	4.7	8.5	0.5	2,800	12	550	3
3282L	85	48	12	11	<0.1	470	<2	1,100	6
3282U	93	4.8	0.06	12	<0.1	740	78	940	4
B Stn	110	-	-	-	-	1,000	-	1,000	-

Bore	NO_3	NO_2	NH_4	P	PO_4	F	$CO_{2\,(aq)}$	
							Fld	Lab
2104U	<0.05	<0.01	<0.1	0.23	<0.01	0.18	299	60
2124U	<0.05	<0.01	0.6	0.23	0.01	0.25	343	100
2173U	6.5	0.13	<0.1	0.35	0.01	0.1	53	7
2175U	<0.05	<0.01	0.4	0.32	0.04	0.2	220	65
2176U	-	-	-	-	-	<0.1	-	-
2178	<0.05	<0.01	0.1	0.52	0.01	0.4	119	56
3135U	0.2	<0.01	<0.1	0.6	0.22	0.1	1,936	15
RWP	0.15	<0.01	0.3	0.26	0.06	0.3	238	70
3282L	0.1	<0.01	9.0	0.35	0.04	0.2	792	88
3282U	0.05	<0.01	0.8	0.29	0.07	0.1	370	43

Notes - Temp. in ^{0}C; Eh in mV; Fld - Field; Lab - Laboratory; RWP & B Stn from May 13, 1998.

The data on groundwater quality obtained during this round of sampling confirmed the trends in specific species, such as high Fe and $CO_{2\ (aq)}$ for bore 3135U, and the degassing of CO_2 between the field and the laboratory. More importantly, the N species are mainly in the form of reduced NH_3 (cf. bores 2124U, 3282L and 3282U), although some bores contain N in an oxidised form as NO_3 (cf. bores 2173U and 3135U). The majority of P is also in a reduced form (P), with minor quantities present in the oxidised form of PO_4^{3-}. The reduced nature of N and P species suggests that reducing conditions are prevalent in HHF groundwaters. The mildly oxidising redox conditions measured in the field appear to be influenced by the use of bailers in groundwater sampling. The variation in speciation of N and P suggests that microbial degradation pathways are complex and are likely to involve more microorganisms than SRB alone, although these do appear as the dominant microbial influence on water quality (which is dominated by SO_4).

The concentrations of dissolved sulfide detected in bore 2124U and the RWP are higher than both April 1997 and October 1996. These high sulfide concentrations are strong evidence of active microbial production of sulfide, as this would be unlikely to be due to chemical reactions alone at the low temperatures found in HHF aquifers. It is not clear if these higher concentrations of sulfide, as well as the variations in N and P speciation, indicate any seasonal variation in microbial activity, as documented by Jørgensen (1977). The TOC concentrations are also high, especially at bore 3135U.

3.8.7 Monitoring Data of October 1998

The analysis for this round of groundwater quality monitoring was the same as that for April 1998, except sulfide, PO_4^{3-} and Al were not included. The laboratory failed to complete the requested analyses on all groundwater samples, and some bores were selected to be resampled and analysed again in late December 1998. Analytical results are given in Table 3.11.

Table 3.11 - Analytical Results for HHF Groundwater, October 1998 (mg/L)

Bore	Temp	pH		Eh	DO	TDS	Na	K
		Fld	Lab					
2124U	17.6	4.76	3.5	119	4.4	1,700	400	1.3
2178	18.7	6.25	6.5	39	2.0	1,900	490	1.6
3135U	17.6	6.46	6.4	27	5.0	940	250	1.3
3609U	17.2	4.63	5.5	125	4.3	740	240	1.4
3610L	18.2	5.63	3.9	72	2.0	930	210	2.2
3610U	18.4	5.09	4.7	102	4.3	1,300	370	1.1
RWP			4.9			4,400	1,300	
3282L	16	3.67	3.2	177	2.6	2,300	750	3.9
3282U	17.1	5.96	6.1	55	3.0	2,300	700	3
B Stn.			7.0			2,700	760	

Bore	Ca	Mg	Fe	SiO_2	F	SO_4	Cl
2124U	12	140	0.28	8.7	0.4	1,000	370
2178	33	65	0.92	24	0.2	1,100	280
3135U	15	56	39	2.8	<0.1	<2	430
3609U	14	49	<0.01	14	0.1	5	450
3610L	82	17	14			140	490
3610U	14	38	0.11			26	840
RWP	56					2,100	540
3282L	7.8	120	4.2	15	0.1	390	1,100
3282U	6	110	<0.01	13	<0.1	610	930
B Stn	13					1,800	920

Bore	NO_3	NO_2	NH_4	P	HCO_3	$CO_{2\,(aq)}$		TOC
						Fld	Lab	
2124U	0.05	<0.01	1.4	0.02	<2	1,038	16	16
2178	0.35	<0.01	0.3	0.03	96	783	26	26
3135U	0.15	<0.01	0.4	0.05	370	>2,000[1]	63	63
3609U	1.2	<0.01	0.5	<0.01	14	722	3	3
3282L	0.6	<0.01	4.5	<0.01	<2	629	11	11
3282U	0.1	<0.01	0.5	0.01	68	1,329	7	7

Notes - Temp. in ^{0}C; Eh in mV; DO - Dissolved Oxygen; Fld - Field; Lab - Laboratory; RWP & B Stn from Nov. 2, 1998; [1] - Bore 3135U failed to reach an identifiable titration endpoint (see text).

The N is mainly in the reduced form of NH_3, with concentrations slightly lower but more consistent than April 1998. The concentrations of P are low. The TOC concentrations are consistently high, especially at bore 3135U. The Dissolved Oxygen (DO) concentrations are moderate, and suggest some weak source of oxygen either in situ or during sampling (ie. bailers).

The dissolved carbon dioxide concentration for bore 3135U is presented as >2,000 mg/L. This is due to the lack of an identifiable end point in the titration. In order to ensure repeatable results, the procedure was performed three times and each time no distinct end point was apparent. At the equivalent of about 2,000 mg/L, the field titration was terminated. This value is similar to the previous field determination of dissolved carbon dioxide from April 1997 and April 1998. The $CO_{2\ (aq)}$ concentrations for the remaining bores were comparable to previous monitoring rounds. The reduction in $CO_{2\ (aq)}$ concentration from the field to the laboratory is significant.

3.8.8 HHF Sediment Analysis for Organic Content

New groundwater monitoring bores were installed in the vicinity of the LYAP in July 1998. The first bore, 3610, was slightly to the north-west of the RWP area with two standpipes and screened at shallow and moderate depths of 15.5 to 18.5 and 29.5 to 32.5 m, respectively. The second bore, 3609, was installed to the south of the LYAP, with one standpipe screened in the HHF at 14 to 20 m, and the second standpipe was screened in the Morwell Formation at 50 to 53 m. The bores were drilled using a cable tool rig, thereby avoiding the use of excessive drilling fluids which may influence groundwater and aquifer processes.

These new bores represented a unique opportunity to obtain relatively undisturbed sediment samples for testing and analysis. A total of four samples of aquifer sediments were obtained from the drill rig for each HHF bore, including one sample from the screen in bore 3609L in the Morwell Formation. The samples were stored in sealed, air-tight plastic bags in a chilled esky, until they were delivered to WSL Consultants for analysis, which included the determination of Total Oxidisable Organic Carbon (OOC) content for each sample. The ratio of fulvic to humic acids was also analysed. The results are presented in Table 3.12.

Table 3.12 - Organic Carbon Analysis of HHF Aquifer Sediments

Bore	OOC (%)	Fulvic:Humic	Bore	OOC (%)	Fulvic:Humic
3609U	2.4	LD	3610U	2.5	7:1
3609U	2.2	LD	3610U	1.9	(fulvic only)
3609L	2.5	1:6	3610U	1.9	LD
3609L	3.5	1:10	3610U	3.1	(fulvic only)
			3610L	2.2	LD

OOC - Oxidisable Organic Carbon.

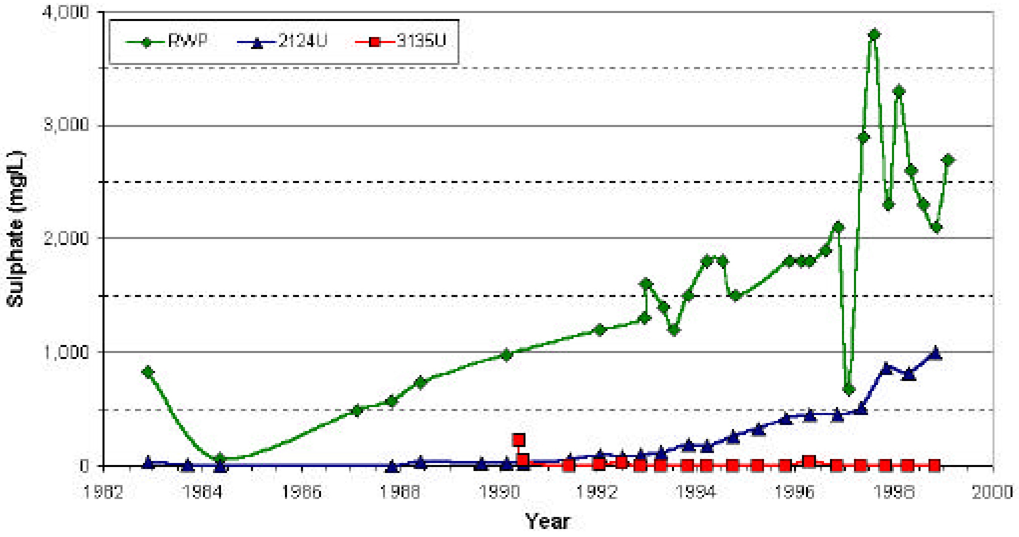
LD - Humic acids could not be speciated due to limits of detection.

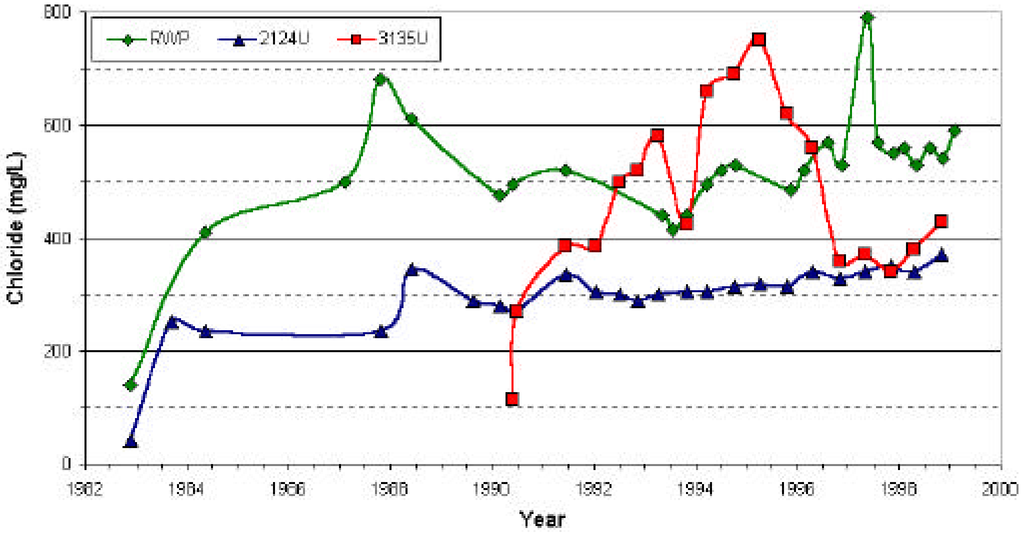
The results show significant quantities of organic matter available within the aquifer sediments. The average OOC is about 2.5%, while there appears to be no distinct pattern of organic acid speciation. This OOC value is within the range reported for marine and aquifer sediments undergoing active SO_4 reduction (Jørgensen, 1977; Murray *et al.*, 1978; Berner, 1971, 1981 & 1982; Berner & Westrich, 1985; Bajjali *et al.*, 1997).

3.8.9 Overall Trends of Groundwater Quality

The additional groundwater quality data collected over the past three years has continued to establish trends and provide a broad basis for more detailed geochemical analysis. The continuing trends for SO_4, Cl and Na are presented in Figure 3.12, and those for TDS and pH in Figure 3.13.

The trends of groundwater quality illustrate that SO_4 at bore 2124U is rising at a similar rate to the RWP, but SO_4 is yet to be detected in bore 3135U. The increase in SO_4 corresponds to similar increases in TDS, showing the signature of ash pond water chemistry. The data collected over the last three years has shown some variation in SO_4 at bore 2124U and the RWP, resembling the variations in SO_4 in LYAP water. Importantly, the SO_4 at the RWP is now approaching that in the LYAP. This suggests that the attenuation capacity of the HHF aquifer sediments, principally controlled by organic content, may be becoming limited due to consumption of the more reactive organic species in the vicinity of the RWP and beneath the LYAP.





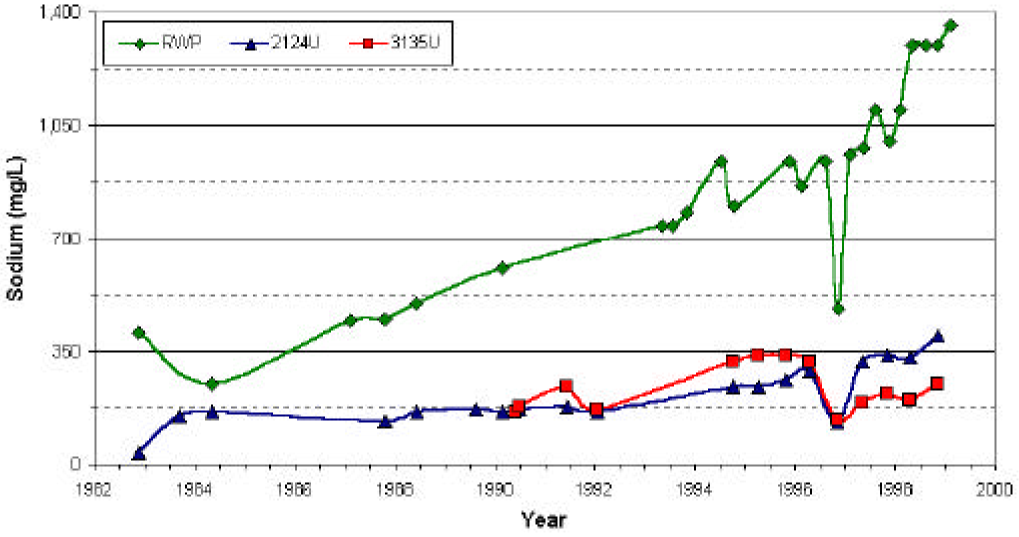


Figure 3.12 - Trends of Sulfate, Chloride and Sodium to January 1999

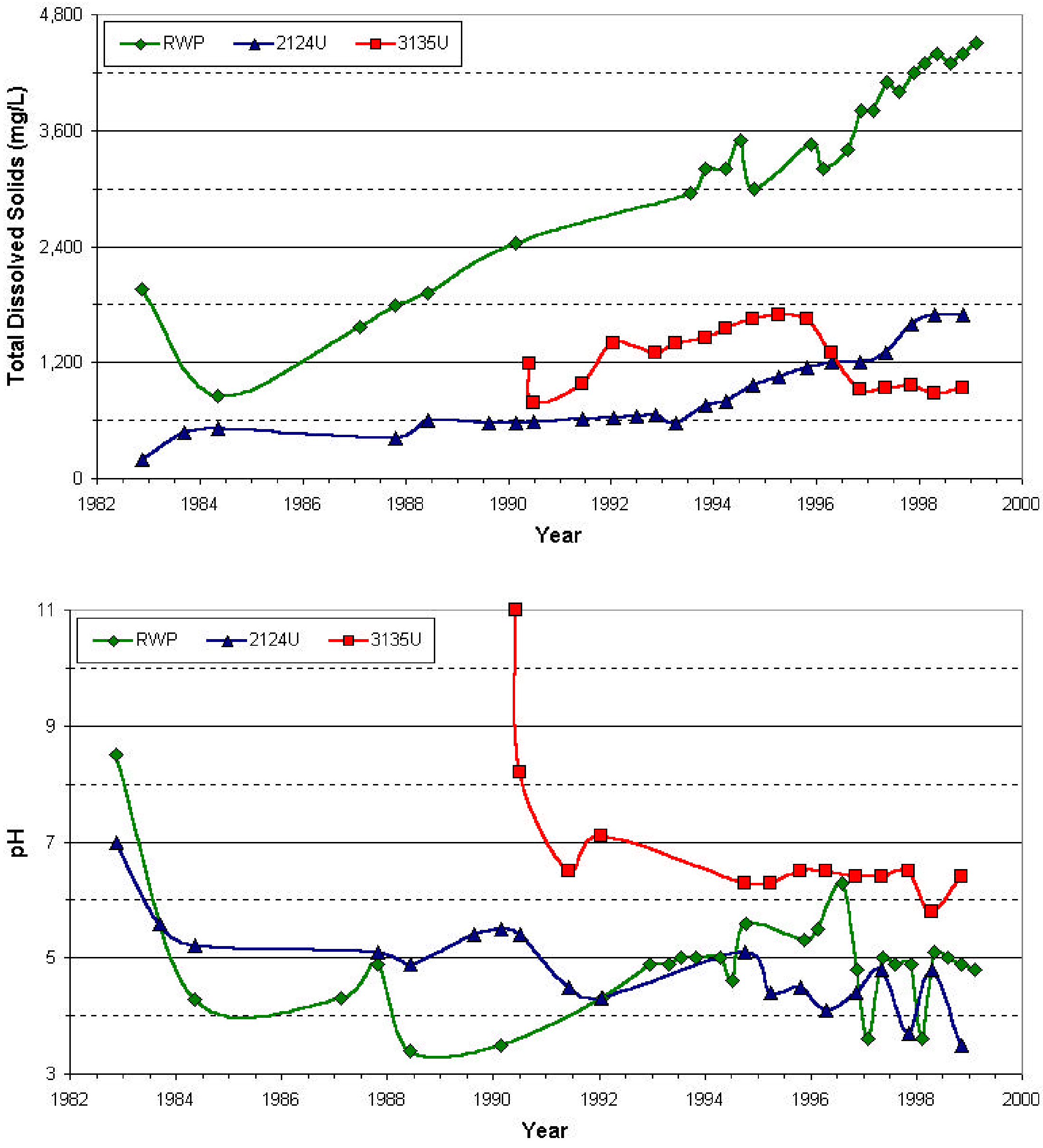


Figure 3.13 - Trends of TDS and pH to January 1999

The Cl concentration of the RWP and bore 2124U continues to be stable, approximately at the same concentration as the LYAP with a small upward trend apparent. The Cl concentration in bore 3135U began to decrease and now appears relatively stable. The Cl concentration of bore 3135U is still similar to that of 2124U and the RWP. This may reflect the slow increase in Cl within the LYAP. The assumption of conservative migration of Cl is therefore still considered to be valid.

The $CO_{2\ (aq)}$ content of bore 3135U is much higher than attributable to SO_4 reduction alone, since the concentration of SO_4 reaching this bore should be low according to the transport analysis in Section 3.5.6. Based on equation 3-11, the molar ratio of CO_2 (or HCO_3^-) to SO_4 is 2:1. The molar concentration of SO_4 is about 0.01 mmol/L (using the 1 mg/L detection limit), compared to the molar concentration of CO_2 at about 44 mmol/L. Even if it is assumed that the maximum groundwater velocity gives a SO_4 concentration of about 1,000 mg/L, this is still only about 10.4 mmol/L. It is difficult therefore to explain the origin of this extra CO_2. It is possible that it is related to degradation of reactive organic species in HHF aquifer sediments by competing bacteria (Knox *et al.*, 1993; Manahan, 1991). The conversion of N and P may indicate further bacterial activity in HHF sediments, although this hypothesis is untested. The recent field data obtained does not allow any interpretation or assessment of possible mechanisms or processes.

The Na concentration is steadily increasing at the RWP, but remains at about background concentrations in bores 2124U and 3135U. The clay content of the HHF sediments is dominantly kaolinite, with minor illite and montmorillonite (Bolger, 1984). The retardation of Na migration is likely to be due to ion exchange and soprtion on these clay surfaces (cf. Fetter, 1993; McBride, 1994; Langmuir, 1997). Without further field or laboratory data it is not possible to assess the cation exchange capacity (CEC) of the HHF aquifer sediments and thus the potential for sodium sorption. The study by Mulder & Pedler (1990) adopted a retardation coefficient of 1.1, based on visual calibration to monitoring data. Their study predicted Na concentrations by 1995 of 670 mg/L in the 2124U area - markedly higher than the 240 to 290 mg/L detected around this time. Since they adopted the same retardation coefficient for Na as that used for SO_4, the only difference in applying the analytical solute transport model from Section 3.5.6 is the source concentration from LYAP seepage to the HHF. The field data for Na is included in Figure 3.11, and shows a poor correlation to the analytical model and properites adopted. Further study of Na behaviour is necessary to properly quantify and assess the migration of Na in HHF aquifers.

The average oxidisable organic carbon (OOC) of HHF aquifer sediments has been determined to be about 2.5%. The source of this organic matter is expected to be reworked coal and peat material from the underlying coal seams during fluvial deposition of the HHF sediments. This provides a bountiful source of organic carbon for SO_4-reducing bacteria. The reactive proportion of this organic material available to SRB, however, is still unknown. Given that peat material is likely to be of lower reactivity, as discussed in Section 3.6.2, it is expected that only a minor proportion of this 2.5% is utilised by the SRB. This correlates with the continuing increase in SO_4 at the RWP and the possibility that the more reactive organic fraction has now been consumed beneath the LYAP and is providing less attenuation of SO_4 as a result. A more detailed study is recommended that can identify the chief organic species present in HHF sediments and their respective geochemical reactivity rates with regards to facilitating SO_4 reduction.

One approach which can be used in the interim is the application of a solute transport model which incorporates the reactive transport of SO_4. This can be used to estimate average reaction rates by calibration to existing field data, and is a popular approach in the literature for a range of marine and sedimentary environments (Berner, 1964, 1980, 1981; Jørgensen, 1978c; Westrich & Berner, 1984; Berner & Westrich, 1985; Middelburg, 1989; Boudreau & Ruddick, 1991). The LYAP has nearly 20 years of monitoring data and thus a solute transport model could be applied by incorporating the kinetic reactions for SO_4 reduction. This approach will be developed for groundwater flow and applied to the western seepage pathway later in this chapter, since most of the cited literature above refers to marine or estuarine sediments.

The nutrient concentrations appear to be sufficient to sustain the activity of SO_4-reducing bacteria (cf. McNab & Dunlap, 1975; Knox *et al.*, 1993; Bedient *et al.*, 1994). Importantly, the chemical speciation undertaken on N and P shows that they are generally in forms of reduced NH_3 and P. This may be explained through a more idealised representation of organic matter decomposition during SO_4 reduction which includes N and P in the organic fraction. Knox *et al.* (1993) present the average composition of organic biomass as $C_{60}H_{87}O_{23}N_{12}P$.

For SO_4 reduction, this formula for organic matter is further simplified and represented as (Richards, 1965; Murray, 1978; Boudreau & Westrich, 1984) :

$$2(CH_2O)_x(NH_3)_y(H_3PO_4)_z + xSO_4^{2-} \rightarrow 2xHCO_3^- + xH_2S + 2yNH_3 + 2zH_3PO_4 \qquad 3\text{-}12$$

where x, y and z are constants, depending on the microorganisms' specific requirements.

This might help to explain the presence of N as NH_3, however, it does not account for the speciation of P. It is possible for some of this NH_3 to be oxidised to form NO_3, given the HHF aquifer has low concentrations of oxygen present. The presence of NO_3 was observed in the monitoring data collected. The reaction, known as nitrification, is generally given as (Manahan, 1991) :

$$2O_2 + NH_4^+ \rightarrow NO_3^- + 2H^+ + H_2O \qquad 3\text{-}13$$

The process of nitrification is also mediated by bacteria, with NO_2 being produced as an intermediate metabolic by-product (Manahan, 1991). The presence of NO_2 was generally not detected in most groundwater samples, except for bore 2173U in April 1998 (see Table 3.10). Bore 2173U also had one of the highest NO_3 concentrations detected in the enhanced monitoring program. The oxidation of N species in HHF aquifers could also act as a mild source of acidity, due to the production of 2 moles of H^+ for every mole of NH_3.

The pH of all groundwaters continues to be mildly acidic at values around 4 to 5. The pH appears to be influenced by the presence of high concentrations of dissolved carbon dioxide ($CO_{2\ (aq)}$), especially at bore 3135U which consistently had the highest $CO_{2\ (aq)}$ concentrations measured in the field. On the basis of the mixing analysis in Section 3.5.7, however, the continuing mild acidity of HHF groundwaters cannot be explained by this process alone. The oxidation of the NH_3 released by organic degradation may be a minor source of acidity. Further mechanisms for acidity will be discussed later in this chapter.

3.8.10 Summary of Monitoring and Sulfate Reduction

On the basis of the additional groundwater quality data collected for this thesis and discussed above, it is argued that the biogeochemical process of SO_4 reduction is a controlling reaction for SO_4 in HHF groundwaters. This leads to strong attenuation of SO_4 during transport. One aspect which has yet to be investigated is the presence of SO_4-reducing bacteria. The field work undertaken to ascertain whether SRB are present within the HHF will now be presented.

3.9 Microbiological Testing of HHF Groundwater

3.9.1 Overview

The previous section presented additional groundwater quality monitoring data and analysis of geochemical processes, and argued that SO_4 reduction was a key biogeochemical process controlling the transport and reactivity of SO_4 in HHF groundwaters. At the typical groundwater temperatures of the HHF (15 to 20 ^{0}C), SO_4 reduction can only occur through the action of specialised sulfate reducing bacteria (SRB), as discussed in Section 3.6.2. The presence of SRB has not been investigated at Loy Yang or in the Latrobe Valley previously. It was necessary, therefore, to obtain samples from the HHF to test for SRB.

The sampling and identification of bacteria or microorganisms within groundwater is a complex and challenging task (Chapelle, 1993; Bedient *et al.*, 1994). The organisms may be free-floating within groundwater, or they may be preferrentially attached to colloidal particles or aquifer sediments (Chapelle, 1993). Further complications arise with SRB due to their general intolerance of oxygen (Postgate, 1984). Ideally, it would be preferrable to obtain both samples of groundwater and aquifer sediments for analysis. At the time of preparing this work in May 1997, no new groundwater bores were being planned from which sediment samples could be obtained. A series of groundwater samples were subsequently obtained for further analysis. The primary objective was to detect SRB in HHF groundwaters, and not a systematic study of microbial ecology. Thus samples of groundwater were considered sufficient for this objective.

3.9.2 Methodology

In July 1997, a series of groundwater samples were obtained by gently and carefully using a bailer. The bores 2105U, 2124U, 3135U, the RWP access shaft and the surface outflow pipe from the RWP were sampled on July 18, and bores 2175U, 2176U, 2178, 3282L and 3282U on July 24, 1997. The samples were stored in sterilised bottles within a chilled esky. They were tested according to APHA (1992) methods for culturing and identification of SRB by EML Consulting Services Pty Ltd. The following methodology and results are based on EML (1997a & 1997b).

The samples were analysed by membrane filtration through sterile 0.45 μm pore-size membranes and incubating on specialised SRB-prepared agar plates for up to 21 days. The bores 2105U and 3135U had higher turbidity and only small volumes of less than 1 mL were filtered. Anaerobic conditions were used in a controlled environment at 30 ^{0}C with hydrogen-based atmosphere. The cultures were examined on an adjacent open bench for no more than 10-15 minutes. The specialised SO_4-reducing agar medium used was prepared according to the required standards in APHA (1992).

3.9.3 Results of SRB Analysis

There was considerable growth during incubation, although there did not appear to be any change observed to the bacterial colonies after about 6 days. The majority of samples produced discrete olive or khaki coloured bacterial colonies, with a typical example shown in Figure 3.14. Some agar plates appeared to be too moist and the bacterial colonies became overgrown and ran into each other (see Figure 3.14). The samples from both the RWP access shaft and bore 2124U, however, were an exception and produced a distinct dark brown colony, suggesting some pyrite formation (black) and thus SO_4 reduction. The colonies produced by bacteria from the RWP sample are shown in Figure 3.15. There was no detection in any sample of *Desulfovibrio* sp. colony forming units (CFU) per 100 mL. Further work was undertaken by EML to attempt to identify the bacteria that were being cultured from the groundwater samples.

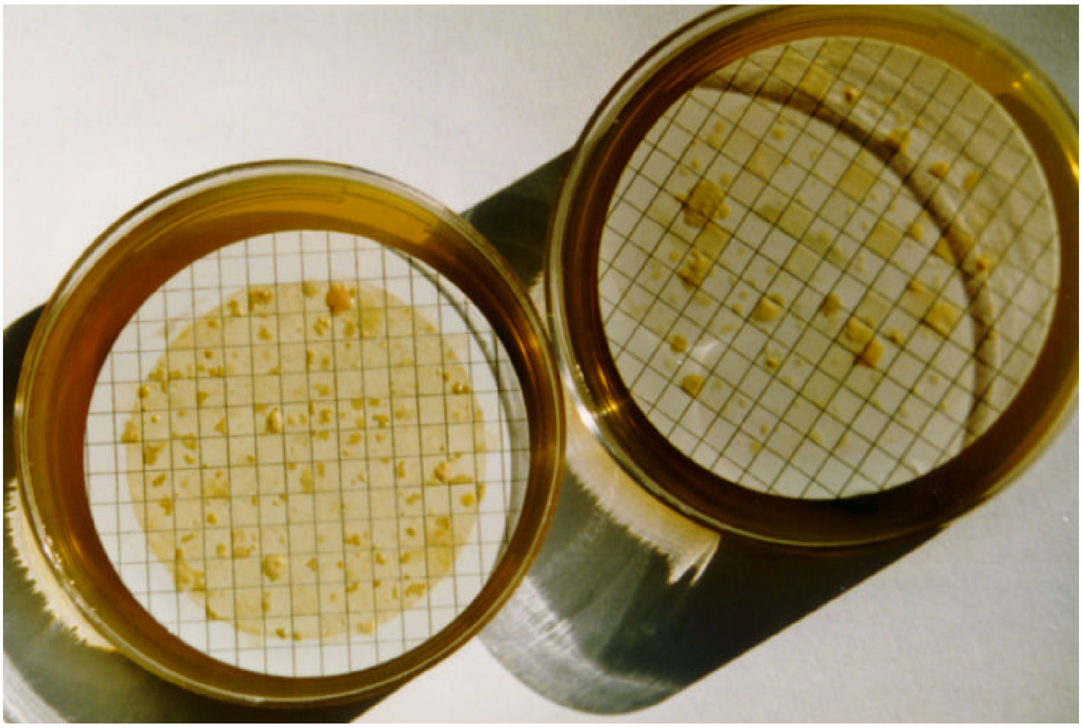


Figure 3.14 - Bacterial colonies from bore 2173U after incubation (10 mL and 1 mL), typical of most colonies cultured from groundwater samples (EML, 1997b)

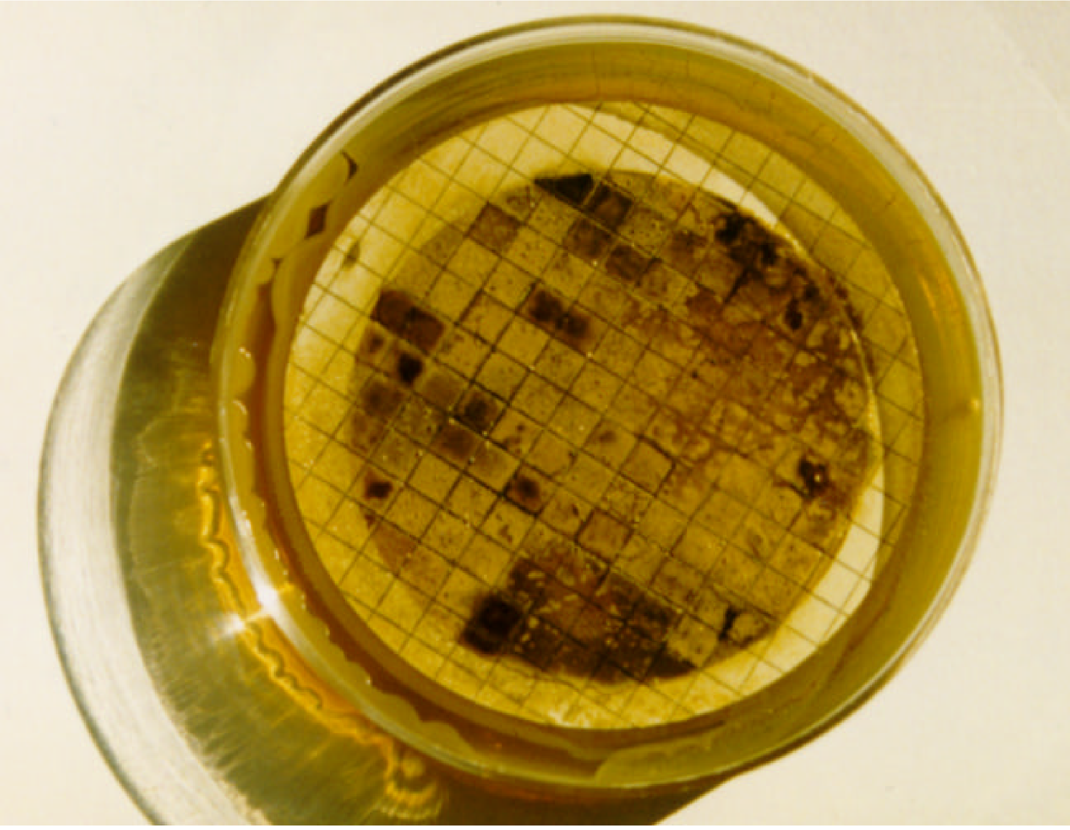


Figure 3.15 - Bacterial colonies from the RWP after incubation (50 mL), similar to the colonies cultured from bore 2124U (EML, 1997a)

The cultured samples from the RWP and bore 2124U were restreaked and recultured on a new agar plate. This failed to produce further dark colonies, instead producing the olive / khaki coloured colonies typical of most groundwater samples tested (see Figure 3.14). Bacterial smears were then prepared from bores 2176U, 2178 and 3282L, heat-fixed, stained by the Grams method and examined under the microscope. Due to the extended age of the samples, the bacteria were staining Gram-negatively and sporulation was occurring. The microscopic examination revealed that some of the bacterial isolates appeared to be SO_4-reducing *Clostridia* sp. or possibly *Desulfotomaculum* sp., a more commonly known SO_4-reducing bacteria. The *Clostridia* sp. examined under the microscope are shown in Figures 3.16 and 3.17. No samples exhibited the microscopic morphology typical of *Desulfovibrio* sp.

3.9.4 Summary of SRB Analysis

The sampling and analysis of HHF groundwaters for SRB has proven to be a challenging task. The samples from bore 2124U and the RWP suggested some degree of SO_4 reduction and hence activity of SRB, while all remaining samples produced olive / khaki coloured bacterial colonies and no direct indication of SRB. All samples appear to have active bacterial populations but no indication of typical *Desulfovibrio* sp. Further investigation by EML suggested that the cultured bacteria may be either *Clostridia* or *Desulfotomaculum* sp. Given the indications of darkening in the cultures from 2124U and the RWP, and the possible presence of *Desulfotomaculum* sp. it would therefore appear reasonable to assume that SRB are active within HHF groundwaters. Further research is required to more accurately determine the bacteria present, preferrably both from groundwater and aquifer sediment samples, as well as determining bacterial population dynamics.

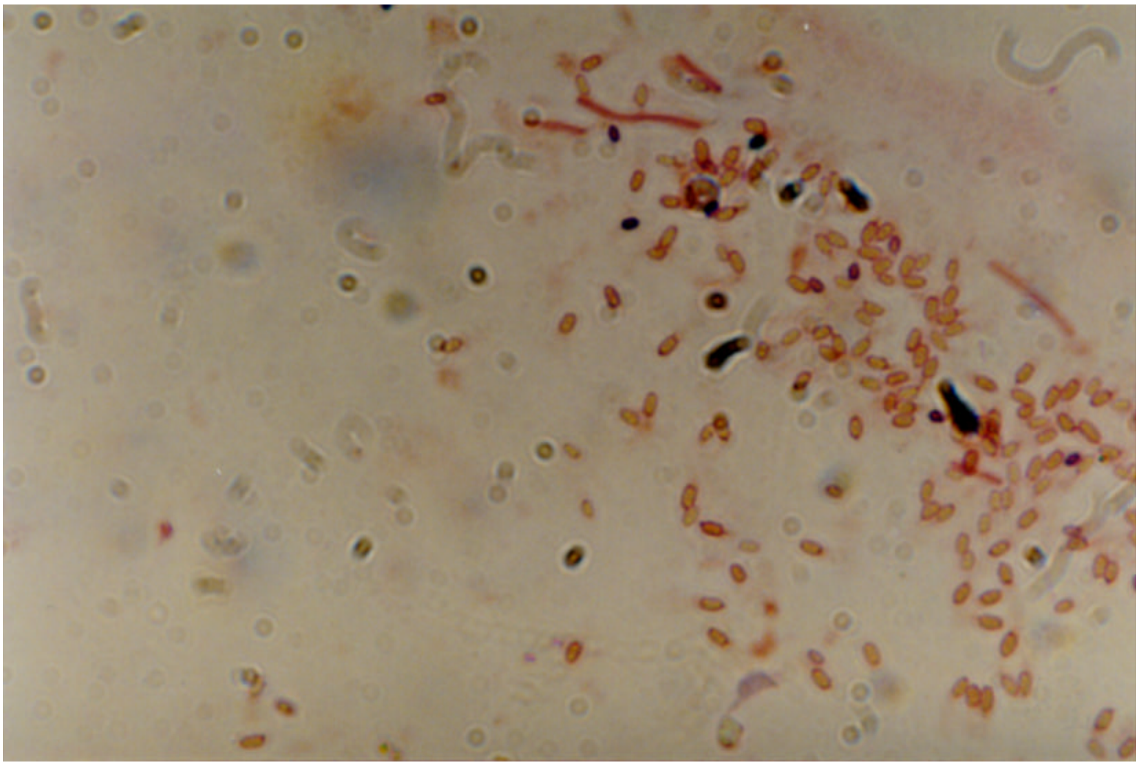


Figure 3.16 - Clostridial spores, separated from vegetative cells. Visualised under oil immersion (x1,000) (EML, 1997b)

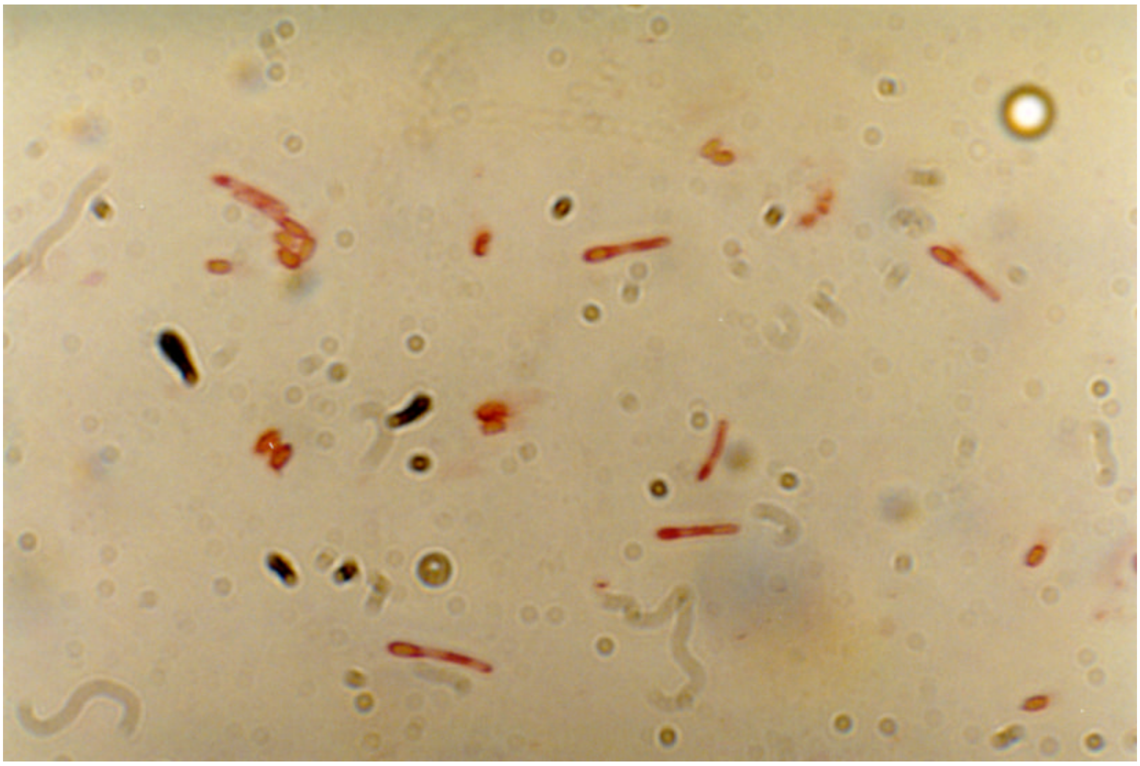


Figure 3.17 - Clostridial cells, rod-shaped, containing terminal endospores. Old cultures now staining Gram-positively. Visualised under oil immersion (x1,000) (EML, 1997b)

3.10 Analysis of Geochemical Processes

In Sections 3.5 to 3.8 the transport of SO_4 in HHF groundwaters was analysed and investigasted in detail. On the basis of observed data, it was argued that the major geochemical control on SO_4 transport is through dissimilatory SO_4 reduction. This attenuation process is evident from the following factors :

- an abundance of organic matter within aquifer sediments;
- hydrogen sulfide can be detected (by odour) and at low concentrations in some bores;
- reduced form of N and P species;
- presence of siderite ($FeCO_3$) and pyrite (FeS_2) in aquifer sediments, which are formed by reaction with the alkalinity and sulfides released by SO_4 reduction;
- indicative presence of SO_4 -reducing bacteria (eg. *Desulfotomaculum* sp.).

Before the construction of the Loy Yang Ash Pond, the abundance of organic matter and the limited supply of SO_4 to groundwater would have constrained the degree of SO_4 reduction and subsequent sulfide production, as described by equation 3-11 and Section 3.6.2. With the commencement of the LYAP and the influx of high SO_4 seepage waters into HHF groundwaters, SO_4 was no longer limiting and higher rates of SO_4 reduction could thus develop. The RWP or western embankment zone of the LYAP could therefore be expected to be accumulating the precipitated sulfides. The main uncertainty remaining in assessing the geochemistry of SO_4 in the HHF is the acid buffering of the groundwater against the influx of 15 years of alkaline seepage from the LYAP. The process of SO_4 reduction generally leads to the consumption of acidity and the release of alkalinity, as per equation 3-11, compared to HHF groundwaters which have maintained or slightly increased in acidity since the detection of seepage in 1982. There are two processes that may act to release or control acidity - carbon dioxide buffering (carbonic acid) and the formation of metal sulfides. These will now be analysed further.

The carbonic acid system is based on the dissolution of gaseous CO_2 (pCO_2) into solution (Stumm & Morgan, 1996; Langmuir, 1997) :

$$\text{at } 15\ {}^0\text{C} \qquad CO_{2\,(g)} \Leftrightarrow CO_{2\,(aq)} \qquad \text{where } K_{eq} = \frac{[CO_{2\,(aq)}]}{[pCO_2]} = 10^{-1.34} \qquad 3\text{-}14$$

where K_{eq} - equilibrium constant

Using 3-14 it is possible to convert from the dissolved concentration measured in the field to partial CO_2 gas pressures (pCO_2). The dissolved CO_2 can then form carbonic acid or H_2CO_3, a diprotic acid. This can release acidity (H^+) according to the following reactions (Appelo & Postma, 1994) :

$$CO_{2\,(aq)} + H_2O \Leftrightarrow H_2CO_3 \qquad 3\text{-}15a$$

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \qquad K_{eq} = 10^{-6.3} \qquad 3\text{-}15b$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \qquad K_{eq} = 10^{-10.3} \qquad 3\text{-}15c$$

The second possible source of acidity is through the sulfide released from SO_4 reduction. The sulfide is thought to precipitate as iron sulfide minerals, and in doing so can release the hydrogen ions (H^+) into solution according to (Dvorak *et al.*, 1992; Stumm & Morgan, 1996; Langmuir, 1997) :

$$M^{2+} + H_2S_{(aq)} \Leftrightarrow MS + 2H^+ \qquad 3\text{-}16$$

On the basis of the high SO_4 seepage over the operational life of the LYAP, it may be possible that the precipitation of sulfides is releasing sufficient acidity to control the pH of HHF groundwaters, due to protons from the hydrogen sulfide or bisulfide.

One approach to ascertain the effect of dissolved CO_2 and sulfides on groundwater chemistry is through the use of geochemical modelling of the aqueous chemistry. A geochemical study of the mineral saturation states of HHF groundwaters will be undertaken using the geochemical model PHREEQC (Parkhurst, 1995). All data used in Table 3.13 is from April 1998, as this represents a reliable and extensive data set.

In this analysis, the following bores and monitoring points were used :

- 3138U Background groundwater chemistry before the influence of ash seepage;
- LYAP Ambient chemistry of the ash pond;
- RWP Seepage collection pit at the toe of the ash pond embankment (200 m west from the LYAP);
- 2124U Intermediate monitoring bore (550 m west from the LYAP);
- 3135U Downgradient monitoring bore (1,350 m west from the LYAP).

Table 3.13 - Groundwater Chemistry Data Used for PHREEQC Analysis

Site	pH	Eh	Na	K	Ca	Mg	Fe	SO_4	HS^-	Cl	HCO_3	$CO_{2\,(aq)}$
3138U	6.5	45	120	3.1	19	7.2	27	23	-	210	-	-
LYAP	9.0	-	1,800	74	360	46	0.27	4,300	-	590	32[1]	-
RWP	4.9	125	1,200	32	64	75	23	2,800	0.5	550	12	238
2124U	4.3	136	330	0.5	8	110	18	810	1.0	340	<2	343
3135U	4.6	38	200	1.6	15	50	130	<5	<0.1	380	310	1,936

Notes - 3138U data is from April 1997, due to no sample from April 1998; LYAP data is from Feb. 1998; pH, Eh (mV) and CO_2 are measured in the field; [1] - CO_3^{2-} concentration is 24 mg/L.

A temperature of 15 ^{0}C was used, according to measured data from groundwater monitoring. The alkalinity was expressed as analysed from monitoring data (as total equivalent $CaCO_3$ for LYAP, and HCO_3 for bores). The concentration of $CO_{2\,(aq)}$ was converted to equivalent partial pressure (in atm) using equation 3-14. The chemistry for each monitoring point was then equilibrated to its respective pCO_2 (measured as dissolved CO_2 for the RWP, 2124U and 3135U, and assumed as atmospheric pCO_2 for the LYAP). The value used for atmospheric pCO_2 was 3.16×10^{-4} atm (or $10^{-3.5}$ atm) (Langmuir, 1997). The sulfate-sulfide redox couple was used to calculate a redox potential, as a comparison to field measured data. The sulfide content of the LYAP and bore 3135U was set equal to the detection limit of 0.1 mg/L. The results from PHREEQC are given in Table 3.14.

Table 3.14 - Geochemical Analysis of HHF Groundwaters : Saturation States

Mineral	Formula	3138U	LYAP		RWP	
			Prior	pCO_2	Prior	pCO_2
Aragonite	$CaCO_3$	-	0.59	0.58	-4.44	-4.63
Calcite	$CaCO_3$	-	0.74	0.73	-4.29	-4.48
Carbon Dioxide	$CO_{2\,(aq)}$	-	-4.77	-4.72	-0.91	-0.63
Siderite	$FeCO_3$	-	-5.73	-0.14	-2.44	-2.64
Dolomite	$CaMg(CO_3)_2$	-	0.81	0.78	-8.29	-8.68
Anhydrite	$CaSO_4$	-2.99	-0.31	-0.31	-1.10	-1.10
Gypsum	$CaSO_42H_2O$	-2.74	-0.06	-0.06	-0.85	-0.85
Hydrogen Sulfide	H_2S	-	-6.93	-7.11	-3.92	-3.92
Mackinawite	FeS	-	-3.89	1.46	-1.45	-1.92
FeS (am)	FeS		-4.62	0.73	-2.18	-2.66
Pyrite	FeS_2	-	24.29	8.07	15.54	9.21
Redox (calc.)	(mV)	-	-299		-28	

Mineral	Formula	2124U		3135U	
		Prior	pCO_2	Prior	pCO_2
Aragonite	$CaCO_3$	-6.15	-6.16	-3.65	-2.90
Calcite	$CaCO_3$	-6.00	-6.00	-3.49	-2.75
Carbon Dioxide	$CO_{2\,(aq)}$	-0.73	-0.47	0.75	0.00
Siderite	$FeCO_3$	-3.37	-3.38	-0.40	0.35
Dolomite	$CaMg(CO_3)_2$	-10.65	-10.67	-6.29	-4.80
Anhydrite	$CaSO_4$	-2.21	-2.21	-4.64	-4.64
Gypsum	$CaSO_42H_2O$	-1.96	-1.96	-4.39	-4.39
Hydrogen Sulfide	H_2S	-3.63	-3.63	-4.95	-4.96
Mackinawite	FeS	-2.27	-2.54	-2.08	-0.59
FeS (am)	FeS	-3.00	-3.27	-2.81	-1.33
Pyrite	FeS_2	14.44	9.02	9.74	8.73
Redox (calc.)	(mV)	11		-20	

Note - "Prior" is before equilibration by PHREEQC to the given pCO_2.

The redox potentials calculated by PHREEQC are generally mildly reducing, correlating with the interpreted conditions in HHF aquifers. The redox potentials measured in the field, which are mildly oxidising, suggest they are influenced by the introduction of oxygen at the ground surface and by the use of bailers in sampling. At the ground surface, the presence of oxygen would lead to strongly oxidising conditions in near surface waters, although at the base of the LYAP where seepage emanates into the HHF (up to 30 m in depth) it is expected that the calculated redox potential would be more realistic due to the lack of oxygen. It is recommended that future sampling investigate the use of down-hole (or in-situ) probes to obtain more accurate field redox values.

The PHREEQC results in Table 3.14 show that the ambient waters in the ash pond are over-saturated with respect to carbonate minerals, and that calcite ($CaCO_3$), aragonite ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) may be expected to precipitate in the ash pond. This is expected, as calcite mineralisation has been identified in ash sediments previously in the Latrobe Valley (Black, 1990a). The geochemistry of ash pond waters and ash leachates is analysed and discussed further in Chapter 7.

The degassing of carbon dioxide observed during groundwater monitoring and chemical analysis can be expected from equation 3-14. Drever (1997) states that for mildly acidic waters the $CO_{2\ (aq)}$ will dissociate to a gas rather than form HCO_3. For bore 3135U, it is important to consider the source of such high concentrations of dissolved CO_2. The reduction of SO_4 produces 2 moles of $CO_{2\ (aq)}$ for every mole of SO_4 (cf. Eq. 3-11). The $CO_{2\ (aq)}$ measured in the field was consistently around 2,000 mg/L or higher, giving about 45 mmol/L. From Section 3.5.6, if the maximum groundwater velocity is assumed for HHF aquifers, the SO_4 concentration would be approximately 1,000 mg/L or about 10 mmol/L. This represents less than one quarter of the SO_4 required to produce the measured $CO_{2\ (aq)}$ at bore 3135U, giving a production of $CO_{2\ (aq)}$ greater than that attributable to SO_4 reduction. The high CO_2 content of bore 3135U is therefore anomalous, assuming it is produced strictly from SO_4 reduction.

As discussed earlier in Section 3.6.2, SO_4 reduction is part of broader biogeochemical processes through which bacteria or microorganisms thrive and break down organic matter (eg. Berner, 1980; Jørgensen, 1983). The SRB can only metabolise short chain labile (reactive) organics, whereas other bacteria are able to effectively degrade the higher molecular mass and less reactive organics, converting them into the short chain organics that SRB can utilise (Jørgensen, 1983). The degradation of the more refractory organic content (generally higher molecular mass organics) of the sediments may be partly responsible for the higher CO_2 content. This hypothesis is preliminary, however, and more detailed microbiological studies and investigations of both dissolved phase and sediment-bound organic compounds would be required to ascertain the source of the high dissolved CO_2 in bore 3135U.

The effect of pCO_2 on siderite ($FeCO_3$) is especially evident. For ambient ash pond water, the difference in the saturation index of siderite before and after equilibration with atmospheric CO_2 is over five orders of magnitude. For bore 3135U, the saturation index of siderite shifts from an undersaturated to oversaturated state after equilibration. This bore also has a consistantly higher Fe concentration than other bores in the vicinity of the LYAP. This change in saturation state for siderite explains its formation within HHF groundwaters in the Loy Yang region, as observed by Bolger (1984).

All water chemistries show significant undersaturation with respect to hydrogen sulfide. The lack of high concentrations of sulfide in most groundwater samples suggests that the sulfide is reacting with aquifer sediments to form insoluble sulfides. The saturation index data for sulfides in Table 3-13 display a wide range, where the formation of the intermediate sulfide minerals, mackinawite (FeS) and greigite (Fe_3S_4), appear to become oversaturated in ash pond waters after equilibration to atmospheric carbon dioxide. The formation of mackinawite and greigite are thermodynamically unstable, and are transition products in the formation of pyrite during bacterial SO_4 reduction (Berner, 1981; Goldhaber & Kaplan, 1974).

The geochemical modelling of dissolved CO_2 and sulfide behaviour has demonstrated the complex controls on groundwater geochemistry. The high $CO_{2\ (aq)}$ concentrations appear to influence groundwater chemistry and also appear to be responsible for the precipitation of siderite in the Loy Yang area, as identified by Bolger (1984). Due to the high quantities of SO_4 in seepage from the LYAP, the formation and subsequent precipitation of sulfides could release acidity. The combination of these two processes could act as acidic buffer in HHF groundwaters. The extended period of time over which this process has been occurring at the LYAP could therefore be expected to lead to the formation of a sulfide zone around the ash pond embankment area. The concentration of sulfides within aquifer sediments has not been tested, and consequently no comparison can be made to concentrations before the onset of ash pond seepage. Bolger (1984) identified the presence of sulfidic minerals in HHF sediments in the Loy Yang area, corresponding well with the above geochemical model.

3.11 Kinetic Modelling of Sulfate Reduction

3.11.1 Introduction

The previous sections have presented observed data and a detailed geochemical analysis of SO_4 behaviour in HHF groundwaters. The process of SO_4 reduction has been argued as a major controlling geochemical reaction for transport in HHF aquifers. As identified earlier in Section 3.6.2, for sufficiently high concentrations of SO_4, the reaction may be treated as a first order kinetic reaction with respect to the oxidation of organic matter and zeroth order with respect to SO_4 reduction (eg. Berner, 1964). There has been nearly 20 years of groundwater monitoring data collected to date and a major one-dimensional seepage pathway has been identified to the west of the LYAP. Thus it is possible to apply a modified form of the advection-dispersion equation (see equation 3-1) to incorporate a reaction term for SO_4 reduction (ie. $(\partial C/\partial t)_R$). This approach, although popular in marine and estuarine sediments (eg. Berner, 1964, 1971 & 1981; Jørgensen, 1978c; Westrich & Berner, 1984; Middelburg, 1989), has not been developed and applied to groundwater systems to the best of the authors' knowledge.

3.11.2 Theoretical Development

The process of SO_4 reduction is a first order kinetic reaction with respect to the oxidation of organic matter and zeroth order with respect to SO_4 reduction (Berner, 1964, 1981). That is, the rate of degradation of organic matter is proportional to the remaining organic matter; while the rate of SO_4 degradation is independent of the SO_4 concentration (Berner, 1964, 1971 & 1981). Mathematically, this becomes :

$$\frac{\partial G}{\partial t} = -\alpha G \qquad \text{and} \qquad \frac{\partial C}{\partial t} = -\beta \qquad \text{3-17}$$

where G represents metabolisable organic content (mg/kg); α is the organic matter reactivity constant (kg/L.day); t is time (day); C is SO_4 concentration (mg/L); and β is the SO_4 degradation rate constant (kg/L.day).

The rate law implies that SO_4 degradation will follow an exponential decline, and has been fitted to observed experimental data from marine and estuarine sediments all over the world (Berner, 1964, 1971 & 1981; Jørgensen, 1978c; Westrich & Berner, 1984; Middelburg, 1989).

It is assumed that the reactivity of organic matter, α, is constant over time (Berner, 1964) and that equation 3-17 applies when there is an infinite source of organic matter relative to SO_4 (Jørgensen, 1978c). This assumption, however, may not be strictly valid for field conditions (Jørgensen, 1978c; Middelburg, 1989). Further assumptions are that SO_4 reduction and organic matter oxidation are the only processes affecting the concentrations of these species and that the adsorption of SO_4 is negligible (Jørgensen, 1978c; Berner, 1980). It is also assumed that steady state flow conditions are present in the system under study (Berner, 1980). The kinetic approach described above is independent of bacterial growth dynamics, thereby simplifying the solute transport model and analysis.

It has been found by numerous authors that the reactivity of organic matter decreases with age since the more reactive organics are consumed first by bacteria (Jørgensen, 1978c & 1983; Berner, 1981; Middelburg, 1989). This has led to the development of multiple component models, such as the Multi-G model (Jørgensen, 1978c; Berner, 1980; Westrich & Berner, 1984), power function model (Middelburg, 1989) and continuum model (Boudreau & Ruddick, 1991) to account for the change in reactivity of the organic species being degraded. Mathematically this is often represented as :

$$\frac{\partial G_T}{\partial t} = \sum(-\alpha_1 G_1 - \alpha_2 G_2 - \alpha_3 G_3 - \alpha_4 G_4 \ldots - \alpha_n G_n) \qquad 3\text{-}18$$

where n - number of total reactive organic species;

$G_T = \Sigma G_n$ total degradable organic carbon;

$\frac{\partial G_T}{\partial t}$ - overall degradation rate of "n" reactive organic species.

When short time periods are being studied, the concentration of reactive organic matter may not become limited, and so the reaction rates will be controlled by the continued presence of these species. Over longer periods, such as geological time frames for example, the more reactive organics will be completely consumed by bacteria, leaving only the less reactive species and reducing overall reaction rates.

For modelling purposes, only two or three reactive organic species are required for time frames of tens of years, but for geological time scales approaching 10^4 to 10^7 years, up to eight components are generally required (Middelburg, 1989). It is important to distinguish the concentration of organic species (G_n) and its respective reactivity (α_n), since G_n is independent of the bacterial process causing degradation (aerobic versus anaerobic) while α_n will vary significantly with the bacteria involved (Westrich & Berner, 1984). In general, α_n varies much more from one group of organic species to another than does G_i (Berner, 1980). Thus the assumption of both organic species and reactivity are important in ensuring a theoretically rigorous approach.

These kinetic rates have been widely studied for marine and estuarine sediments, where organic rich sediments accumulate on the ocean floor and the ambient seawater provides a plentiful source of SO_4 (Berner, 1964, 1971, 1980, 1981 & 1982; Jørgensen, 1978a, 1978b & 1978c; Langmuir, 1997). However, for fresh groundwater systems, there has been relatively few studies published (eg. Dockins *et al.*, 1980).

There is a lack of detailed field data concerning organic matter speciation and reactivity in the HHF at the Loy Yang site, although the earlier discussion suggested a lower reactivity due to the likely terrestrial (coal or peat) source for the organic matter. There is, on the other hand, over 15 years of groundwater monitoring data. On the basis of hydrogeology, groundwater velocities and the earlier discussion of the geochemistry of sulfate reduction (see Section 3.6), it would appear reasonable to assume a single overall reaction rate for organic degradation and SO_4 reduction. Therefore the approach of Berner (1964) will be used to estimate the rates of SO_4 reduction with a one-dimensional solute transport equation incorporating the kinetics of this reaction.

3.11.3 Kinetic Solute Transport Modelling of Sulfate

The equation describing reactive solute transport (3-6) was given earlier in Section 3.5.6. It will be assumed that sorption processes can be neglected in the transport of SO_4 (ie. retardation factor is 1). From equation 3-11, the rate of organic matter degradation is twice the rate of SO_4 degradation, an approach used by Westrich & Berner (1984) and Appelo & Postma (1994). By substituting equations 3-11 and 3-17 into 3-6, it is possible to derive the overall solute transport equation for SO_4 which incorporates the kinetic reduction of SO_4 as :

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} - \frac{1}{2}\alpha G \qquad \text{3-19}$$

On the basis of 3-11 and 3-19, in groundwater with a continuing high influx of SO_4, there will be a progressive depletion of organic matter along the flowpath. Given the strong tendency of the sulfide to precipitate with Fe, this should also enrich the flowpath with sulfides.

The above equation will be applied to model the migration of SO_4 west from the LYAP. Since Cl is known to migrate in a conservative manner, the sum of reactions affecting its concentration will be zero (retardation factor or R = 1). The field data for Cl can therefore be calibrated with realistic groundwater flow and transport parameters from the model (ie. the velocity and hydrodynamic dispersion coefficient). The same values for velocity and dispersion can then be used for reactive SO_4 transport.

3.11.4 Numerical Solution of the 1-D Kinetic Model

A block-centred explicit, upward finite difference scheme (Zheng & Bennett, 1995) was used to solve the 1-D solute transport and kinetic reaction model described by 3-19. The detail of this technique is provided in Appendix A1. The following boundary and initial conditions were adopted (Zheng & Bennett, 1995) :

Initial Conditions : $C(z,0) = C_0$ $G(z,0) = G_0$ $z \geq 0$ 3-20a

Boundary Conditions : $C(0,t) = f(t)$ and 3-20b

$z = Z_{max}$ $\frac{\partial C}{\partial z} = 0$ $t \geq 0$ 3-20c

where f(t) is the input concentration function for a particular solute (eg. variable or constant SO_4/Cl), C_0 and G_0 the background concentrations of SO_4 and reactive organic matter, respectively, and Z_{max} the maximum flow length. Equation 3-20c represents a zero concentration flux diffusion boundary, depicting the point where, mathematically, no solute transport will occur.

The control of numerical dispersion is achieved through using a high spatial and temporal discretisation (low Courant and Peclet numbers; see details in Appendix A1). The finite difference scheme is subject to the following stability criteria :

$$\Delta t \leq \frac{\Delta z^2}{2D_x + v\Delta z} \qquad 3\text{-}21$$

The change in the concentration of the organic matter will depend on the rate at which it is consumed by SRB in the HHF aquifer. The rate of organic matter degradation is given by the rate of change with time of organic content. By starting from an initial reactive organic concentration in the aquifer sediments, G_0, the new concentration will be the initial value minus the rate multiplied by time, given by the following relationship :

$$G_{k+1} = G_k - \frac{\partial G}{\partial t}\partial t \quad = G_k\,(1 - \alpha.\partial t) \qquad 3\text{-}22$$

where k - is time step or iteration number.

A computer code of the numerical model was developed using the FORTRAN 77 language (Lahey, 1994) on an IBM-compatible personal computer running Microsoft DOS (see Appendix A2 for listing of the source code).

3.11.5 Calibration of the 1-D Kinetic Model

Two different approaches were used for approximating the source leachate concentrations emanating from the base of the Loy Yang Ash Pond. Firstly, a constant source concentration was assumed on the basis of the average concentration within the LYAP (Cl - 590 mg/L; SO_4 - 3,950 mg/L). Higher concentrations were used compared to Section 3.5.6 to allow for the increased concentrations of SO_4 and Cl through to the mid 1990's. Secondly, the variable concentration of SO_4 and Cl over time within the LYAP was assumed on the basis of compiled monitoring data from 1982 to present.

The source functions of SO_4 and Cl within the ash pond used for this modelling are those presented in Figure 3.5 (Section 3.5.1). Similar to Section 3.5.6, the modelling of Cl migration was used to estimate the most appropriate groundwater velocity and value of hydrodynamic dispersion, based on a comparison of field and model data. This was achieved through visual best fit. The same velocity and dispersion values were then used for SO_4 modelling, where further visual calibration was performed based on the rate constant and initial organic content of the aquifer.

The background concentrations of SO_4 and Cl were assumed as the initial concentrations in the model (cf. equation 3-20a). The concentrations chosen of 140 mg/L for Cl and 30 mg/L for SO_4 were based on Mulder & Pedler (1990) and the more recent data presented in Section 3.8.

3.11.6 Results of the Kinetic Solute Transport Model

The results for modelling the transport of Cl west from the LYAP are given in Figure 3.18. The following parameters were determined by visual calibration to the observed Cl migration pattern - linear groundwater velocity of 0.05 (m/day) and hydrodynamic dispersion coefficient of 6 (m^2/day). These values are within expected ranges, with hydrodynamic dispersion based on Fetter (1993) and the velocity correlating with previous work (Mulder & Pedler, 1990) and that calculated based on hydraulic gradients in the HHF groundwater. (Refer to Section 3.5.6 for comparison).

Using the flow and transport parameters from the calibration to Cl data, the following results were obtained for kinetic SO_4 reduction, shown in Figure 3.19. The initial organic matter contentration (G_0) found to provide the best visual fit was 1,250 mg/kg (0.125% by aquifer sediment mass) and the organic degradation rate constant, α, was 0.001 kg/L.day (or 1,000 mg/L.day). The initial rate of SO_4 reduction, therefore, is approximately 0.63 mg/l.day (based on $\frac{1}{2}\alpha G_0$). This corresponds well to values reported in the literature (Jørgensen, 1978a, 1978b & 1978c; Devol & Ahmed, 1981; and others).

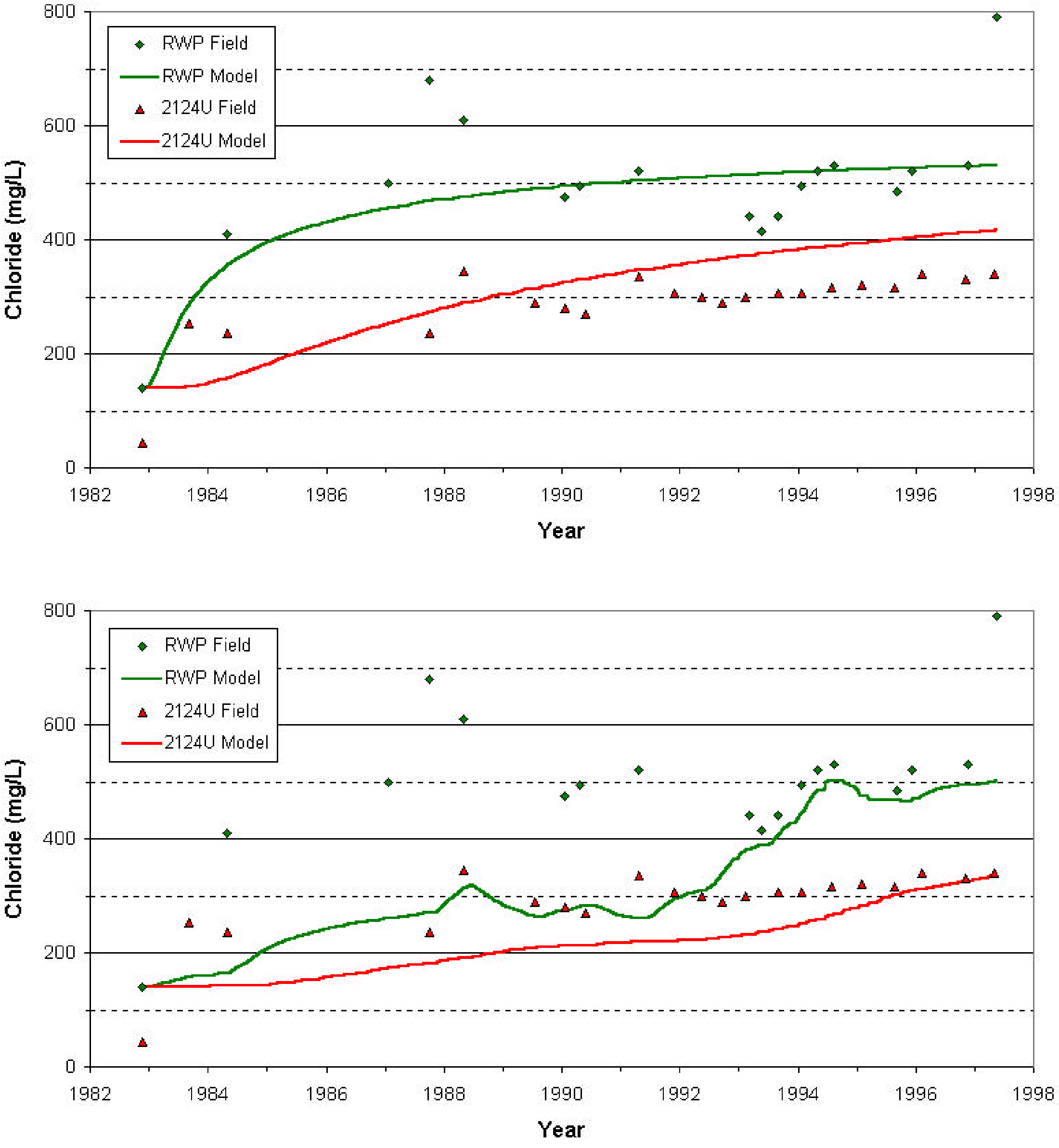


Figure 3.18 - Calibration to Chloride Migration : Constant (top) and Variable (bottom)

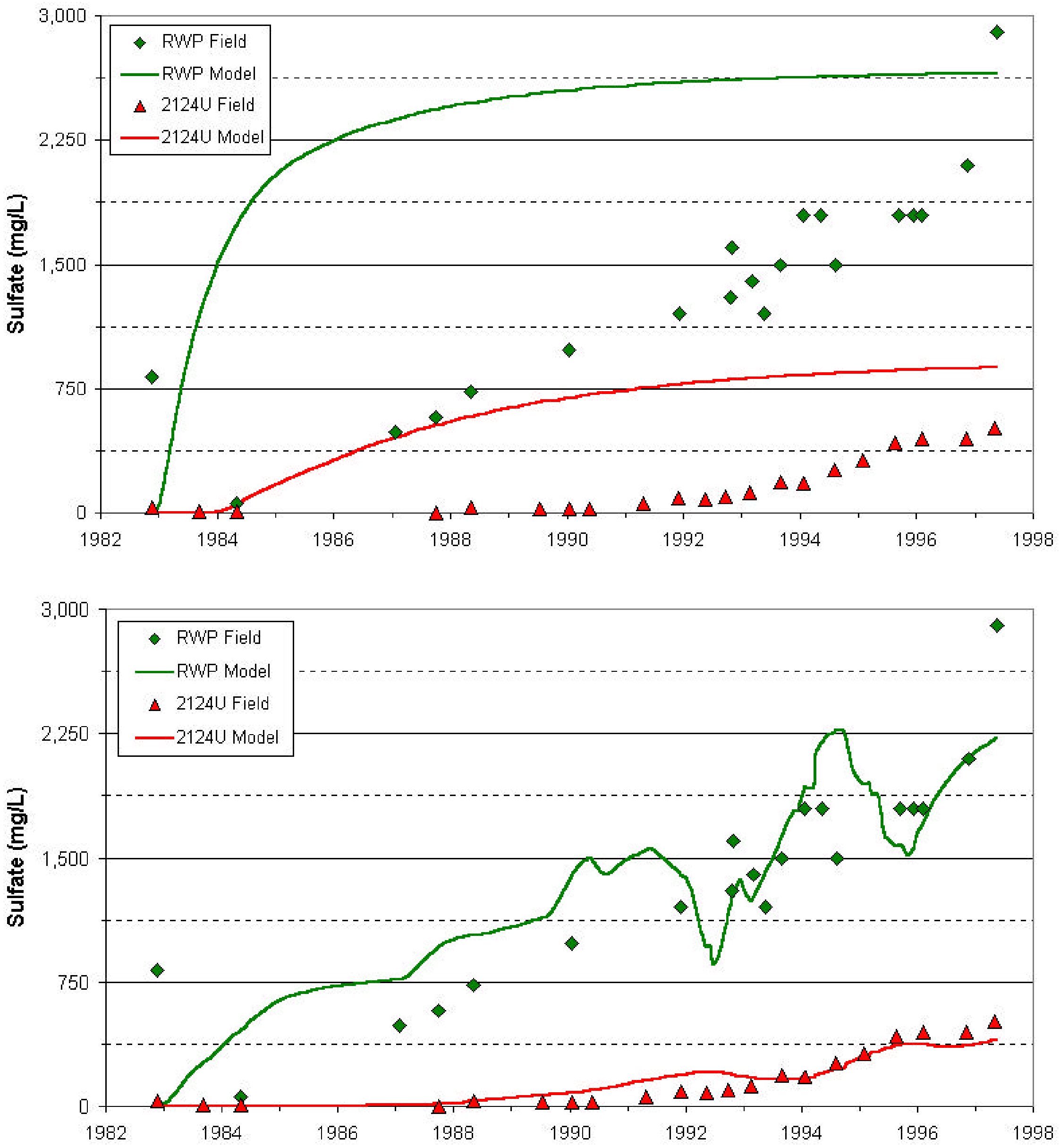


Figure 3.19 - Calibration to Sulfate Migration : Constant (top) and Variable (bottom)

3.11.6 Sensitivity Analyses and Discussion

The effect of changing the velocity, hydrodynamic dispersion, initial organic matter concentration and the organic degradation rate constant was analysed with the model.

The groundwater velocity is constrained by the known hydraulic gradients of the HHF in the vicinity of the LYAP and the hydraulic conductivity of the aquifer. The linear groundwater velocity of 0.05 m/day adopted is within the lower range expected. The higher hydraulic pressure within the LYAP relative to the groundwater levels in the HHF, however, creates a faster velocity adjacent to the LYAP, which decreases due to the lower hydraulic gradients as the seepage and groundwater flows to the west towards bore 3135U. The higher the groundwater velocity, the sooner that high SO_4 concentrations emerge at the RWP. This may create a sharper breakthrough for Cl also (refer to Figure 3.10) but this fails to correlate with the migration of SO_4. It must be pointed out that the hydrogeologic flow system of HHF groundwater and seepage at the LYAP is in reality a complex three-dimensional problem, and the above modelling approach has simplified it to a one-dimensional analysis. Thus the adopted groundwater velocity of 0.05 m/day was considered realistic in light of the previous analytical work in Section 3.5.6.

The adopted value of hydrodynamic dispersion was varied in model runs. The model was not found to be significantly affected. This is due to the long flowpath involved and the small groundwater velocity.

Sensitivity analyses show that a higher organic content attenuates the migration of SO_4 too strongly, while a lower concentration attenuates the migration of SO_4 too weakly. The concentration of SO_4 in bore 2124U and the RWP is therefore either below detection or too high, respectively, compared to the observed field monitoring data. The organic matter content used in the kinetic model (0.125%) is lower than the aquifer sediment analyses presented earlier (2.5%). This is most likely due to different reactivities (α) of the organic species in HHF aquifer sediments, as discussed in Sections 3.6 and 3.7.

The time scale modelled of 15 years corresponds to the timescales used in Berner (1964, 1971, 1980), Westrich & Berner (1984), Jørgensen (1978c), and Middleburg (1989). The organic degradation rate (α) derived by the above kinetic model is within the range of these authors. It is important to note that the α value used above represents the average reactivity of organic matter in the HHF aquifers over the 15 year time period modelled, and also corresponds to values reported in the cited literature. The value of α was varied in model runs, and a similar effect was noted as that observed in changing the reactive organic fraction. If a higher value of α was used, the attenuation of SO_4 was too strong and the resulting model predictions for SO_4 were below the measured field data, whereby if a lower value of α was used the predictions of SO_4 were much higher than the field data. It is likely that a multi-species approach to organic matter reactivity would allow more accurate modelling of SO_4 reduction and organic degradation reactions. It is also likely that there is a degree of variation in α in the HHF sediments (Charbeneau & Weaver, 1992).

The more recent monitoring data presented and discussed in Section 3.8 demonstrated a continuing trend of increasing SO_4 at the RWP and bore 2124U (shown above in Figure 3.15). The low proportion of reactive organic matter in the HHF, on the basis of modelled SO_4 transport, may help to explain this behaviour. The small but reactive organic fraction has now been consumed by SO_4-reducing bacteria in the HHF beneath the LYAP and in the vicinity of the RWP and bore 2124U, leaving only the more refractory and less reactive organic species. For modelling predictions over a longer time period, it would therefore be necessary to consider this variability in organic matter reactivity.

On the basis of the limitations and sensitivities discussed above, the one-dimensional kinetic solute transport model for SO_4 does give a reasonable approximation to the observed field data. Further research is required to verify the reaction parameters for SO_4 and organic matter, however, the approach does provide an important basis for continued monitoring and environmental assessment of the Loy Yang Ash Pond and its seepage influences on HHF groundwaters.

3.12 Summary of Seepage, Groundwater Chemistry and Aquifer Biogeochemistry

The regional geology and hydrogeology of the Latrobe Valley and the local geology and hydrogeology at the Loy Yang Ash Pond has been presented. A history of the seepage problems at the LYAP was updated and reviewed. There are two known areas of ash pond seepage to date, to the west of the LYAP towards the Overburden Dump and to the north towards the B Station Bench. It is considered unlikely that seepage will apear to the east or the south in the near future. The review of seepage history, complex geology and hydrogeology led to a focus on the shallow Haunted Hill Formation aquifer system, as the western seepage path could be identified as an approximate linear seepage pathway for simplified solute transport analysis. The seepage waters predominantly consist of Na, SO_4 and Cl concentrations elevated above background concentrations in the HHF aquifers.

The analysis of solute transport rates for SO_4 in comparison to those Cl suggested strong controlling reactions for SO_4, which needed to be taken into account in the analysis of seepage migration. Investigation of possible chemical mechanisms (retardation or sorption) and mixing calculations of seepage and groundwater showed that these were not capable of providing the attenuation of SO_4 migration being observed in HHF aquifers at the LYAP. A review of the geochemistry of SO_4 indicated that bacterial SO_4 reduction could be a major process affecting the transport of SO_4, given the presence of organic matter within HHF aquifer sediments and hydrogen sulfide gas in monitoring bores. A program of expanded groundwater monitoring and analysis was undertaken in conjunction with Loy Yang Power to determine if SO_4 reduction was occurring in HHF aquifers. This program included detailed chemical analysis of groundwater samples, and the presence of organic matter and SO_4-reducing bacteria in HHF aquifer sediments.

The groundwater monitoring results showed the occurrence of quite active chemistry. Hydrogen sulfide gas, detected by odour during sampling, was generally below detection limits, although a few samples registered significant concentrations. There was high concentrations of dissolved carbon dioxide and dissolved organic matter, essential to allow SO_4-reducing bacteria to remain active. There were sufficient concentrations of the biological nutrients, N and P, were available. Current information suggested that the N was mostly present in reduced form, compared to P which was present in an oxidised form.

Two new groundwater bores were installed near the LYAP in July 1998. The opportunity was taken to collect a series of HHF sand samples and these were tested for the concentration of oxidisable organic carbon (OOC) and the ratio of humic to fulvic acids. The average OOC was 2.5%, ranging from 1.9% to 3.5%. These values are similar to those from the literature and should be more than sufficient to sustain active microbial populations and therefore reduction of SO_4. The ratio of humic to fulvic acids was variable and did not appear to be consistent. Given that the expected source for the organic matter within HHF sediments is reworked coal and peat materials from underlying coal seams, only a small proportion of the OOC is expected to be utilised by SO_4-reducing bacteria over the time scale analysed of about 18 years.

Analysis of groundwater samples for bacteria capable of SO_4 reduction suggested that bacteria were present, and were possibly *Desulfotomaculum* sp. or *Clostridia* sp. Further work is required to more accurately ascertain the type of bacteria present in HHF aquifers and their specific nutrient and growth dynamics which may affect the attenuation rates of elevated SO_4 derived from the LYAP.

The continuing trends of major solutes in HHF groundwater, such as Na, SO_4 and Cl were analysed. In the Relief Well Pit area adjacent to the western embankment of the LYAP, the concentration of SO_4 is steadily increasing in both the RWP and bore 2124U, with the higher concentration in the RWP now approaching that in the ash pond. This steady increase is attributed to the degradation of the more reactive organic species in HHF sediments, giving a lower overall rate of SO_4 reduction and therefore attenuation. The distant monitoring bore 3135U continues to show no detectable SO_4 by late 1998.

In the absence of laboratory or field data, the kinetic rate controls on SO_4 reduction were investigated through the use of a one-dimensional numerical solute transport model, applied to the western seepage pathway. The model was based on the kinetic oxidation of organic matter as a first-order reaction, where the rate of the reaction is proportional to the remaining concentration. On the basis of the chemical reaction describing SO_4 reduction, the rate of SO_4 reduction is assumed to be half of the rate for organic matter oxidation. The governing solute transport equation was numerically solved using a block-centred, upward finite difference scheme was used to solve the equation through a computer program written in FORTRAN 77. Two approaches for the source leachate (seepage) concentrations were used - constant concentration and variable chemistry of the ash pond. The model was first applied to the migration of Cl from the LYAP, since Cl is a conservative species and does not undergo any chemical reactions. Based on the fit to Cl data, the model was then applied to SO_4 migration incorporating kinetic SO_4 reduction. The model, when the variable chemistry of the ash pond was used as the source concentrations, provided a realistic fit and description of SO_4 migration and monitoring to date. The rate of SO_4 reduction determined by this model was approximately 0.63 mg/L.day.

Chapter 4

Static Leachability Studies

The results of work investigating the leachability and soluble mass of the ash at varying points within the Loy Yang power station is presented. The available soluble mass, the solubility of salts and trace elements within the ash, and the suitability of field leached ash excavated from the Loy Yang Ash Pond for classification as fill material according to regulatory (EPAV) criteria is discussed.

4.1 Research on Leached Ash

The literature review presented in Chapter 2 noted that most of the research on ash leaching and disposal investigated precipitator ash, which has a considerably higher available mass for leaching compared to ash excavated from a disposal pond. Previous research on the leachability of ash excavated from an ash pond in the Latrobe Valley was summarised in Section 2.2.5 (pages 25 to 29). The work of Black (1988) and McKinley (1995) is essentially the only leaching studies specifically on Loy Yang ash, the former being precipitator ash and the latter leached ash from the Loy Yang Ash Pond. The laboratory study by Black (1988) did not include analysis of trace elements, which are of environmental importance. In contrast, the field study by McKinley (1995) only examined trace elements. A further issue identified in Chapter 2 was the leaching effect of the hydraulic ash slurry system. The slurry system acts to begin leaching the ash during the time the dry ash is first mixed with water inside the power station (see Figure 2.1) up until the time when the ash slurry is disposed of into the ash pond. This leaching effect during slurrying has not been quantified previously at Loy Yang. There is, therefore, a need for a more comprehensive study of ash quality and leachability within the Loy Yang complex. As part of the current research program, a static (batch) leaching study of the available soluble mass within the ash at various points across the Loy Yang Ash Pond delta was undertaken in late 1995. Further chemical testing of ash within the hydraulic ash slurry system was undertaken in early 1996 concurrently with samples obtained of dry precipitator ash before mixing with water (the start of leaching).

4.2 Static Leaching Tests on Leached Ash

4.2.1 Overview of Methodology

A total of twelve samples of leached ash were obtained from the near surface of the delta of the Loy Yang Ash Pond. The samples were retrieved from about 10 to 15 cm depth, below the surface. For consistency, the sampling locations approximated those of McKinley (1995) (see Figure 2.6, page 28). Site 4 could not be sampled due to the higher water level in the LYAP at the time of sampling. The sampling sites were considered to have been 6 to 12 months in age (Pentland, 1995). The leached ash samples were obtained by shovel and stored in large plastic sample bags. The ash was well mixed in each bag and small sub-samples were extracted for chemical testing.

A chemical elutriation analysis was performed by Analabs Pty Ltd (now Australian Environmental Laboratories (AEL) Pty Ltd) on each sample to determine the concentrations of major and trace elements. The elutriation test involved maintaining with the ash in contact with the leachate at a constant pH of 4 using nitric acid (HNO_3), to simulate aggressive leaching conditions. The pH was maintained for approximately 24 hours. The test was developed by Analabs (through their laboratory certification) and is a variation of the Elutriation Procedure of the EPAV (EPAV, 1986). This test was chosen to assess the total availability of leachable salts and trace elements from the ash.

The three ash samples which showed the overall highest concentrations were then resampled from the large sample bag and subjected to more intensive testing and chemical analysis. These three leached ash samples were analysed using a "Total Decomposition" technique, similar to the total chemical concentration used by the early SECV testing. The total concentration of the various elements within the ash allows comparison to leachable quantities. Further subsamples from these particular leached ash samples were then subjected to a dual (sequential) batch leaching test. Each new sample was separately batch leached with neutral and acidic leaching solutions, based on the ASTM batch test standards ASTM D 4793-93 and D 5284-93 (ASTM, 1994).

The batch tests used 100 g samples in 2 litres of water, giving a liquid to solid ratio of 20:1, and shaken for about 18 hours. The neutral solution was distilled water and the acidic solution used was nitric acid, initially set to a pH of about 4 (but not maintained throughout the 18 hours, as per the ASTM standard). After the first 18 hours, the leachate solution was filtered, removed and sent to Analabs for chemical analysis. The remaining ash was subjected to a further 2 litres of leaching for 18 hours and the subsequent leachate analysed, making the total liquid to solid ratio about 40:1. A dual batch test was chosen due to the lower soluble mass expected for ash from the ash delta. To ensure adequate quality control for EPA purposes, all equipment was acid washed and rinsed thoroughly with distilled/deionised water.

4.2.2 Results of Static Leachability Testing

The results of the Elutriation Tests performed by Analabs on the 12 samples are presented in Tables 4.1 and 4.2, on a mg/kg leached basis. These results were compared to the regulatory criteria from EPAV (1986). The majority of samples were within these criteria, with three samples exhibiting leachable concentrations for Ba or Hg above or near these values. These were sites 1, 5 and 9, and were chosen for further testing and analysis. The total concentration analysis for sites 1, 5 and 9 are given in Tables 4.3 to 4.4. The results of the leachate concentrations determined from the static leaching tests are presented in Tables 4.5 to 4.8.

Table 4.1 - Elutriation Test : Acid Digestible Major Elements (mg/kg) (dry basis)

Site	Ca	Mg	Na	K	SO_4	Cl	Moisture Content[1]
1	48,000	47,000	13,000	810	6,600	850	66
2	30,000	37,000	10,000	980	nd	nd	56
3	64,000	47,000	3,100	410	6,500	61	55
5	42,000	33,000	12,000	1,500	4,100	1,000	55
6	3,200	3,200	2,000	210	140	8.4	18
7	6,800	9,600	9,700	1,700	1,500	140	59
8	9,100	10,000	2,700	470	nd	nd	20
9	56,000	46,000	8,300	820	88	<5	58
10	6,100	6,700	3,600	980	1,100	nd	65
11	2,200	3,400	4,600	1,100	390	66	54
12	12,000	16,000	4,600	790	530	96	58
13	1,900	2,900	4,600	1,200	nd	760	54

[1] - % w/w; as sampled and received by Analabs. nd - no data.

Table 4.2 - Elutriation Test : Acid Digestible Trace Elements (mg/kg) (dry basis)

Site	Ba	Cd	Cr	Co	Mo	Ni	Sn	Hg
1	550	1.3	18	7.7	11	15	39	1.5
2	330	1.2	23	19	9.3	29	34	1.1
3	380	0.9	20	18	10	25	38	1.1
5	490	0.8	28	9	12	21	35	2.0
6	170	0.6	18	6	9	11	10	0.16
7	170	0.3	57	12	8	22	21	1.3
8	210	0.5	22	9	10	20	19	0.44
9	440	1.0	27	19	12	32	36	1.2
10	92	0.9	34	7	<5	15	14	0.91
11	82	0.1	55	7	5	16	12	0.71
12	180	1.0	39	14	8	23	20	0.67
13	78	0.6	56	7	5	15	12	0.62
Average	264	0.77	33	11	8.3	20	24	0.98
EPAV	400	5	250	50	40	100	50	2.0

Table 4.3 - Total Concentration : Major Elements (%) (dry basis)

Site	SO_4	CaO	MgO	Na_2O	K_2O	Cl
1	1.36	11.08	15.82	1.75	0.13	0.16
5	1.81	9.37	11.05	2.60	0.32	0.14
9	2.58	9.37	11.70	1.40	0.16	0.02

Table 4.4 - Total Concentration : Trace Elements (mg/kg) (dry basis)

Site	As	Ba	Cd	Cr	Co	Cu	Pb	Mo	Ni	Sn	Hg	Zn
1	14	1,362	2	53	10	41	<50	<10	34	<3	0.39	154
5	33	908	<2	102	18	51	<50	<10	64	7	2.15	96
9	22	724	<2	79	29	32	<50	<10	54	3	0.52	76
EPAV		400	5	250	50			40	100	50	2	

Table 4.5 - Acidified Sequential Batch Test : Major Elements in Leachate (mg/L)

Site	Batch Extract	Na	K	Ca	Mg	SO_4	Cl	CO_3	HCO_3	TDS
1	1	380	21	42	0.11	400	80	66	0	1,200
1	2	51	5.6	76	0.11	110	8.8	40	0	400
5	1	230	13	49	0.06	360	81	120	0	860
5	2	16	2.2	93	0.06	110	9.3	120	0	860
9	1	140	14	46	0.29	310	2.4	110	0	360
9	2	21	5	52	0.43	120	<0.5	45	6	300

Table 4.6 - Acidified Sequential Batch Test : Trace Elements in Leachate (mg/L)

Site	Batch Extract	Ba	Cd	Cr	Co	Mo	Ni	Sn	Hg
1	1	0.16	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
1	2	0.35	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
5	1	0.13	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
5	2	0.29	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
9	1	0.10	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
9	2	0.16	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005

Table 4.7 - Neutral Sequential Batch Test : Major Elements in Leachate (mg/L)

Site	Batch Extract	Na	K	Ca	Mg	SO_4	Cl	CO_3	HCO_3	TDS
1	1	330	19	38	0.11	140	54	66	0	1,200
1	2	48	5.5	82	0.18	50	8.9	60	0	420
5	1	210	12	45	0.09	120	70	160	0	380
5	2	14	2.1	89	0.08	50	7.4	130	0	800
9	1	150	15	45	0.53	340	2.1	56	5	680
9	2	12	3.6	60	0.31	110	<0.5	47	0	270

Table 4.8 - Neutral Sequential Batch Test : Trace Elements in Leachate (mg/L)

Site	Batch Extract	Ba	Cd	Cr	Co	Mo	Ni	Sn	Hg
1	1	0.16	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
1	2	0.37	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
5	1	0.14	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
5	2	0.27	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
9	1	0.11	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005
9	2	0.22	<0.01	<0.03	<0.03	<0.05	<0.03	<0.05	<0.0005

4.2.3 Discussion and Analysis of Results

The pH of the leachates was not determined from the sequential batch tests, although strong alkaline conditions can be inferred from the absence of bicarbonate and the high carbonate concentrations within the leachate. It is important to note that there is no requirement in ASTM (1994) to maintain the acidic pH. Thus the alkaline nature of the ash was stronger than the original acid leaching solution, and this feature appears to have limited the solubility or leaching of most trace elements, with the exception of Ba. The strong alkaline nature is most likely due to the high lime (CaO) content, based on the total concentration of Ca in Table 4.3. The measured decrease in concentrations from the first to the second extraction indicate that further extractions would not contribute significantly to the total mass leached from the aged ash samples.

The concentrations of most elements decreased significantly in the second extraction, except for Mg which is stable and Ba and Ca, which both increased in concentration in the second extraction. This can be explained through leaching the more soluble salts in the first extraction, primarily gypsum ($CaSO_4$), thenardite (Na_2SO_4) and halite (NaCl). The dissolution and leaching of these minerals are less dependent on the pH of the leachate and can therefore leach more readily. The available mass of SO_4 is therefore mostly removed in the first extraction. On the basis of the equilibrium dissolution of a mineral (Fetter, 1993; Appelo & Postma, 1994; Langmuir, 1997), the small remaining SO_4 minerals give rise to a lower SO_4 and higher Ca concentration. The higher Ba concentration suggests that it is present in the ash as insoluble barite ($BaSO_4$), due to the higher Ba concentration as the SO_4 concentration decreases. The geochemical controls on ash leachate will be analysed in greater detail in Chapter 7.

The concentration of Ba within the various ash samples is variable. It is noteworthy that the elutriation tests gave an average concentration of leachable Ba of about 264 mg/kg, compared to the EPAV criteria of 400 mg/kg. In contrast, the total concentration analyses, gave an average Ba of about 890 mg/kg. This is further evidence of the importance of assessing the leachable fraction in ash, which appears low for Ba.

It is possible to calculate the amount of each element in the ash before the batch leaching test and the amount leached out into solution, thereby determining the "leachability" of each element in the aged ash. The concentration of each element in the ash is converted to mg/kg and the mass leached into solution is calculated from :

$$\text{Mass Leached per kg of Dry Aged Ash} = \frac{C_1V_1 + C_2V_2}{\text{Sample Mass}} \quad \text{mg/kg} \qquad 4\text{-}1$$

where V_1 and V_2 is the leachate volume (2 litres), C_1 and C_2 are the respective leachate concentrations (mg/L), and the sample mass of aged ash is 0.1 kg.

The total mass leached is the sum of all elements leached from both batch tests. Results are presented in Table 4.9. The leachability fractions for the major elements of the aged ash can be calculated by :

$$\text{Leachability Fraction (\%)} = {}^{C_L}\!/_{C_A} \times 100 \qquad 4\text{-}2$$

where C_L - concentration leached from the ash (mg/kg);

C_A - total concentration in the ash (mg/kg).

Table 4.9 - Total Mass Leached from Leached Ash Samples (mg/kg)

		Ca	Mg	K	Na	SO_4	Cl	CO_3	Ba	Total Mass Leached[1]
1	A	2,360	4.4	532	8,620	10,200	1,776	2,120	10.2	25,623
1	W	2,400	5.8	490	7,560	3,800	1,258	2,520	10.6	18,044
1	T	79,188	95,407	1,079	12,982	13,558	1,550	-	1,362	
5	A	2,840	2.4	304	4,920	9,400	1,806	4,800	8.4	24,081
5	W	2,680	3.4	282	4,480	3,400	1,548	5,800	8.2	18,202
5	T	66,967	66,640	2,656	19,288	18,118	1,400	-	908	
9	A	1,960	14.4	380	3,220	8,600	48	3,100	5.2	17,328
9	W	2,100	16.8	372	3,240	9,000	42	2,060	6.6	16,837
9	T	66,967	70,560	1,328	10,386	25,797	230	-	724	

Notes : A - Acid; W - Water (neutral); T - Total.

The average leachability fractions for the acidic and the neutral (water) static tests are presented in Table 4.10. By calculating the overall average leachability from the six results, the order of leachability can be established as :

Cl (79%) > SO_4 (40%) > Na (40%) > K (29%) > Ca (3.4%) > Ba (0.8%) > Mg (0%)

Table 4.10 - Average Leachability Fraction (%)

	Ca	Mg	K	Na	SO_4	Cl	Ba	Overall
Acid	3.4	0.0	29.8	41.0	53.5	88.2	0.8	2.23
Water	3.4	0.0	28.0	37.6	27.2	70.0	0.9	1.77

On the basis of the data in Table 4.10, the average mass leached from was approximately 2%. There would appear to be a slightly higher mass leachable if acidic solutions are used (2.23%) compared to neutral solutions (1.77%). All of these above values are significantly lower than results reported for Morwell Ash Pond sediment (12%) (Black, 1990a), Yallourn Ash Pond Sediment (6.5%) (Black, 1990b) and precipitator ash at Loy Yang (19.2%) (Black, 1988). There are no criteria available from the EPAV for soluble salt concentrations in wastes.

The main conclusions from this study :

- leached ash is strongly alkaline and shows a strong alkaline buffering capacity;
- the concentrations of SO_4, Cl, Na and K decreased from the first to the second extraction by approximately one order of magnitude;
- the concentration of Mg was found to remain uniform;
- the concentrations of Ca and Ba approximately doubled from the first to the second extractions;
- the alkaline conditions retard the leaching of all trace elements analysed, with the exception of Ba; and
- the leached ash exhibits a low degree of leachability (about 2% by mass).

4.3 Leaching Effect of the Hydraulic Ash Slurry System

The ash disposal system at Loy Yang is via hydraulic pumping as a slurry to the ash pond where the slurry is deposited sub-aqueously (refer to Figure 2.1, page 13). It was highlighted in the literature review that earlier SECV research had shown that such pumping leaches a significant proportion of soluble salts from the ash (Bone and Schaap, 1980). Their work was conducted at the Hazelwood power station. No comparable study has yet been undertaken at Loy Yang. In order to ascertain the effect of slurry pumping on ash leaching at Loy Yang, a sampling and analysis program was undertaken in late February and early March 1996.

A total of five series of samples were obtained, four samples from Loy Yang Power (LYA) and one sample from Edison Mission Energy (LYB). Each sampling run included a sample of ash and slurry water from within the power station complex (ie - relatively fresh ash and before the leaching effect of pumping, labelled the “Inlet”) and a sample of ash and slurry water from the discharge pipes at the ash pond, labelled the “Outlet”. The ash was separated by on site filtering through a 75 µm filter. The slurry water samples were analysed for major elements and a suite of trace elements. The ash samples were only tested for SO_4 and Cl concentrations, as these comprise most of the leachable ash mass. All results are presented in Tables 4.11 to 4.13.

Samples of unleached (dry) precipitator ash and coal quality were obtained during this work. There is no access to sample dry fly ash from the electrostatic precipitators before mixing with water at Loy Yang A, although the slightly newer precipitator design at Loy Yang B allowed access to dry ash before mixing with water through a maintenance port. One sample of unleached precipitator ash was obtained from an electrostatic precipitator unit at Loy Yang A undergoing cleaning and maintenance during this period. Two samples of Loy Yang B dry precipitator ash were obtained. The quality of the coal supplied to each utility is essentially the same, since it is supplied by the coal preparation plant adjacent to the Loy Yang open cut. Any differences in ash morphology relate to the minor design differences between each utility. The coal quality data was supplied courtesy of Loy Yang Power. All results are in Tables 4.14 to 4.16.

Table 4.11 - Slurry Water Chemistry (Early 1996) : Major Elements (mg/L)

	29-02-96		05-03-96		07-03-96[1]		12-03-96		15-03-96	
	I	O	I	O	I	O	I	O	I	O
pH	9.2	9.2	11.0	11.1	10.8	10.6	11.6	9.6	10.2	10.1
Eh[2]	-	-	280	300	300	300	320	330	310	300
TDS	7,800	7,500	5,900	4,600	12,000	10,000	7,300	7,300	8,400	7,800
EC[2]	1,145	1,125	822	701	1,790	1,430	1,295	961	1,138	1,056
Na	1,900	1,800	1,600	1,100	2,900	2,700	1,800	1,800	2,200	2,000
K	89	89	77	59	140	120	82	85	0.3	93
Ca	370	370	240	560	480	460	440	440	460	410
Mg	73	66	0.13	110	110	120	150	160	5.3	6.2
SO_4	4,500	4,300	3,200	2,400	6,500	5,600	4,000	4,000	4,850	4,500
Cl	745	720	500	370	1,000	750	635	630	595	560
CO_3	70	57	110	130	190	200	68	58	150	140
HCO_3	45	60	-	-	48	120	64	60	65	52

I - initial ash slurry within power station; O - output ash slurry at the ash pond.

[1] - Loy Yang B sample; [2] - Eh (redox) in mV and EC in mS/m.

Table 4.12 - Slurry Water Chemistry (Early 1996) : Trace Elements (μg/L)

	29-02-96		05-03-96		07-03-96[1]		12-03-96		15-03-96	
	I	O	I	O	I	O	I	O	I	O
As	-	-	3	<1	1	<1	8	9	16	18
Ba	60	50	70	110	110	70	60	50	90	70
B	4,100	4,000	2,400	3,600	5,400	4,500	3,500	3,400	3,700	3,300
Cd	<5	<5	<2	<2	<2	<2	<10	<10	<10	<10
Cr	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Co	<30	<30	<30	<30	<30	<30	<30	<30	<30	<30
Cu	60	60	<30	50	110	30	150	170	<30	<30
Pb	30	<30	40	90	90	100	130	120	<30	<30
Hg	<0.5	<0.5	<0.5	<0.5	<0.5	2	2.3	2.8	0.6	2
Mo	<50	<50	90	70	90	70	90	90	80	70
Ni	40	40	<30	<30	<30	<30	<30	<30	<30	<30
Sn	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Se	240	240	225	36	65	61	420	420	390	340
Zn	50	40	<30	50	60	30	170	500	<30	60

[1] - Loy Yang B sample.

Table 4.13 - Leachable Mass (Early 1996) : Sulfate and Chloride (mg/kg) (dry basis)

	Sulfate			Chloride		
Date	Inlet	Outlet	%Diff.[1]	Inlet	Outlet	%Diff.
29-02-96	12,000	7,300	-39.2	2,000	960	-52
05-03-96	5,500	10,000	81.8	540	620	14.8
07-03-96	22,000	23,000	4.5	2,200	1,400	-36.4
12-03-96	18,000	6,300	-65	1,100	510	-53.6
15-03-96	9,000	8,100	-10	840	960	14.3

[1] - Calculated from the percentage increase (+) / decrease (-).

Table 4.14 - Precipitator Ash Quality at Loy Yang (Early 1996) : Major Elements

	Exp.[1]	Black	Loy Yang A	Loy Yang B	
(%)	Furnace	(1988)	20-03-96[2]	7-03-96	7-05-96[3]
SiO_2	2.5	41.6	55.9	6.6	6.56
SO_3	1.9	5.6	5.39	19.3	25.6
CaO	2.3	3.5	3.45	10.3	14.82
MgO	7	7.9	4.84	10.2	15.17
Na_2O	3.3	7.8	6.7	12.7	13.45
K_2O	0.17	0.43	0.23	0.69	0.32
Al_2O_3	22.8	17.6	6.92	11.6	3.24
Fe_2O_3	14.9	7.5	7.81	5.3	7.13
Cl	<0.1	1.4	0.33	0.31	2.09
TiO_2	<0.1		0.76	1.3	0.2
MnO			0.04	0.16	0.05
CO_3				5.2	0.88
P_2O_5			0.03	0.05	0.01
LOI		9.2	5.66	21.1	11.77
Sum		102.53	98.06	104.81	101.29

[1] - Loy Yang Experimental Furnace samples from Bone & Schaap (1980); [2] - Sample provided by Loy Yang Power during cleaning and maintenance of a precipitator at Loy Yang A; [3] - Further bulk sample provided by Edison Mission Energy.

Table 4.15 - Coal Quality at Loy Yang (Early 1996) (%)

Date	Location	Moisture[1]	Ash[2]	Na[2]	Al[2]	Ca[2]	SiO_2[1]
29-02 AM	Stage 2, LYA	65.0	1.7	0.05	0.01	0.02	1.01
5-03 AM	Stage 1, LYA	61.0	1.7	0.13	0.00	0.00	0.75
7-03 AM	Stage 14, LYB	61.5	1.5	0.17	-	-	-
12-03 AM	Stage 2, LYA	62.8	1.0	0.21	0.08	0.08	0.00
15-03 AM	Stage 2, LYA	64.1	1.7	0.08	0.01	0.03	0.00

LYA - Loy Yang A; LYB - Loy Yang B. [1] - As received at the power station; [2] - % Dry basis.

Table 4.16 - Precipitator Ash Quality at Loy Yang (Early 1996) : Trace Elements

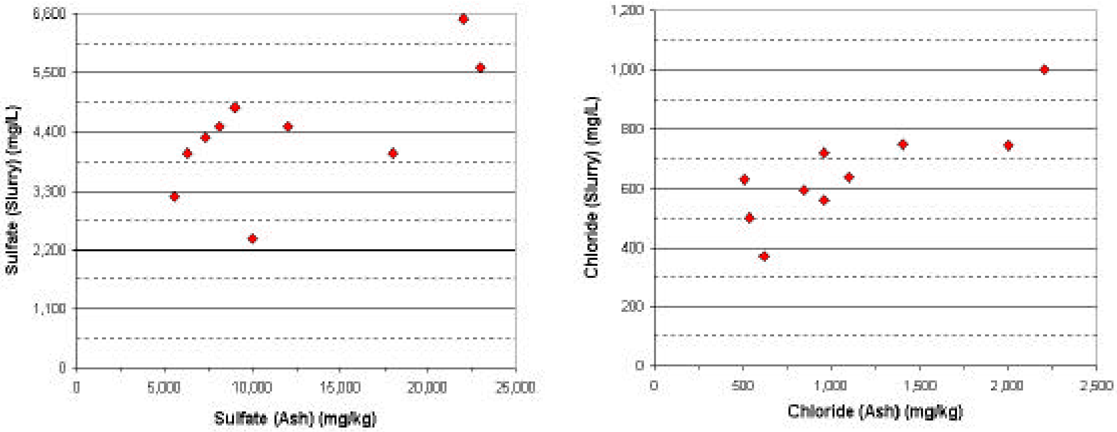
mg/kg	As	Ba	B	Cd	Cr	Co	Cu	Pb	Hg	Mo	Ni	Se	Sn	Zn
LYA[1]	4.1	120.8	49.3	<0.5	13.5	8.8	13	2.5	0.23	<5	11.8	<5	<5	23
LYB[2]	7.9	33	630	<0.5	8.0	4.0	28.5	5.0	1.45	<5	10	18.5	<5	86.5
1980[3]	71	1,800	190	3.9	310	74	140	220	3.2	69	130	26	-	140

[1] - Loy Yang A, Sampled 20-3-96; [2] - Loy Yang A, Sampled 7-5-96; [3] - Data from Loy Yang Experimental Furnace (Bone & Schaap, 1980).

The coal quality data is generally uniform, showing the effects of blending at the coal preparation plant adjacent to the open cut, undertaken to minimise fouling of the boilers and thereby optimise station performance (Waring *et al.*, 1996). The influence of Ca on the alkaline strength of the ash slurry water quality can be seen by comparing the data in Tables 4.11, 4.14 and 4.15. The high calcium oxide (lime) content of the ash, particularly at Loy Yang B, allows the pH to reach up to 11. Importantly, the proportion of soluble species in the dry precipitator ash samples appears to be higher than the ash samples obtained by filtering slurry water. The concentration of trace elements within the precipitator ash samples is generally low, especially compared to the early studies in 1980 at the Loy Yang Experimental Furnace. The coal quality and precipitator ash data demonstrate the need to consider ash and slurry water quality as a function of the coal quality over time.

The concentrations of SO_4 and Cl in the slurry water and the slurry ash appear to correlate some degree, as shown in Figure 4.1. This would be expected as the SO_4 and Cl are generally present in relatively soluble mineral forms in the ash and would dissolve into solution quite rapidly. There is wide variability in the measured concentrations of SO_4 and Cl within the filtered ash. This may be due to the expected variability of the ash or the residence time of the slurry within the hydraulic transport system. The average residence time within the hydraulic slurry system is approximately 15 to 30 minutes on average, although it can reach up to an hour or more if the internal pumps in the power station are temporarily turned off (Pentland, 1995). This time corresponded to the time taken to move from sampling the inlet within the power station to the discharge outlet at the ash pond.

Figure 4.1 - Correlation of Sulfate and Chloride in Ash and Slurry Water



There is an average decrease in SO_4 concentration in the filtered ash from the inlet to the outlet of approximately 5.6%, although excluding the value of 81.8% as a statistical outlier the average becomes much greater at 27.4%. The average decrease in Cl concentration from the inlet to the outlet was 22.6%. The data on ash and slurry water quality demonstrates that there is leaching occurring within the hydraulic transport system at Loy Yang, although a degree of caution is necessary in extrapolation based on the limited data set obtained.

This initial leaching appears to help the leaching of the ash once it has been deposited into the disposal pond. The previous section, 4.2, demonstrated that ash excavated from the ash pond delta after 6 to 12 months deposition had a soluble mass about one order of magnitude lower than precipitator ash, consistent with the analytical data obtained on precipitator ash in Table 4.14. The decrease in SO_4 and Cl concentration in the ash between the inlet inside the Loy Yang power station and the outlet (discharge) at the ash pond ranges from about 6% to 27%. Given the fact that a significant proportion of the soluble mass in the ash is due to soluble SO_4 and Cl salts, this decrease caused by the hydraulic slurry system is therefore significant.

4.4 Summary of Static Tests on Leached Ash

The results of static leaching tests and chemical analysis of ash from the Loy Yang Ash Pond and the ash and slurry water at the inlet and outlets of the hydraulic ash transport system has been presented. The data and analysis show that the soluble mass of ash excavated from the LYAP after about 6 to 12 months deposition is very low, especially compared to unleached (dry) precipitator ash. The static or batch tests showed the solubility to be about 2%, slightly higher if acidic solutions are used in testing. It is important to note that most trace elements did not leach in measurable quantity in the static tests, with the exception of Ba at low concentrations. The hydraulic ash slurry system, which collects the dry precipitator ash, mixes it with water and pumps the slurry to the ash pond for disposal, does appear to have a leaching effect on the ash during transport. The chemistry of the slurry water and ash can be related to the coal quality and precipitatpor ash being processed at the respective power stations at that time. Overall, the low leachability and chemical quality of ash excavated from the Ash Pond are within EPAV criteria for classification as fill material.

The significance of these test results is that they show the importance of characterising the source material for disposal. For example, if the static tests were conducted on precipitator ash yet the ash for disposal was excavated from the ash pond, the static testing would significantly overestimate the leachable fraction and therefore potential environmental impacts from such disposal. The extrapolation of static test data to the field is difficult, however, as highlighted from the literature in Chapter 2. The higher liquid-to-solid ratios and more aggressive conditions used in static or batch-type testing clearly do not reflect the expected field conditions at a potential disposal site. Therefore, having a realistic understanding of the chemical quality of the waste is important in assessing such sites in the context of their expected field conditions.

Chapter 5

Field Leachability Studies

The results of the construction and operation of 2 field leaching cells are presented. These cells were used to simulate the leaching effects and moisture flow behaviour of disposed ash within the overburden. A detailed flow and chemical monitoring regime was followed, allowing the compilation of inflow versus outflow data and a mass balance of solutes within the ash and leachate. These studies provide the basis for solute transport models of ash leaching and solute migration.

5.1 Engineering Design and Construction

To verify the long-term behaviour of leached ash under unsaturated conditions, as opposed to the saturated conditions which batch tests simulate, trial leaching cells were constructed at Loy Yang in late June 1997. Due to the climate of the region, two individual cells were constructed with one cell remaining open to rainfall while the second cell had an external 5,000 litre water tank installed for regular irrigation. The cells were constructed in a special purpose ash platform located above the maximum water level of the pond and within the south-western confines of the Ash Pond catchment (see the bottom left corner of LYAP, Figure 1.3, Chapter 1). The two cells were respectively named the Dry Cell and the Wet Cell. It was considered that by building two separate cells, natural leaching rates and flow behaviour could be established while an accelerated leaching test could be conducted on the second cell by adding water regularly to reach much higher pore volumes of leaching.

The design and construction of each cell was identical, with an area of 5 m by 5 m at the surface and a height of 3 m. The liner used was 2 mm thick High Density Polyethylene plastic (HDPE) and a 75 mm drainage layer was installed at the base consisting of subrounded aggregate at 3 to 5 mm diameter (approximate only). A layer of geotextile (Bitton Cloth, about 5 mm thickness) was used to separate the ash layer from the drainage layer and prevent fine particle migration and possible clogging of the leachate collection pipe within each cell. A design outline is given in Figure 5.1.

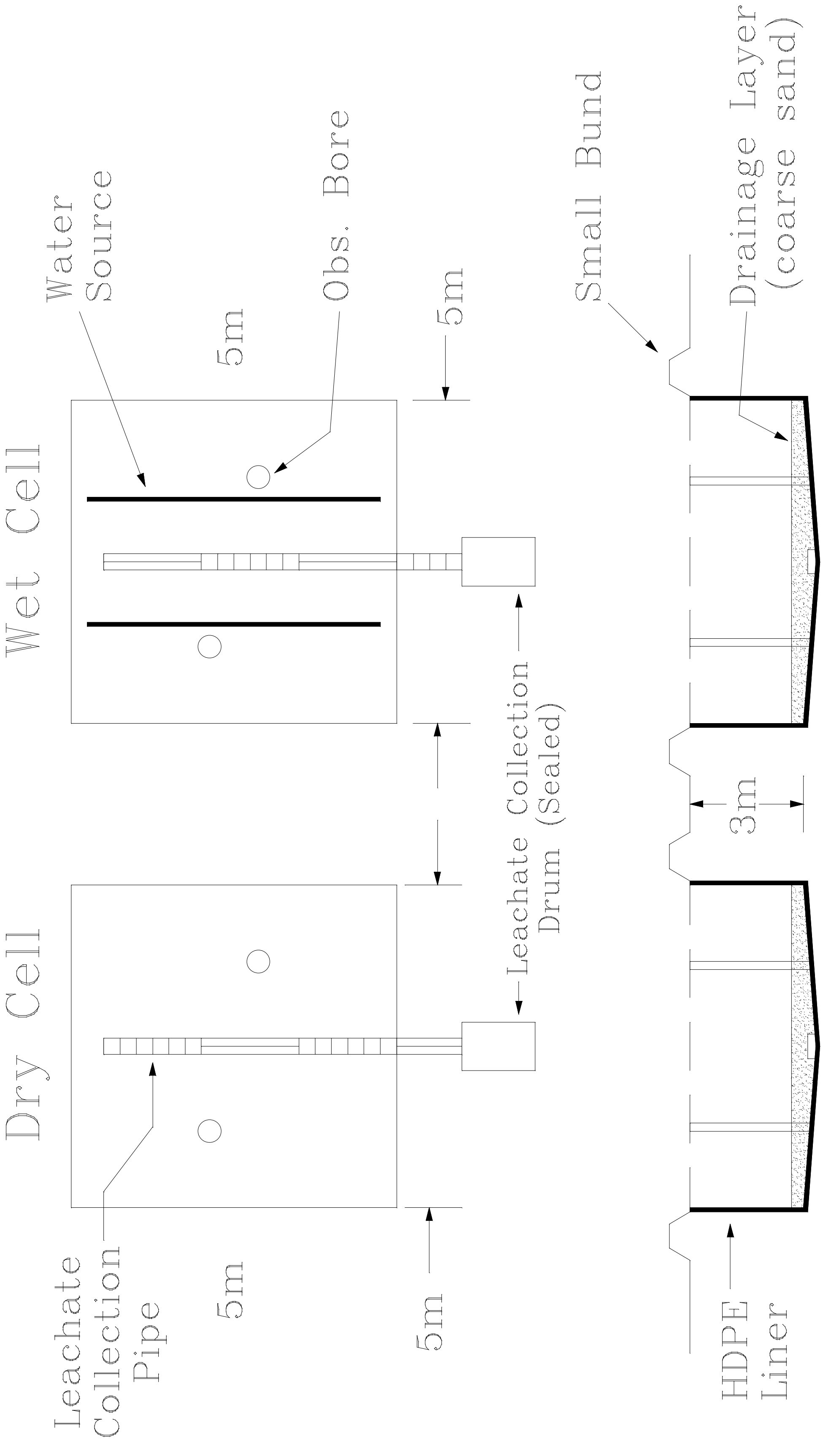


Figure 5.1 - Engineering Design of Field Leaching Cells (approximate scale only)

The potential for puncture of the HDPE liner by the coarse drainage layer is low. The puncture resistance was assessed using a method from Koerner (1998) and the analysis indicated a very high factor of safety for the design of the cells.

The coarse drainage layer, and possibly the geotextile, can act as a capillary break (cf. Koerner & Daniel, 1997). The amount (and rate) of leachate emanating from the base of an ash layer will depend on the permeability and moisture condition of underlying soils or materials. In the field situation, disposal sites are located on natural clays, which are unsaturated at the time of ash placement, compared to the cells which included the geotextile, drainage layer and HDPE. The low permeability of clays, even after saturation by percolating leachate, leads to localised mounding in the ash layer, whereas the drainage layer has a very high permeability and no mounding can occur due to rapid lateral discharge. The cells, therefore, provide a base condition which is likely to provide an overestimation of leachate generation under field conditions.

The cells were located in the south-western corner of the ash pond catchment (refer to Figures 1.2 and 1.3). A special platform of ash was constructed one week earlier by the placement of ash over an area about 20 m by 8 m, to a depth of between 3.5 to 5 m. The ash was sourced from the delta of the Loy Yang Ash Pond, identified as leached ash in Chapters 2 and 4. The surface level of the platform was the same as the top of the dam wall. Installation of the two cells was identical, with the Dry Cell located on the eastern half and the Wet Cell on the western half of the platform. A distance of about 8 m separated the 2 cells. An area of 5 by 5 m was surveyed by hand, followed by excavation of this area to a depth of about 3 m. The sides of the excavation were maintained at an angle of about 45^0 from the surveyed area (for safety reasons). For the Wet Cell, an straight excavation to the north was dug to allow for the leachate pipe, while for the Dry Cell the leachate collection pipe was laid through an excavation to the east. The bottom 0.5 m of the hole was kept vertical for easier installation of the HDPE. The HDPE was laid out across the excavation and carefully checked for any holes, cracks or possible points of weakness (none were found). The leachate collection pipe, 50 mm diameter PVC, was placed on the HDPE into a thin groove (about 25 mm) dug into the ash, with thick slots sawn into the pipe about every 5 cm to a depth of 25 mm in the pipe.

A 50 mm hole was cut into the HDPE liner and the leachate pipe placed through this. The hole was carefully sealed around the pipe using a special tape supplied with the HDPE. Water was poured onto the hole to check for possible leaks, and none were found. The coarse aggregate for the drainage layer was then carefully placed on the HDPE liner and manually levelled to achieve a thickness of about 75 mm. Four steel poles were installed vertically at each corner of the cell, rising to the surface of the platform. Horizontal cross members (steel pipe), were connected between each vertical pole at about 1.5 and 3 m to provide structural support. The HDPE was pulled across the horizontal members and ash was placed inside the cell by the excavator. The ash was compacted by the bucket of the excavator about every 0.5 m. After a depth of 1.5 m had been achieved, the outside of the excavation was backfilled to ensure stability. Further ash was placed inside the cell and compacted by the excavators' bucket. Every care was taken to ensure no ripping or holes were allowd to develop in the HDPE during construction. After filling the cell with ash, the excess HDPE was used for a bund wall on each side, thereby preventing surface runoff from entering the cell. Special attention was given to prevent preferrential flow along the wall of the cells. The platform and trial cells are shown in Figure 5.2. The construction sequence is shown in Appendix A3.

The density of ash within each cell was generally similar to that found in current and proposed ash dump sites within the Loy Yang Overburden Dump, based on similar construction techniques and previous investigations (eg. Kacavenda, 1994; Kacavenda & McKinley, 1994; see Section 2.2.5, Table 2.7). The density data obtained will be presented under the results for each cell.

A collection tank volume of about 12 mm (300 litres) was installed at the outlet of each leachate collection pipe, sufficient to hold a maximum rainfall event typical of the Latrobe Valley, after allowing for storage within the ash and regular monitoring. The Wet Cell had an three lines of irrigation spray jets installed, sufficient to achieve an irrigation rate of about 11 mm/hr (or 0.075 L/s, based on the external tank volume of 5,000 litres), making the total time for one tank of water to irrigate the Wet Cell approximately 18 to 20 hours. The irrigation jets covered approximately 80% of the surface area of the cell (see Figure 5.3).

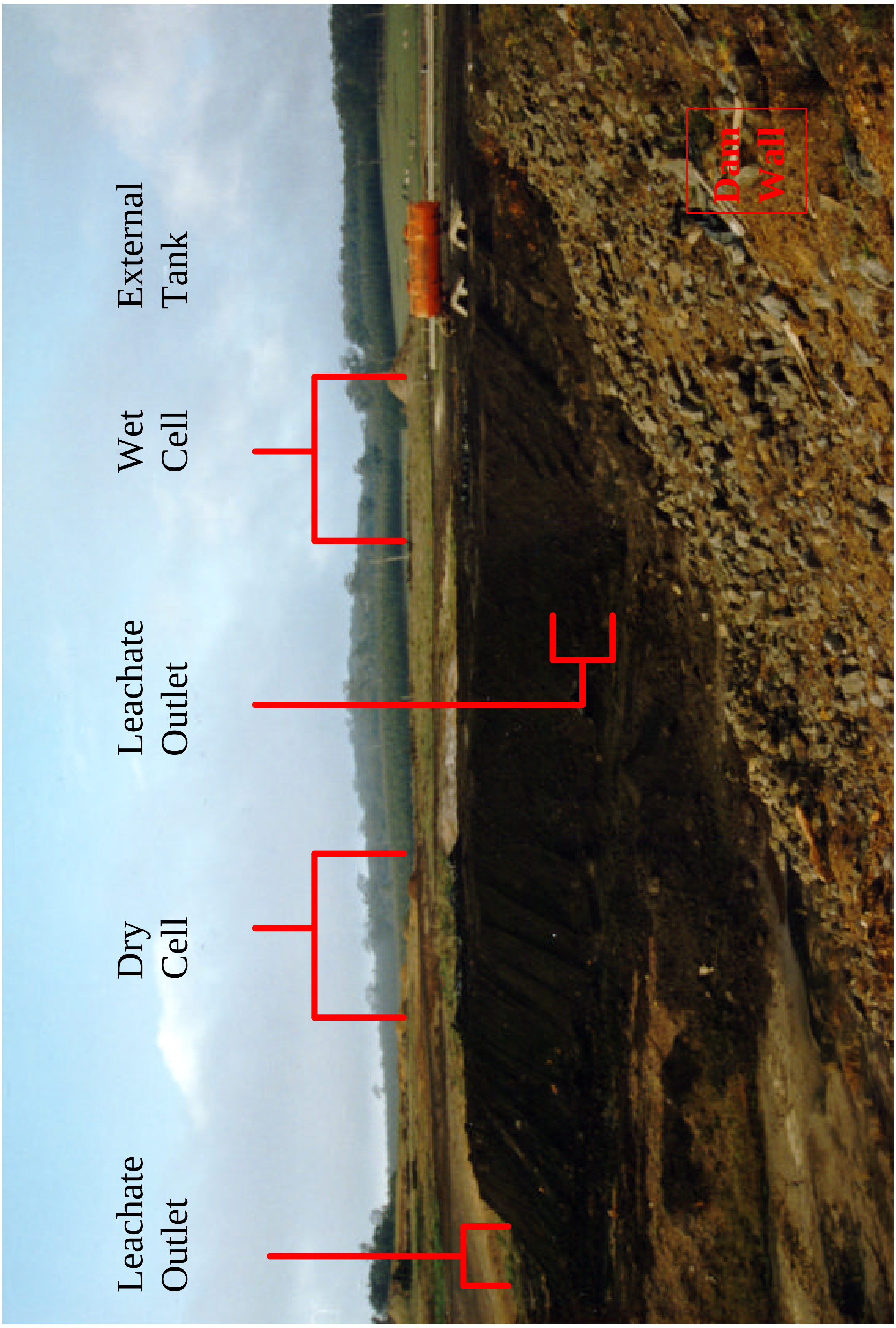


Figure 5.2 - Field Leaching Cells, June 1997 (as constructed; see Fig. 1.3 for location)
(Ash platform constructed for the trial cells; dam wall across top right corner)

5.2 Operation and Monitoring Regime

5.2.1 Overview of Methodology

The operational and monitoring period of both cells lasted from July 1997 to August 1998. A detailed calculation of total inflow and outflow was established for each cell, whereby rainfall, external water and total outflow of leachate was monitored.

The water used to refill the external tank for irrigation of the Wet Cell was derived from the Loy Yang High Quality Water system (a processed water stream available from within the Loy Yang complex), and was tested regularly for water quality. The tank was allowed to irrigate the Wet Cell about once every two to three weeks, and both the leachate flow rate emanating from the collection pipe and the total volume collected per event was monitored closely. Samples of rain water were also obtained from the Loy Yang weather station and chemically tested for comparison.

Samples of leachate from each cell were obtained, when available, approximately every two weeks or more frequently when required, and analysed for a complete suite of cations, anions, trace elements, pH and redox conditions of the leachate. A series of ash samples were taken at the time of construction of each cell, and further surface samples and a series of ash samples at various depths were taken approximately every three to four months. All laboratory analytical work of leachate and ash samples was performed by WSL Consultants Pty Ltd, under contract to Loy Yang Power Ltd. In combination with the inflow, outflow, ash and leachate analyses, a detailed solute balance was calculated for each cell. The geochemistry of ash leachate is analysed in Chapter 7, which incorporates the further laboratory leaching studies presented in Chapter 6.

The internal moisture profile of each cell was intended to be regularly monitored using a neutron moisture probe[1], however, there were difficulties in interpreting the data. There was a large degree of variability and no statistically acceptable regression could be determined to make use of the data. The neutron probe data has thus not been included.

---

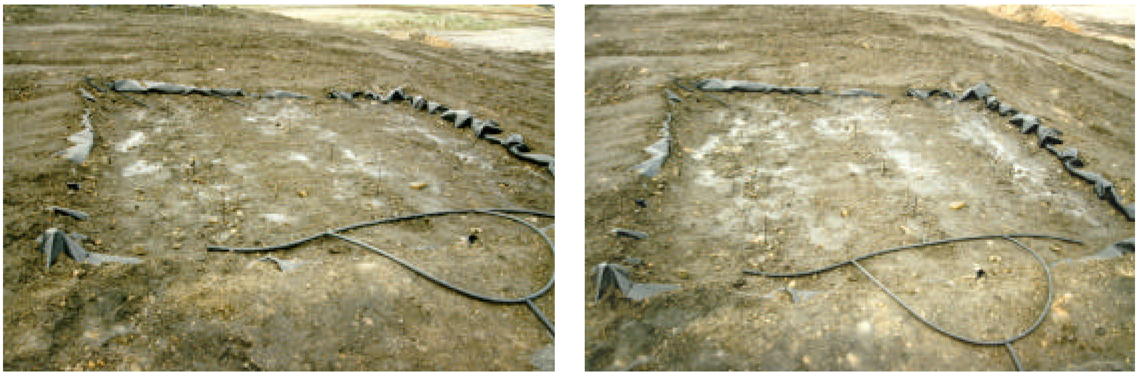
[1] - CPN Corporation model 503 DR neutron depth moisture probe, made available for use by Dr Sam Yuen, Dept. of Civil & Environmental Engineering, University of Melbourne.

The vertical moisture profile was determined when ash samples were obtained by hand-augered boreholes. The boreholes were drilled at six monthly intervals and provided ash samples for chemical analysis and moisture content (based on oven drying of samples). The bores, after completion of sampling, were carefully backfilled to prevent any preferrential flow path developing. Great care was also taken to avoid drilling beyond the drainage layer and into the HDPE.

5.2.2 General Observations During Operation

The ash was not observed to consolidate significantly, based on visual inspection and monitoring of each cell. The depth of ponded water in the Wet Cell, however, did increase gradually over time during the operation of the trial. The irrigation rate was maintained at an approximately constant flow rate throughout the trial, with the filters in the pipe and jets regularly cleaned to prevent fine particle clogging, and hence this is not considered a possible cause. The phenomenon of increasing ponded depth was not physically measured, but can be seen on the photo sequence presented in Figure 5.3. These photos suggest a reduction in permeability in the near-surface over time. The causes of this behaviour are unclear, but may include mineral precipitation (eg. iron hydroxides) or algal growth (Bouwer, 1996; Houston, 2000). It is not clear if consolidation was a further mechanism, although this is considered to be a reasonable possibility.

An important observation is that although the irrigation was generally uniform across most of the cell, small pockets of ash remained dry due to the gentle undulations in surface contours (especially towards the edges and the bunded sides). This has been taken advantage of, with samples of ash collected including samples from an area of saturated or inundated ash and from an area near the edge that remained dry during irrigation. Thus the effect of this different water content on ash leaching behaviour can be assessed. The results of this are discussed further in Section 5.5.4.



August 1997 September 1997

November 1997 December 1997

April 1998 July 1998

Figure 5.3 - Irrigation of the Wet Cell Over Time

The total rainfall over the 14 month operational and monitoring period from July 1997 to mid-August 1998 was 596 mm. The average annual rainfall in the Latrobe Valley is approximately 850 mm (July to June), and the lower rainfall during the field trials is considered to be due to the El Nino Southern Oscillation creating drier climatic conditions across Australia[2]. The trial cells, therefore, were run in an unusually dry year.

---

[2] - Courtesy of the Bureau of Meteorology, Melbourne, VIC.

During the summer months, under conditions of high temperatures and relatively dry air (compared to winter months), a thin, discontinuous salt film of up to 1 mm could be formed on the surface of the cells and the ash platform. This process was hastened if strong winds were present. The salt was very fine grained and could be dispersed with prevailing strong wind gusts. It would not be sufficient to form a solid crust, however, and easily dissolved and leached back into the ash at the next rainfall event.

Research on this behaviour has not been included in this study. Experience elsewhere, such as gold mines in Western Australia with hypersaline tailings (eg. Fahey, 1997, Fahey & Newson, 1997; Newson & Fahey, 1998) suggests that evaporation rates can be significantly reduced at high salinities and where thick crusts are formed. If the crust is removed, the evaporation rates can be within 55% to 75% of potential evaporation rates. Therefore, the discontinuous, thin crust formed on occasions during the summer months at Loy Yang should not significantly limit evaporation rates from the surface of the ash. On the basis of this work, it is assumed that the lower overall salinity of leached ash does not provide a significant degree of osmotic suction within the ash. The formation of salt crusts and the potential osmotic suction created within pore fluids are recommended for further research, to ascertain if the above assumptions are indeed valid for ash management in the Latrobe Valley.

Overall, the Dry and Wet Cells demonstrated moderate permeability and quick response to the various irrigation or inflow events and changing climatic conditions.

5.3 Climate Data and Influent Water Quality

The climate data was gathered by the Loy Yang weather station, situated close to the north-western corner of the Ash Pond. The parameters monitored were rainfall, daily pan evaporation (Class A pan, monitored by Loy Yang staff), minimum and maximum temperature, and relative humidity, and wind speed. Average monthly climate data for Loy Yang is summarised in Table 5.1 (daily climate data is provided in Appendix A4). For comparison, average monthly Latrobe Valley climate data is shown in Figure 5.4.

Table 5.1 - Average Monthly Climate Data for Loy Yang July 1997 to August 1998

1997	July	Aug.	Sep.	Oct.	Nov.	Dec
Rainfall (mm)	43.2	57.2	55.2	54.4	69.6	20.7
Pan Evaporation (mm)	16.9	64.2	58.9	121	123	237
Max. Temperature (^{O}C)	nd	nd	nd	20.0	22.0	23.9
Min. Temperature (^{O}C)	nd	nd	nd	8.6	10.5	11.9
Max. Rel. Humidity (%)	nd	nd	nd	95	94	93
Min. Rel. Humidity (%)	nd	nd	nd	54	54	47
Daily Wind Speed (km/hr)	nd	nd	8.2	10.8	9.9	11.5

1998	Jan.	Feb.	Mar.	Apr.	May	June	July	Aug.
Rainfall (mm)	50.4	62.2	7.2	29.9	32.4	51.2	40.8	27.2
Pan Evaporation (mm)	102	149	165	57.7	53.2	32.7	27.0	32.0
Max. Temperature (^{O}C)	27.2	26.7	24.2	nd	15.6	13.0	11.3	14.0
Min. Temperature (^{O}C)	15.0	12.9	11.8	nd	8.8	5.9	4.1	6.6
Max. Rel. Humidity (%)	94	94	94	nd	96	99	99	99
Min. Rel. Humidity (%)	48	45	49	nd	74	72	77	69
Daily Wind Speed (km/hr)	10.8	9.7	9.6	9.7	9.4	7.3	8.1	7.3

Note - nd is No Data (due to equipment malfunction). Available data is taken from daily pan evaporation monitoring by staff from Loy Yang Power Ltd.

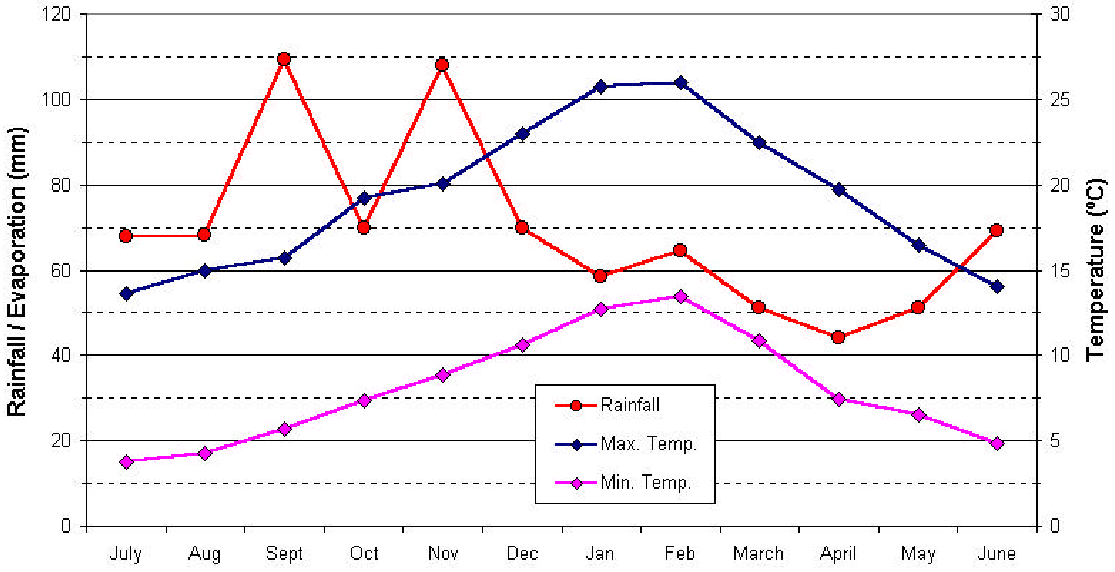


Figure 5.4 - Average Climate Data for the Latrobe Valley[3]

---

[3] - data courtesy of the Bureau of Meteorology, Melbourne, VIC.

Samples of rainfall water were taken from the rain gauge at the weather station and from the external tank at the Wet Cell and analysed for water quality. All samples had a salinity approximately less than 60 mg/L, with generally minor amounts of Al and Zn. Results are given in Table 5.2. The high Mo, Cr, Ni and Zn values recorded for the rainfall sample on 25-08-97 are anomalous. Investigations suggested that the metal surfaces within the rainfall gauge may be responsible for this anomaly. Further rainfall samples after this date were obtained by plastic bucket.

Table 5.2 - Average Influent Water Quality [1,2] (mg/L)

Date		pH	EC	Eh	TDS	Na	K	Ca	Mg	Fe	Al	SiO_2
18-08-97	T	7.0	10	345	55	12	0.95	3.1	1.6	5.8	0.29	6.7
25-08-97	R	7.0	4.2	-	13	9.6	0.54	1.7	1.1	1.3	0.19	0.5
24-02-98	T	6.7	8.9	370	56	9.0	0.25	3.3	1.6	1.3	0.12	7.0
14-04-98	R	5.7	11	450	50	-	-	-	-	-	-	1.0
17-06-98	T	7.5	8.7	290	48	7.7	0.96	2.3	1.2	5.6	0.67	5.5
29-06-98	R	6.3	7.0	394	35	-	-	-	-	-	-	0.3
13-08-98	T	6.8	7.3	285	50	7.7	1.1	2.9	1.5	1.6	0.18	5.6

Date		SO_4	Cl	HCO_3	As	Ba	Cr	Cu	Mo	Ni	Zn
18-08-97	T	9	13	10	0.001	0.01	<0.01	<0.02	-	-	-
25-08-97	R	1.6	6	2	0.001	<0.01	0.30	0.04	1.1	0.18	0.27
24-02-98	T	6	12	6	<0.001	0.02	-	0.02	<0.01	0.002	0.03
14-04-98	R	7	22	-	-	-	-	-	-	-	-
17-06-98	T	2	12	16	-	-	-	-	-	-	-
29-06-98	R	1	10	4	<0.001	0.02	0.09	<0.01	<0.01	0.01	0.26
13-08-98	T	5.6	12	8	<0.005	0.02	<0.01	<0.01	<0.01	<0.01	0.03

Notes : EC in mS/m; Eh in mV (redox). T - Influent Tank; R - Rainfall.

[1] - All samples have <2 mg/L CO_3. The sample from 24-02-98 had F < 0.3 and NO_3 of 0.35 mg/L.

[2] - B <0.01, Cd <0.001, Co <0.01, Pb <0.010, Hg <0.001, Se <0.01 and Sn <0.01 mg/L.

5.4 Results of Dry Cell Monitoring

5.4.1 Physical Properties

The geotechnical characteristics of the Dry Cell were determined in July 1998, including porosity and density, and are presented in Table 5.3. It was intended to determine these properites at construction, however, this was delayed. The samples were obtained from hand-auger drilled holes into the cell for ash sampling. A sampling tube was used to obtain undisturbed ash samples. The soil properties were determined in the laboratory at Victoria University. The values are similar to those measured for nearby Ash Dump sites, which the Dry Cell was designed to simulate (McKinley, 1998). There appears to be increasing moisture content and degree of saturation with depth, a phenomenon observed within the Ash Dump site (Pentland, 1998) and is thought to be influenced by self-weight consolidation, drainage of excess initial pore water, equilibration of pore pressures and the capillary break effect of the underlying drainage layer.

Table 5.3 - Geotechnical Properties of the Dry Cell

Site & Depth	Moisture Content	Density (kg/m^3)		Void Ratio	Porosity	Degree of Saturation
		Wet	Dry			
SC - 0 m	85.9%	1,111	598	2.92	74.5%	68.9%
NC - 0 m	86.2%	847	455	4.15	80.6%	48.7%
NC - 1.4 m	86.4%	1,027	551	3.25	76.4%	62.3%
NC - 2.6 m	96.2%	1,153	588	2.98	74.9%	75.5%

SC - South Central corner; NC - North Central corner.

5.4.2 Moisture Content Profile

The moisture content profile of the Dry Cell was determined at various times throughout the trial, including at the time of construction. The samples obtained in June 1997 (at the time of construction) were oven dried and weighed to calculate moisture content. These samples were obtained by dividing the cell into quarters, and collecting an ash sample from the approximate centre of each quarter. The June 1997 results are given in Table 5.4. As expected, there is no discernible pattern, with the average moisture content approximately 107.3% (or about 1,764 mm of stored water in the pore space of ash).

Table 5.4 - Vertical Moisture Content : June 1997 (as constructed)

Depth	Corner	Moisture Content	Depth	Corner	Moisture Content	Depth	Corner	Moisture Content
0 m	SE	106.6%	1.4 m	SE	110.5%	2.6 m	SE	105.0%
0 m	SW	107.8%	1.4 m	SW	120.1%	2.6 m	SW	111.0%
0 m	NW	99.6%	1.4 m	NW	91.1%	2.6 m	NW	99.0%
0 m	NE	113.4%	1.4 m	NE	118.0%	2.6 m	NE	105.5%
(top)			(middle)			(base)		

Two boreholes were drilled into the Dry Cell in January 1998, aiming to serve three functions. Firstly, provide ash samples for a vertical profile of leaching processes. Secondly, provide subsamples for moisture content determination via oven drying. Thirdly, the installation of 75 mm diameter aluminium access tubes (external) to trial a neutron probe for regular non-invasive and non-destructive moisture monitoring of the ash profile. The moisture data from these two boreholes is given in Table 5.5.

Table 5.5 - Vertical Moisture Content : January 1998

South-West Corner		North-East Corner	
Depth (m)	Moisture Content	Depth (m)	Moisture Content
0.1	68.0%	0.1	65.5%
0.55	58.1%	0.4	74.6%
1.21	90.7%	0.7	92.4%
1.56	79.7%	1.21	89.4%
1.71	75.7%	1.51	82.7%
2.12	66.4%	1.8	83.0%
2.36	86.9%	2.25	85.6%
2.63	89.8%	2.57	92.4%
2.67	89.3%	2.79	88.2%
2.85	37.1%	2.8	76.6%
		2.99	57.1%

Note - Drainage layer was observed >2.75 m. Care was taken to avoid drilling through the HDPE base.

Unfortunately, the use of the neutron probe was hampered due to difficulty in calibrating the probe data to the measured moisture data. A statistically acceptable regression was not possible given the scatter of the probe data and lack of response to the small changes in volumetric moisture within the ash profile. The neutron probe data has thus not been included. It is recommended that different techniques to assess the in-situ moisture content of ash be researched further to ascertain a viable and cost-effective technique for compliance monitoring of ash disposal sites.

The moisture data from July 1998, near the end of the trial, is provided in Table 5.3. The values ranging from 86% to 96% (about 1,458 mm) suggest a considerable evaporative effect due to the small quantities of drainage from the cell. The effect of evaporation appears to decrease with depth. Further analysis of the water balance will be presented later in this section.

5.4.3 Cumulative Flows

The flow components within the Dry Cell consist of rainfall, evaporation, drainage and change in moisture storage within the ash profile. The cumulative inflow is equal to the sum of the rainfall. Over the full year of the study, only minor quantities of leachate were generated, almost all of which was within the first 60 days of operation. The flow rates of leachate were also quite low. The results are shown in Figure 5.5 (the full data set is provided in Appendix A5).

The high initial leachate flow rate on day 0 (start of monitoring, 3 days after construction) is the result of a bend in the outflow pipe preventing immediate discharge. This problem was rectified and did not prove problematic afterwards. The initial discharge drained the water accumulated within the pipe and drainage layer, and hence flow rates would have quickly equilibrated to match the flow emanating from the ash layer into the drainage layer.

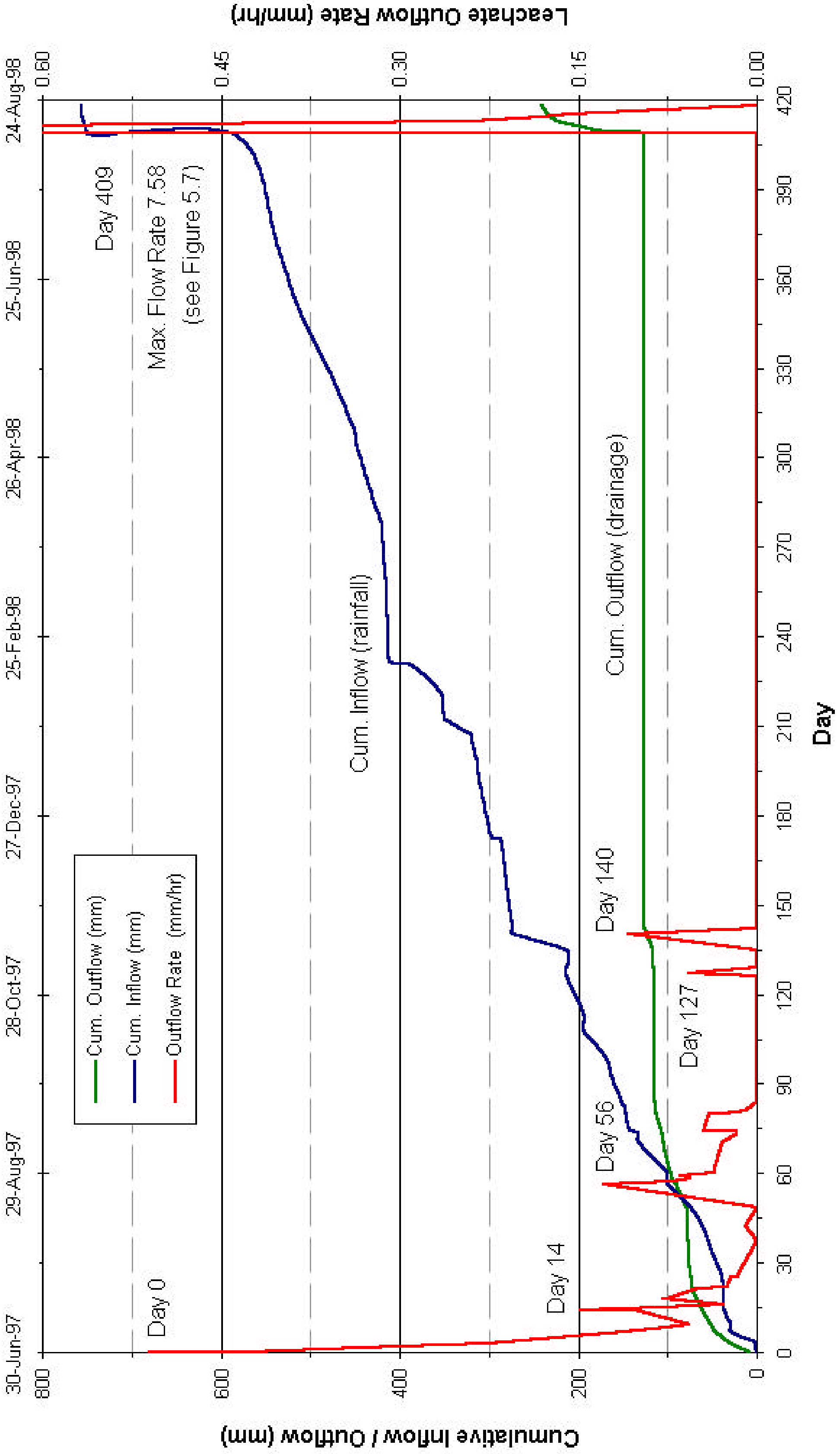


Figure 5.5 - Hydraulic Performance of the Dry Cell

During the first 50 days, a total of about 79 mm of leachate was generated, compared to a cumulative inflow (rainfall) of 74 mm. By day 60, the leachate generated was about 96 mm and cumulative inflow 100 mm. This shows an initial excess of outflow over inflow (cf. Figure 5.5), on the basis of measured data. This is most likely due to the sparse nature of the measured data during this time. The total outflow volume is estimated as the area under the flow rate versus time graph by linear interpolation. This presents a tendency to overestimate the outflow since a linear flow rate is assumed between measured data points compared to the exponential decline in flow rates. In addition, the initial leachate discharge may also be influenced by self-weight consolidation of the ash within the cell and equilibration of pore pressures leading to minor leachate generation. This behaviour has been observed at the current Ash Dump site (Pentland, 1998).

The only occurrence of leachate flow after this time was during a period of high rainfall in early November (1997). This event, however, produced only a very small quantity of leachate volume - less than 12 mm compared to approximately 60 mm of rainfall. The low flow rates were also difficult to measure accurately due to their dripwise nature. The remaining rainfall (~ 48 mm) has been held in soil moisture storage and gradually lost through evaporation. The flow rate data for the first 160 days is presented in Figure 5.6.

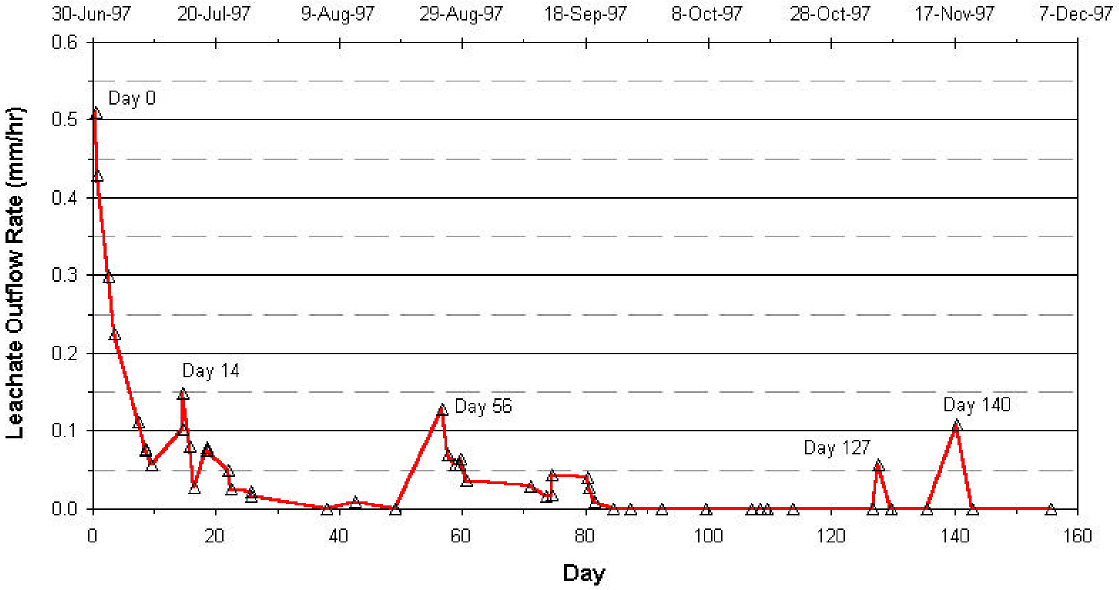


Figure 5.6 - Leachate Outflow Data, Days 0 to 160

A point of note is that a total of 92.4 mm of rainfall fell between Jan. 23 (day 207) and Feb. 17 (day 232), 1998, and yet there was no leachate generated. This corresponds to the higher temperatures and low rainfall during December and early January.

To obtain further samples of leachate from the Dry Cell, the irrigation tank was shifted from the Wet Cell and allowed to irrigate the Dry Cell on August 8, 1998 (day 408). A total of 160 mm (4,000 litres) was irrigated over a period of 10 hours (a rate of 16.0 mm/hr). Three leachate samples were obtained for analysis over succeeding days. The estimated volume of leachate collected was 115.6 mm, about two-thirds of the input. The response of the ash showed an initial delay with no leachate emanating from the collection pipe until 1 day after the start of irrigation (day 409). The leachate flow rate rapidly increased from this point, reaching a maximum value of 7.6 mm/hr just over four hours later. It also decreased just as rapidly, declining to 1.8 mm/hr after a further nine hours. The leachate outflow data for this event is given in Figure 5.7.

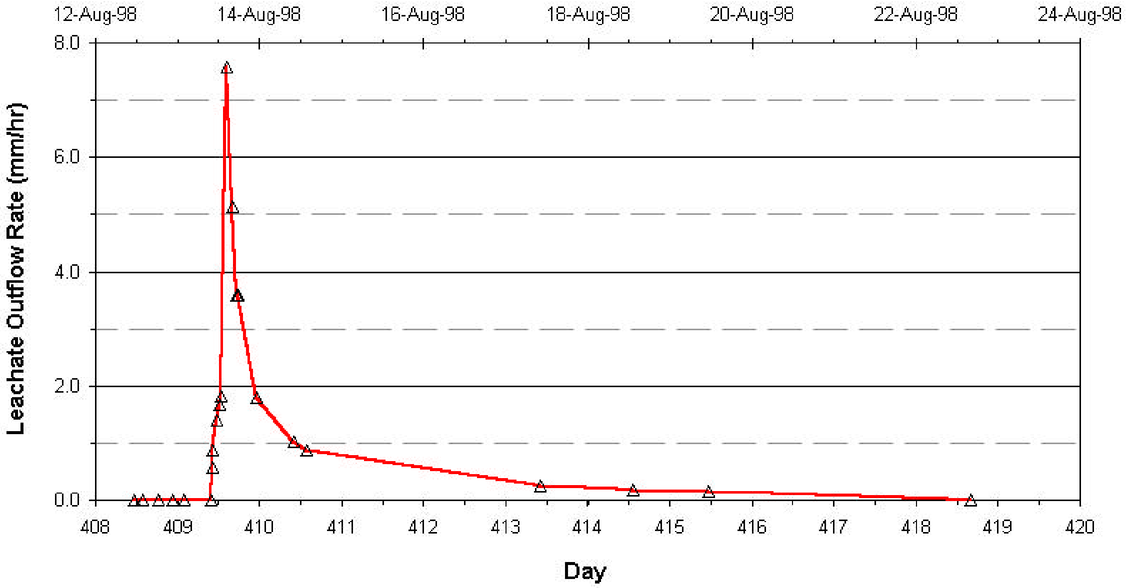


Figure 5.7 - Leachate Outflow Data, Days 408 to 420

By completion of the field trial in August 1998, approximately 755.8 mm of rainfall (including the extra tank water) entered the cell, whereas only 241.2 mm of leachate has been calculated to discharge from the cell (half of this discharge is attributed to the tank of water added). Given that the pore volume of the Dry Cell is approximately 2,298 mm, the Dry Cell has not reached any significant stage of field leaching with about one tenth of a pore volume of leachate generated to date.

5.4.4 Water Balance of the Dry Cell

Given the monitoring data collected during operation of the Dry Cell, it is possible to analyse the water balance over this period. The water balance comprises rainfall, irrigation, evaporation, change in soil moisture storage and drainage (leachate). The climate data monitored by Loy Yang includes Pan Evaporation, a measure of the total potential evaporation from a free water surface. In contrast, evaporation in the cell is from the ash surface and this is known as Actual Evaporation and represents the actual loss of water from the pore volume (Wilson *et al.*, 1994). The Actual Evaporation has not been measured in the operation and testing of the Dry Cell. On the basis of collected data, it is possible to calculate the Actual Evaporation from inflow, storage and drainage data. The values for these components are summarised in Table 5.6. By considering the cell as a single volume, the water balance can be considered as (eg. Koerner & Daniel, 1997; Blight, 2000) :

$$\text{Actual Evaporation} = \text{Inflow} - \Delta(\text{Soil Storage}) - \text{Drainage} \qquad \text{5-1}$$

Table 5.6 - Components of the Dry Cell Water Balance Over Time (mm)

	Total Inflow	Soil Moisture	Drainage	Pan Evaporation	AE
30-06-97	0	1,764	0	0	
Change	+349.1	-432	+125.7	+723.0	+655.4
28-01-98	349.1	1,332	125.7	723.0	
Change	+406.7	+126	+115.5	+516.6	+165.2
22-08-98	755.8	1,458	241.2	1,239.6	
Overall	+755.8	-306	+241.2	1,239.6	+820.6

The first six months shows that the calculated actual evaporation is about 90% of the pan (or potential) evaporation, compared to the second six months where the calculated actual evaporation is about 32% of pan evaporation. This reflects the initial loss of water held in storage at the start of the trial, which is not replenished through rainfall or inflow. Overall, the calculated actual evaporation is about two thirds of the pan evaporation. The extent of actual evaporation would vary depending on seasonal climatic conditions at the Loy Yang site.

5.4.5 Leachate Chemistry

The water quality of leachate discharged from the Dry Cell was measured in the early months of its operation and during artificial irrigation at the end of monitoring in August 1998. A total of 15 samples were collected and analysed for major ions and a suite of trace elements (Al, As, B, Ba, Cu, Co, Cr, Cd, Hg, Mo, Ni, Pb, Se, Sn, Zn). There were no samples between November 1997 and August 1998 because no leachate was generated from the base of the cell. The results are given in Tables 5.7 and 5.8.

The initial samples of leachate gave only slightly oxidising conditions (Eh around +25 to +45 mV). However, this was quickly increased to a stronger oxidising state with the redox value stabilising for the remainder of the study around +260 to +280 mV. The leachate is moderately to highly saline, being dominated by Na, SO_4 and Cl. The leachate is moderately alkaline, with the pH varying around 8.5 to 9. The concentration of iron in Dry Cell leachate was generally less than 0.2 mg/L. Most trace elements were either very low or below detection limits, which would be due to the alkaline nature of the leachate. However, the notable exceptions are B, Ba, Mo and Se, which consistently register in the leachate with distinct trends over time. The following elements were consistently at or below detection limits (mg/L) : Cd <0.001, Co < 0.01, Cr < 0.01, Cu < 0.01, Pb < 0.01, Hg < 0.001, Ni < 0.01 and Sn < 0.01.

There has been no discernible pattern in the leachate data, apart from being of similar magnitude. The small leachate sample obtained in November 1997 gave a much higher salinity. This result may be due to the long time between samples (i.e. a higher residence time), which allowed more chemical constituents to dissolve or diffuse from the ash matrix. The extra time also allowed a progressively lower moisture content within the ash profile due to evaporation, effectively concentrating the leachate (suggested by the higher Cl concentration of this sample). With the advent of a high rainfall period (days 120 to 140), this water was flushed out from the ash through advective flow with minimal mixing due to the low volumes. There does not appear to be any increase in trace element concentrations with this sample (except higher Se), only an increase in salinity. Further analysis of trace element geochemistry is given in Chapter 7.

Table 5.7 - Leachate Quality : Major Ions (mg/L)

Date	pH	EC	Eh	TDS	SO_4	Cl	HCO_3	CO_3	F	NO_3
30-06-97	7.7	1,100	-	8,700	-	-	-	-	-	-
30-06-97	7.6	1,100	-	9,100	-	-	-	-	-	-
30-06-97	7.9	1,200	26	9,400	3,100	740	110	-	-	0.32
02-07-97	7.9	1,300	-	10,000	-	-	-	-	-	-
03-07-97	9.0	1,300	47	10,000	3,500	700	70	36	-	0.19
07-07-97	9.3	1,300	42	11,000	2,600	720	46	64	-	0.33
18-07-97	8.9	1,600	280	11,000	8,500	630	56	52	-	-
25-07-97	8.9	1,400	258	11,000	6,300	730	48	48	-	-
04-08-97	8.8	1,400	-	10,000	6,800	790	-	-	-	-
07-08-97	8.6	1,500	290	10,000	6,000	790	92	28	-	-
18-08-97	9.1	1,500	280	10,000	6,200	760	50	50	-	-
04-11-97	8.7	2,100	-	17,000	13,000	1,100	-	-	-	-
13-08-98	8.3	1,700	276	-	9,200	720	210	24	0.4	4.0
13-08-98	8.4	1,600	283	14,000	7,200	720	120	28	0.4	2.6
14-08-98	8.5	1,600	280	14,000	8,100	720	120	20	0.4	2.4

Note - pH in units; Eh (redox) in mV; EC (elec. Cond.) in mS/m.

Table 5.7 (cont'd) - Leachate Quality : Major Ions (mg/L)

Date	Na	K	Ca	Mg	Fe	Al	SiO_2
30-06-97	-	-	-	-	-	-	-
30-06-97	-	-	-	-	-	-	-
30-06-97	3,300	80	110	74	<0.01	0.06	9.5
02-07-97	-	-	-	-	-	-	-
03-07-97	3,500	110	93	25	<0.01	0.26	8.5
07-07-97	3,500	110	100	25	<0.01	0.99	9
18-07-97	3,500	120	130	27	0.09	1.40	8.7
25-07-97	2,100	96	110	22	0.06	0.16	8.5
04-08-97	3,400	-	120	42	-	-	-
07-08-97	3,500	100	130	43	0.04	0.13	10
18-08-97	3,400	70	120	52	0.13	0.08	11
04-11-97	5,800	-	160	70	0.83	-	-
13-08-98	4,200	120	210	220	0.13	0.16	9.7
13-08-98	3,800	130	150	130	0.05	0.09	7.4
14-08-98	3,800	130	160	130	0.06	0.09	7.7

Table 5.8 - Leachate Quality : Trace Elements (mg/L)

Date	As	B	Ba	Mo	Se	Zn
30-06-97	-	-	-	-	-	-
30-06-97	-	-	-	-	-	-
30-06-97	0.007	2.2	0.17	0.28	0.89	<0.01
02-07-97	-	-	-	-	-	-
03-07-97	0.009	2.7	0.18	0.32	0.59	<0.01
07-07-97	0.009	2.9	0.17	0.33	0.30	<0.01
18-07-97	0.006	2.4	0.07	0.26	0.84	0.01
25-07-97	<0.01	0.9	0.03	0.08	0.70	<0.01
04-08-97	0.009	-	0.14	0.31	0.095	<0.01
07-08-97	0.007	3.0	0.14	0.33	0.40	<0.01
18-08-97	0.014	3.0	0.03	-	0.97	<0.01
04-11-97	0.003	-	0.03	0.39	2.2	<0.01
13-08-98	<0.005	2.8	0.16	<0.01	3.1	0.08
13-08-98	<0.005	3.4	0.15	<0.01	3.6	0.05
14-08-98	<0.005	3.5	0.14	<0.01	3.8	0.06

5.4.6 Ash Quality

During the full year study period, ash samples were collected from the Dry Cell and analysed for major and trace elements. These included surface samples taken approximately every three months, and two hand-augered boreholes for vertical sampling every six months. The boreholes were carefully backfilled to ensure no preferrential flow path existed after drilling. A total of 26 ash samples were collected. The results are given in Tables 5.9 and 5.10. For trace elements, comparison of the averages to the EPAV clean fill criteria are also included. There is no discernible pattern in the ash chemistry, except for the typical variability found in ash samples. The average concentrations of trace elements are within EPAV criteria for consideration as fill material, as highlighted earlier in Section 2.2.5, with only a small number of samples near or marginally above the criteria for certain elements (such as Ba with 11 samples and Hg with 5 samples). This further demonstrates the lower leachability of ash excavated from the Loy Yang Ash Pond.

5.4.7 Summary of the Dry Cell

The Dry Cell has provided important data on likely leachate generation rates and leachate chemistry. The ash is holding most rainfall (or applied water) within porous storage, signifying the unsaturated nature of the ash. For the majority of the trial, no leachate was generated, and it took persistent rainfall over an extended period before very small quantities were generated in November 1997. A further period of persistent rainfall in late January-February 1998, however, failed to generate discharge of leachate.

The leachate that was generated is of moderate salinity, dominated chiefly by Na and SO_4, with minor amounts of Cl, Ca, Mg and K. The trace elements detected in the leachate were As, Ba, B, Mo, Se, and to a lesser extent Zn. Most elements analysed for were very close to or below detection limits.

The unsaturated and evaporative behaviour of the Dry Cell suggests that these processes are crucial in modelling and predicting moisture flow, leachate and geochemistry.

Table 5.9 - Ash Quality : Major Elements (% dry basis)

Date	Site[1]	SO_4	Cl	Na	K	Ca	Mg	Fe	Al	A.I.	LOI
07-07-97	0 m NW	0.76	0.073	1.9	0.150	4.0	6.2	4.1	3.4	58	28.6
07-07-97	0 m SE	0.69	0.070	1.6	0.110	3.6	5.5	3.6	2.7	59	24.3
07-07-97	1.5 m C	0.73	0.073	1.9	0.140	3.5	5.2	4.0	3.3	56	28.9
07-07-97	3 m C	0.88	0.072	1.2	0.110	3.4	4.9	3.8	2.5	62	28.3
20-10-97	0 m C	0.76	0.180	1.6	0.130	2.9	4.5	4.7	3.0	66	20
20-10-97	0 m SW	1.20	0.180	1.5	0.120	2.9	4.3	5.6	3.1	67	23
03-02-98	0.10 SW	0.52	0.090	0.84	0.075	2.3	4.5	3.3	2.6	62	20
03-02-98	1.21 SW	0.58	0.084	1.1	0.080	3.2	4.6	2.9	2.4	63	19
03-02-98	2.12 SW	0.45	0.057	1.2	0.120	3.0	4.5	4.2	3.3	70	17
03-02-98	2.67 SW	0.52	0.067	1.3	0.130	3.2	5.2	4.1	3.2	67	19
03-02-98	0.10 NE	0.46	0.089	1.1	0.120	2.7	3.9	3.8	2.9	64	21
03-02-98	1.21 NE	0.72	0.082	0.58	0.041	2.1	3.4	1.9	1.6	56	20
03-02-98	1.80 NE	0.72	0.077	0.93	0.090	3.4	5.5	3.8	2.8	62	18
03-02-98	2.79 NE	0.53	0.067	0.74	0.071	2.2	3.7	2.8	2.2	62	18
19-05-98	0 m N	0.48	0.160	1.6	0.160	3.1	4.4	4.8	3.4	65	13
19-05-98	0 m S	0.63	0.120	1.6	0.160	2.9	4.4	5.3	3.9	54	13
07-08-98	0 m N	0.23	-	0.94	0.110	2.6	4.1	5.8	3.7	64	30
07-08-98	0.30 N	0.54	-	1.4	0.110	3.0	5.1	5.8	3.7	63	20
07-08-98	0.75 N	0.59	-	1.6	0.110	3.6	7.1	7.4	4.8	49	22
07-08-98	1.50 N	0.48	-	1.1	0.100	2.9	5.0	5.4	4.4	60	17
07-08-98	2.75 N	0.52	-	1.5	0.120	3.0	4.9	6.1	3.7	65	21
07-08-98	0 m S	0.18	-	0.75	0.093	2.7	3.5	4.8	3.3	62	20
07-08-98	0.30 S	0.86	-	1.2	0.095	3.7	7.1	6.0	4.1	51	17
07-08-98	0.75 S	0.6	-	1.1	0.110	3.4	5.1	4.8	3.6	60	16
07-08-98	1.50 S	0.36	-	1.2	0.089	2.5	3.6	4.7	3.2	66	16
07-08-98	2.50 S	0.59	-	1.4	0.120	3.3	6.2	5.8	4.6	57	21
Average		0.66	0.096	1.29	0.113	3.0	4.7	3.9	2.9	62	20.7

[1] - “2.79 NE” is depth 2.79 m North East corner. LOI - Loss On Ignition; A.I. - Acid Insoluble; NE - North East corner; SW - South West corner; C - Centre.

Table 5.10 - Ash Quality : Trace Elements (mg/kg) (dry basis)

Date	Site	As	B	Ba	Cd	Cr	Co	Cu
07-07-97	0 m NW	<5	160	280	<0.2	29	19	36
07-07-97	0 m SE	6.6	110	330	<0.2	34	16	27
07-07-97	1.5 m C	9.4	150	330	0.4	31	26	37
07-07-97	3 m C	8.9	140	320	<0.2	33	18	38
20-10-97	0 m C	2.6	150	430	0.1	45	30	42
20-10-97	0 m SW	6.5	160	460	0.13	62	20	49
03-02-98	0.10 SW	<5	160	270	<0.2	35	24	43
03-02-98	1.21 SW	<5	230	160	<0.2	34	28	42
03-02-98	2.12 SW	6.2	150	420	<0.2	33	25	38
03-02-98	2.67 SW	<5	180	240	0.3	33	20	40
03-02-98	0.10 NE	7.7	180	320	<0.2	30	17	41
03-02-98	1.21 NE	8.5	230	160	<0.2	35	24	45
03-02-98	1.80 NE	7.5	210	170	<0.2	40	23	45
03-02-98	2.79 NE	8	170	230	<0.2	36	26	40
19-05-98	0 m N	10	160	420	<0.1	38	18	42
19-05-98	0 m S	7	160	320	<0.1	34	19	37
07-08-98	0 m N	<5	150	440	<0.2	30	420	38
07-08-98	0.30 N	<5	160	650	<0.2	36	19	45
07-08-98	0.75 N	<5	200	560	<0.2	37	17	57
07-08-98	1.50 N	<5	190	420	<0.2	33	23	42
07-08-98	2.75 N	<5	160	320	<0.2	33	24	41
07-08-98	0 m S	<5	140	580	<0.2	31	18	36
07-08-98	0.30 S	<5	250	400	<0.2	56	22	64
07-08-98	0.75 S	<5	170	490	<0.2	32	22	34
07-08-98	1.50 S	<5	130	460	<0.2	27	20	35
07-08-98	2.50 S	<5	150	200	<0.2	36	18	34
Average[1]		7.4	169	304	0.23	36	22	40
EPAV (1993)		30		400	5	250	50	

Note - C is "Centre"; NE - North-East and the like. [1] - Excluding values below detection limits.

Table 5.10 (cont'd) - Ash Quality : Trace Elements (mg/kg) (dry basis)

Date	Site[1]	Hg	Mo	Ni	Pb	Se	Sn	Zn
07-07-97	0 m NW	2.4	<5	43	7.6	7.9	<5	75
07-07-97	0 m SE	2.1	<5	33	7.7	11	<5	64
07-07-97	1.5 m C	1.6	<5	35	9.1	12	<5	78
07-07-97	3 m C	2.2	<5	35	13	<5	<5	74
20-10-97	0 m C	-	7	37	12	<5	<5	80
20-10-97	0 m SW	-	10	41	13	<5	<5	85
03-02-98	0.10 SW	0.6	<5	45	12	<5	<5	80
03-02-98	1.21 SW	1.1	<5	45	12	<5	<5	73
03-02-98	2.12 SW	0.69	<5	42	10	<5	<5	89
03-02-98	2.67 SW	0.81	<5	39	13	<5	<5	88
03-02-98	0.10 NE	0.56	<5	38	10	<5	<5	140
03-02-98	1.21 NE	1.2	23	46	9.5	7.7	<5	80
03-02-98	1.80 NE	1.2	<5	47	12	<5	<5	92
03-02-98	2.79 NE	1.1	<5	46	13	<5	<5	93
19-05-98	0 m N	1.2	4.6	32	9.5	5.0	<1	84
19-05-98	0 m S	1.3	3.4	33	13	5.5	<1	75
07-08-98	0 m N	1.4	<5	130	7.3	<5	<5	84
07-08-98	0.30 N	2.5	<5	34	12	<5	<5	120
07-08-98	0.75 N	2.1	<5	42	14	<5	<5	140
07-08-98	1.50 N	1.7	<5	42	<5	<5	<5	110
07-08-98	2.75 N	1.6	<5	41	13	<5	<5	110
07-08-98	0 m S	1.3	<5	40	8.4	<5	<5	76
07-08-98	0.30 S	1.6	<5	110	15	<5	<5	150
07-08-98	0.75 S	1.4	<5	42	11	<5	<5	76
07-08-98	1.50 S	1.8	<5	33	12	<5	<5	88
07-08-98	2.50 S	1.4	<5	34	10	<5	<5	91
Average		1.29	9.6	40	11	8.2	<5	84
EPAV (1993)		2.0	40	100			50	

5.5 Results of Wet Cell Monitoring

5.5.1 Physical Properties

The geotechnical characteristics of the Wet Cell were determined in July 1998, including porosity and density, and are presented in Table 5.11. It was intended to determine these properites at construction, however, this was delayed. The sampling methodology was the same as that used for the Dry Cell (see Section 5.4.1). The values are similar to those for the nearby Ash Dump site and the Dry Cell. Similar to the Dry Cell, the moisture content and degree of saturation appear to increase with depth.

Table 5.11 - Geotechnical Properties of the Wet Cell

Site & Depth	Moisture Content	Density (kg/m^3) Wet	Dry	Void Ratio	Porosity	Degree of Saturation
C - 0 m	86.0%	832	447	4.23	80.9%	47.6%
NW - 0 m	81.3%	812	448	4.22	80.9%	45.0%
NW - 1.4 m	85.1%	1,080	583	3.01	75.1%	66.1%
NW - 2.6 m	93.7%	1,127	582	3.02	75.1%	72.6%

C - Central corner; NW - North Western corner.

5.5.2 Moisture Content Profile

The moisture content of the Wet Cell was determined at the time of construction and at further times throughout the trial. The samples obtained in June 1997 during construction were oven dried and weighed to calculate moisture content. These were sampled based on dividing the cell into quarters, and collecting an ash sample from the approximate centre of each quarter. Results for June 1997 are given in Table 5.12. There is no apparent pattern, with the average moisture content approximately 91.9% (about 1,420 mm), slightly lower than the Dry Cell. Two boreholes were drilled into the Wet Cell in January 1998, serving the three functions as outlined for the Dry Cell. The moisture data from these two boreholes is given in Table 5.13. The neutron probe data has not been included.

Table 5.12 - Vertical Moisture Content : June 1997 (as constructed)

Depth	Corner	Moisture Content	Depth	Corner	Moisture Content	Depth	Corner	Moisture Content
0 m	SE	88.9%	1.4 m	SE	87.9%	2.6 m	SE	83.6%
0 m	SW	84.7%	1.4 m	SW	97.2%	2.6 m	SW	92.0%
0 m	NW	83.0%	1.4 m	NW	101.5%	2.6 m	NW	94.5%
0 m	NE	100.0%	1.4 m	NE	86.6%	2.6 m	NE	102.6%

Table 5.13 - Vertical Moisture Content : January 1998

South-East Corner		North Central	
Depth (m)	Moisture Content	Depth (m)	Moisture Content
0.25	91.7%	0.3	105.5%
0.70	89.3%	0.8	86.1%
1.10	95.2%	1.23	87.7%
1.65	93.5%	1.63	91.3%
1.92	81.3%	1.82	98.0%
2.18	89.2%	2.35	95.3%
2.58 (1)	101.3%	2.65	103.0%
2.58 (2)	92.6%	2.71	94.0%
2.58 (3)	90.0%	2.73	86.2%

Note - 3 samples from the SE borehole were obtained at 2.58 m.

5.5.3 Cumulative Flows

The flow components within the Wet Cell also demonstrated unsaturated soil behaviour, although higher inflow rates took place into this cell. After construction in late June 1997, the Wet Cell exhibited similar flow rates to the Dry Cell from the leachate discharge pipe. The leachate flow rate decreased over the first few weeks as the ash consolidated. However, as the external water supply was added, the peak flow rate of leachate increased with each addition of water. The decrease in the leachate flow rate following each event was rapid. The peak flow rate for each of the first few events of adding water showed an increasing trend. The results are shown in Figure 5.8. The full set of leachate flow rate, inflow and outflow data and graphs are presented in Appendix A6. Each graph has about 3 events over a period of up to 50 days or less.

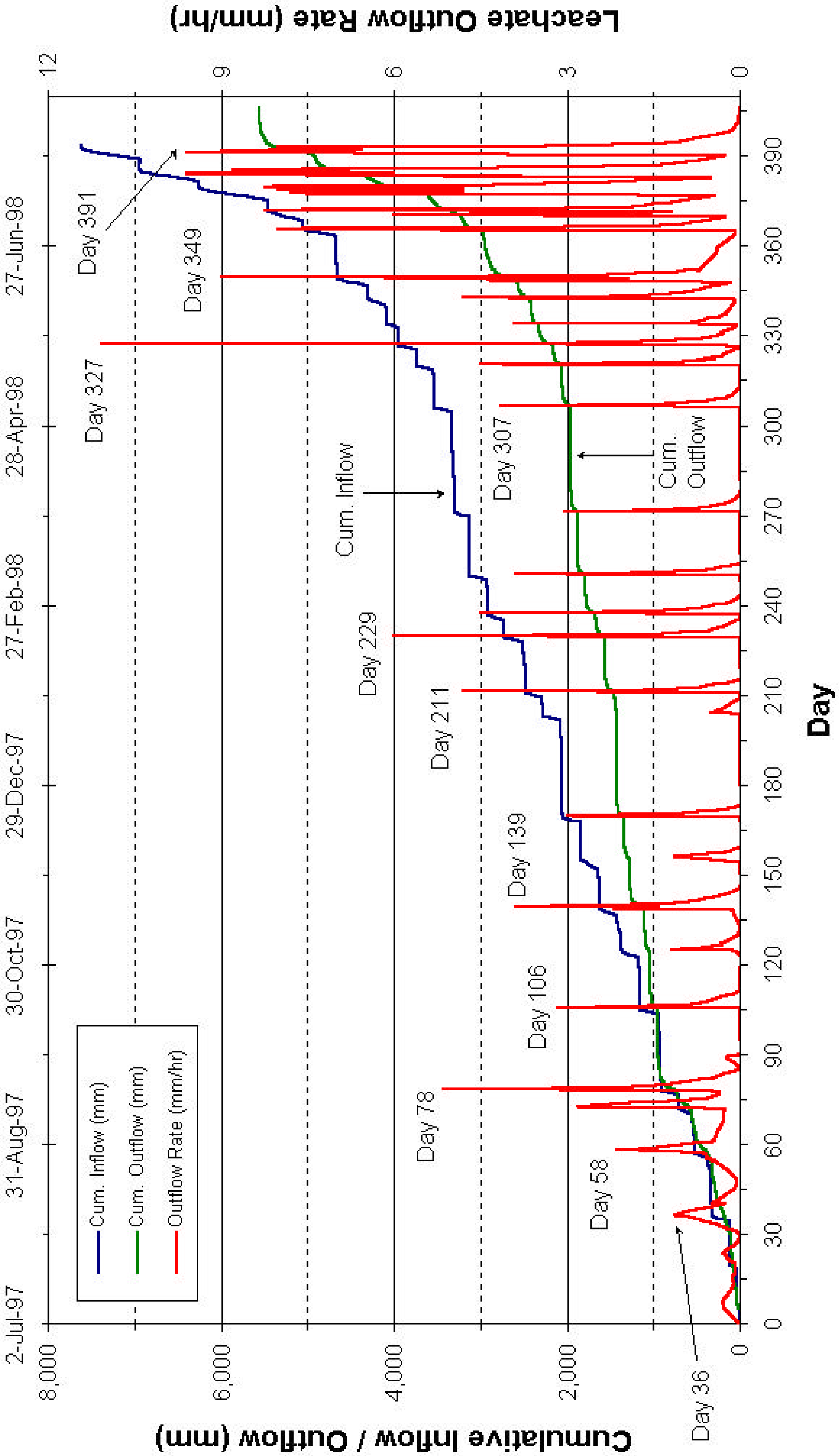


Figure 5.8 - Hydraulic Performance of the Wet Cell

For the first few months of operation there were some occasions where the estimated outflow from the Wet Cell slightly exceeded the inflow from rainfall and the source tank. As indicated earlier for the Dry Cell, this initial excess may be influenced by the use of linear interpolation in the calculating the volume of leachate outflow, by self-weight consolidation of the ash within the cell and/or equilibration of pore pressures leading to minor leachate generation. This is thought to explain the early data for the Wet Cell, where the outflow marginally exceeds inflow at some points.

In general, the variation in peak flow rate for each event of adding water can be explained on the basis of unsaturated flow mechanics. For an unsaturated soil system, the hydraulic conductivity of a soil depends on its moisture content (or storage), and thus the flow velocity is also dependent on moisture content. As the moisture content of the ash profile increases with the addition of water, the hydraulic conductivity increases and higher flow rates through the ash profile can be achieved. This is particularly highlighted by the lower flow rates achieved through the summer months, shown in Figure 5.9 (days 150 to 230, i.e. 29 Nov. 1997 to 7 Feb. 1998). The first addition of tank water around days 156 and 204 gave low leachate flow rates, compared to the successive events on days 170 and 211, respectively, which generated significantly higher leachate flow rates.

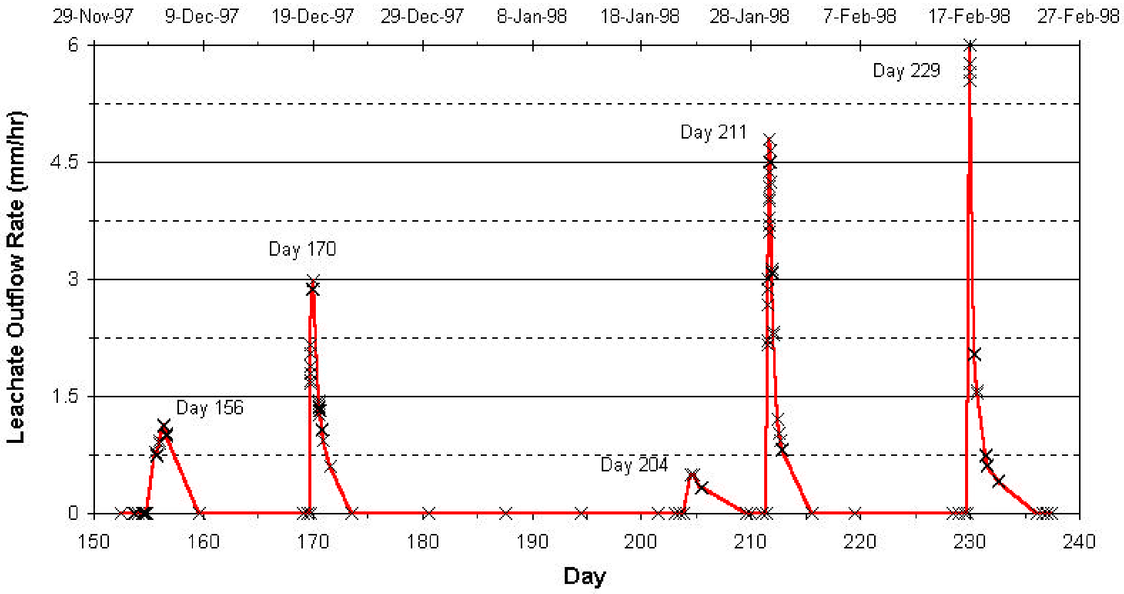


Figure 5.9 - Increasing Maximum Leachate Flow Rates During Summer

The event on day 204 (22 Jan. 1998) demonstrates that despite a full tank of 200 mm added to the cell, the overall flow rate (and volume) was very low, indicating that the majority of the water was held in soil storage due to the much drier profile (longer period between events and semi-arid climatic conditions). This corresponds to the low rainfall during December and January to this point, with increasing summer heat and dry air conditions. The next two events (day 211, 29 Jan. 1998; and day 229, 16 Feb. 1998), however, achieved two of the highest outflow rates recorded to that point in time. The soil moisture deficit of the ash profile had been reduced by the influx of water on day 204, allowing water to flow through the ash profile relatively rapidly. The majority of rainfall in both January and February also fell just a few days before these events, ensuring a moist ash profile near the surface before these two events. A total of 92.4 mm fell between January 23 and February 17, 1998.

For the last two months of operation, an accelerated program of irrigation was undertaken, where up to four tanks per week were added in quick succession to maintain near-constant irrigation for the first few days of the week. Again, typical unsaturated soil behaviour is evident. As the second or third tanks of water were added to the cell, the peak outflow rate also increased, indicating a higher permeability due to a higher moisture content profile within the ash. For the final weeks in July 1998, the outflow rate almost approached the inflow rate, suggesting that the ash was close to behaving as a saturated soil, where the hydraulic conductivity may have been controlled by saturated behaviour. Alternatively, this situation may also represent the case where the hydraulic gradient approaches unity (near-saturation), based on the ponding occurring by this time, and the inflow rate is therefore equal to the hydraulic conductivity for the prevailing soil moisture content and climatic forcing conditions.

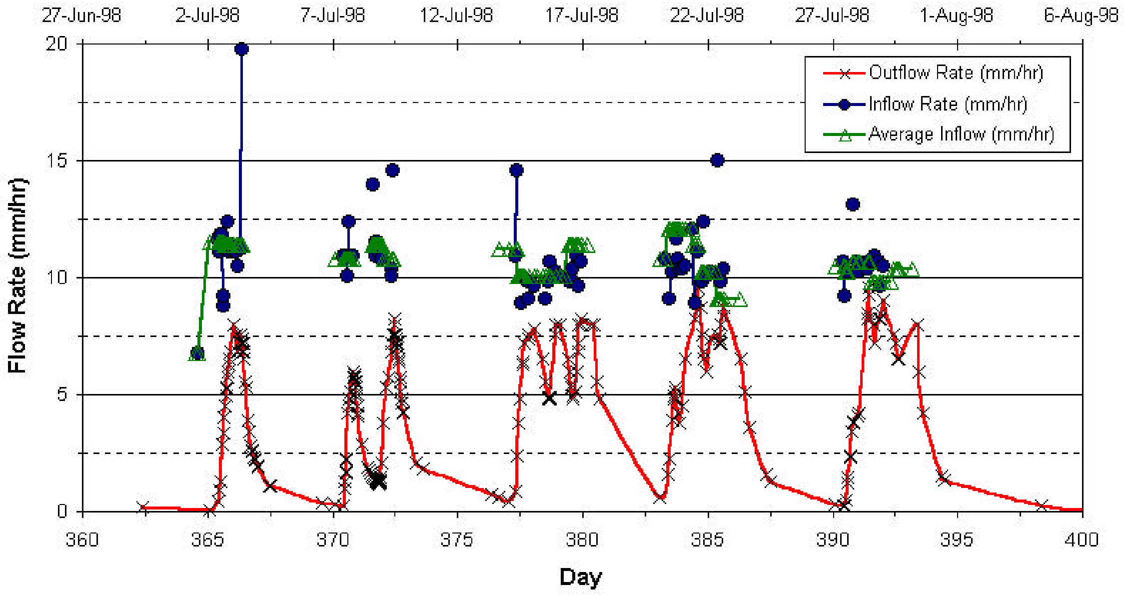


Figure 5.10 - Increasing Leachate Flow Rates During Winter From Irrigation

One important pattern to note is the respective gradients of the Inflow and Outflow curves. During both the Winters of 1997 (up to day 120; 30 Oct. 1997) and 1998 (from day 330; 28 May 1998), the ratio of the gradient of cumulative outflow to the gradient of cumulative inflow is about unity (the quantity of water entering the cell is approximately the same as that discharging). By Spring 1997 (~ day 200; 18 Jan. 1998), however, the outflow-to-inflow ratio begins to decrease. This ratio is lowest during Summer (~ day 260; 19 Mar. 1998), and begins to increase again during Autumn 1998 (~ day 330; 28 May 1998). This is expected since the evaporative demand during Summer is higher and therefore less water is available for discharge as leachate.

A total of approximately 7,616.8 mm of combined rainfall and source tank water has entered the cell, whereas about 5,555.2 mm of leachate has been calculated to discharge from the cell. Given the pore volume of the Wet Cell at about 2,340 mm, this represents about 2.4 pore volumes of active leaching (based on leachate discharge).

5.5.4 Water Balance of the Wet Cell

The water balance over the operational period is now analysed for the Wet Cell. The water balance comprises rainfall, irrigation, evaporation, change in soil moisture storage and drainage (leachate). The values for these components are summarised in Table 5.14, based on equation 5-1 and the approach used earlier for the Dry Cell.

Table 5.14 - Components of the Wet Cell Water Balance Over Time (mm)

	Total Inflow	Soil Moisture	Drainage	Pan Evaporation	AE
30-06-97	0	1,420	0	0	
Change	+2,304	+14	+1,455	+723.0	+835
28-01-98	2,304	1,434	1,455	723.0	
Change	+5,313	-97	+4,100	+516.6	+1,310
22-08-98	7,617	1,337	5,555	1,239.6	
Overall	+7,617	-83	+5,555	+1,239.6	+2,145

The first six months gives a calculated actual evaporation rate about 15% higher than the pan (or potential) evaporation rate, compared to the second six months where the calculated actual evaporation rate is about 250% higher. Overall, the calculated actual evaporation exceeds pan evaporation by 173%. The cause of this excess is unclear, but the following factors can be taken into account. First, there is a small error in the cumulative calculation of both inflow and outflow, and this could conservatively be expected to be of the order of 5 to 10% of the figures above (based on the author's knowledge of flow events and cell behaviour). Second, the water balance would be altered if there were leaks through the HDPE base of the cell, although this is not considered likely due to the near-unity ratio of inflow and outflow volumes in July 1998. Third, Blight (2000) argues that saturated soil, compared to free-standing water, can give rise to higher actual than pan evaporation rates since soil is undulating and provides a higher effective surface area. The increase in actual over pan evaporation is only slight (up to 30%), however, and Blight's data could not account for the differences above (although if the error was at 10%, then the above calculations are closer to pan evaporation). The ash does have a high porosity and thus could accomplish higher actual evaporation rates. Clearly this is an area for further research.

5.5.4 Leachate Chemistry

A total of 52 leachate samples were collected from the Wet Cell, and results are given in Tables 5.15 to 5.18 and Figures 5.11 and 5.12. The leachate quality is graphed as normalised concentrations with respect to the average leachate concentration between July and September 1997, when concentrations were approximately constant.

The initial leachate obtained was of similar salinity concentration and chemistry to the leachate from the Dry Cell, being dominated by Na, SO_4 and Cl and of moderately alkaline pH. The salinity and concentration of major elements remained constant for about three months, from where they decreased until the end of the trial. The same trace elements were also leached at similar concentrations to the Dry Cell.

The initial samples of leachate had slightly oxidising conditions (around +45 mV). However, this subsequently increased to much stronger oxidising conditions with the redox state stabilising around +300 to +380 mV. As the irrigation rate was increased in July and August 1998, the redox state began to decrease to about +160 to +180 mV.

There was an average decrease of about 90.3% in most major elements between July 1997 and August 1998, especially Na, SO_4 and Cl (which account for the majority of leachate salinity). The concentration of iron in Wet Cell leachate was always less than 0.5 mg/L. There were some trace elements leached, namely Al, As, B, Ba, Mo and Se. The change in leachate concentrations over time was not as marked for trace elements as for major elements, except for B, the concentration of which actually increased over the trial period. The average leachate chemistry over time is presented in Tables 5.15 and 5.16. The leachate chemistry through the trial is presented in Figures 5.11 and 5.12, based on the concentration relative (normalised) to the initial concentration over the first 3 months. The following elements were consistently near or below detection limits (all mg/L) : Cd <0.001, Cr <0.01, Co <0.01, Cu <0.01, Pb <0.01, Hg <0.001, Ni <0.01, Sn <0.01 and Zn <0.01. There were a small number of samples that registered Cr, Co, Cu, Ni and Zn; however these were close to detection limits and are not considered significant. The full trace element results are given in Appendix A6.

Table 5.15 - Average Leachate Quality : Major Parameters[1] (mg/L)

Date	pH	Eh	TDS	SO_4	Cl	HCO_3	CO_3	F	NO_3	SiO_2
July-Sept. '97	9.2	282	11,000	6,780	671	38	68	1.4	0.39	9.3
Dec. '97	9.3	301	7,300	4,100	300	40	60	1.6	0.70	10
March '98	8.3	380	5,700	3,800	150	110	2	1.4	0.25	8.7
15 June '98	9.2	340	3,100	2,000	100	30	44	1.0	0.35	7.5
29 July '98	10.0	162	1,000	480	28	-	68	1.2	.06	6.5
Decrease (%)	-	-	90.9	92.9	95.8	-	-	-	-	-

[1] - Eh (redox) in mV.

Date	Na	K	Ca	Mg	Fe
July-Sept. '97	3,467	119	130	26	0.06
Dec. '97	2,300	85	90	15	0.07
March '98	1,800	84	77	9.8	0.24
15 June '98	950	46	38	10	-
29 July '98	330	20	15	2.4	0.01
Decrease (%)	90.5	83.2	88.5	90.8	-

Table 5.16 - Average Leachate Quality : Trace Elements (mg/L)

Date	Al	As	B	Ba	Mo	Se
July-Sept. '97	0.81	0.009	3.3	0.07	0.26	0.81
Dec. '97	0.21	0.006	4.9	0.03	0.13	2.0
March '98	0.64	0.003	7.9	<0.01	0.11	1.5
15 June '98	0.05	0.003	4.3	0.02	0.06	0.22
29 July '98	0.46	<0.005	4.8	<0.01	<0.01	0.08
Change (± %)	-43.8	~ -66.7	+145.4	~ -85.7	-96.2	-90.1

Table 5.17 - Leachate Quality : Major Ions (mg/L)

Date	pH	EC	Eh	TDS	SO_4	Cl	HCO_3	CO_3	F	NO_3
07-07-97	9.5	1,200	44	9,800	2,500	630	40	84	-	-
18-07-97	9.3	1,800	270	11,000	9,300	750	14	92	-	-
25-07-97	9.3	1,400	280	11,000	5,800	740	22	88	-	-
04-08-97	8.1	1,500	-	11,000	8,600	700	-	-	-	-
07-08-97	8.8	1,300	320	11,000	6,400	770	90	20	-	-
11-08-97	8.8	1,600	310	11,000	6,400	740	28	60	-	-
18-08-97	9.2	1,600	290	11,000	7,200	800	40	70	-	-
25-08-97	9.5	1,700	-	11,300	7,400	720	34	52	-	-
01-09-97	9.8	1,700	280	11,000	6,800	660	16	92	-	-
08-09-97	10.1	1,500	280	11,000	6,500	560	<2	120	-	-

[1] - pH in pH units; EC in mS/m; Eh (Redox Potential) in mV.

Table 5.17 (cont'd) - Leachate Quality : Major Ions (mg/L)

Date	pH	EC	Eh	TDS	SO_4	Cl	HCO_3	CO_3	F	NO_3
15-09-97	9.8	1,400	280	11,000	7,900	720	2	96	-	-
22-09-97	9.7	1,300	270	11,000	6,700	640	38	72	1.4	0.1
29-09-97	9.4	1,300	280	11,000	6,900	600	54	68	1.4	0.56
20-10-97	8.8	1,400	280	9,400	6,700	480	76	24	1.5	0.5
27-10-97	8.5	1,500	296	11,000	6,600	550	84	12	1.4	-
04-11-97	9.5	1,100	-	7,800	5,500	340	-	-	-	-
10-11-97	9.4	1,300	280	9,200	4,800	410	20	80	-	-
17-11-97	8.7	1,200	290	8,800	5,800	420	78	40	1.7	-
24-11-97	9.5	1,200	290	8,600	5,500	390	34	76	1.5	-
01-12-97	9.5	1,100	280	8,600	6,000	370	44	68	1.6	-
08-12-97	9.3	1,000	292	7,900	4,500	340	36	60	1.8	-
23-12-97	9.3	990	301	7,300	4,100	300	40	60	1.6	0.7
27-01-98	9.0	930	300	6,800	4,100	260	66	36	1.2	0.85
02-02-98	9.1	930	-	7,000	4,200	240	48	44	1.5	0.6
02-02-98	8.2	1,700	-	13,000	8,400	820	-	-	-	-
23-02-98	9.4	950	370	6,100	4,200	180	44	56	1.4	-
02-03-98	9.4	790	350	6,000	2,900	170	48	50	1.5	0.3
10-03-98	9.2	740	346	5,300	2,900	140	64	36	1.4	0.48
17-03-98	8.9	790	390	5,000	2,800	150	60	40	1.6	0.5
23-03-98	8.3	880	380	5,700	3,800	150	110	2	1.4	0.25
07-04-98	8.3	700	220	5,000	3,300	130	90	<2	1.3	0.35
15-04-98	8.2	840	250	5,100	3,600	130	110	<2	1.3	1.4
04-05-98	8.2	1,100	-	7,600	4,400	610	-	-	-	-
18-05-98	9.0	700	315	5,200	2,700	130	54	24	1.1	0.55
19-05-98	9.3	600	330	4,500	2,700	120	42	14	1.1	0.45
25-05-98	9.7	570	320	4,100	2,900	98	18	68	-	-
01-06-98	9.4	290	314	1,800	600	45	22	72	1.5	0.12
15-06-98	9.2	520	340	3,100	2,000	100	30	44	1.0	0.35
17-06-98	9.5	530	290	3,500	2,500	93	24	52	-	-
22-06-98	9.5	560	253	3,600	1,600	510	32	52	1.0	0.41
29-06-98	9.5	640	330	4,400	2,900	140	44	36	-	-
06-07-98	9.5	440	330	3,100	2,100	89	8	72	-	-
13-07-98	9.8	500	325	3,500	2,500	110	34	68	1.0	0.18
16-07-98	9.9	320	178	1,900	1,100	51	-	72	1.2	0.13
21-07-98	9.8	280	182	1,400	990	36	-	52	1.1	0.09
22-07-98	9.9	250	174	1,300	890	36	-	56	1.1	0.07
27-07-98	9.7	210	189	1,400	920	43	<5	68	1.0	0.25
29-07-98	10.0	160	162	1,000	480	28	-	68	1.2	0.06

Table 5.17 (cont'd) - Leachate Quality : Major Ions (mg/L)

Date	Na	K	Ca	Mg	Fe	Al	SiO_2
07-07-97	3,500	110	110	22	0.03	0.29	8.5
18-07-97	3,400	120	100	24	<0.01	1.3	9.7
25-07-97	2,100	90	100	31	0.03	0.07	11
04-08-97	3,700	-	140	36	-	-	-
07-08-97	3,600	100	160	60	0.07	0.22	9.8
11-08-97	3,800	120	130	21	0.05	0.32	7.9
18-08-97	3,600	110	120	24	0.03	0.08	7.5
25-08-97	3,500	120	140	19	0.25	1.4	9.4
01-09-97	3,300	140	150	18	<0.01	0.68	0.55
08-09-97	3,300	110	130	11	<0.1	1.3	8.5
15-09-97	4,000	130	130	21	0.22	1.4	11
22-09-97	4,000	130	120	14	0.1	1.9	11
29-09-97	3,600	150	120	16	<0.01	1.1	7.4
20-10-97	3,200	120	140	32	0.07	0.12	12
27-10-97	3,400	120	160	35	<0.1	1.2	16
04-11-97	2,600	-	110	24	0.09		-
10-11-97	2,700	110	130	26	<0.01	0.07	-
17-11-97	2,700	110	140	22	<0.01	0.12	-
24-11-97	2,500	95	110	16	-	0.22	-
01-12-97	2,600	110	120	16	0.23	0.38	1.2
08-12-97	2,500	92	110	19	0.03	0.2	11
23-12-97	2,300	85	90	15	0.07	0.21	10
27-01-98	2,100	77	100	24	0.09	0.09	12
02-02-98	1,800	73	86	15	<0.01	0.19	-
02-02-98	2,700		380	65	-	-	-
23-02-98	1,900	89	92	13	0.25	0.2	7.7
02-03-98	1,700	97	86	9	<0.01	0.25	7.5
10-03-98	1,600	73	75	12	0.17	0.48	8.7
17-03-98	1,900	89	82	10	0.12	0.25	8.0
23-03-98	1,800	84	77	9.8	0.24	0.64	8.7
07-04-98	1,600	78	75	10	0.04	0.28	7.5
15-04-98	1,600	76	66	10	0.11	0.17	7.5
04-05-98	2,500	-	160	43	<0.1	-	-
18-05-98	1,750	85	90	9.5	0.1	0.18	4.9
19-05-98	1,400	68	68	14	0.1	0.33	4.9
25-05-98	1,200	68	54	6.5	<0.01	0.3	-
01-06-98	610	34	15	6	0.3	0.55	8.5
15-06-98	950	46	38	10	-	0.05	7.5
17-06-98	1,200	57	45	11	0.1	0.27	7.0
22-06-98	1,100	64	65	8.2	0.28	0.4	6.2
29-06-98	1,400	78	85	11	0.1	0.28	5.5
06-07-98	910	49	64	9.2	0.34	0.44	6.2

Table 5.17 (cont'd) - Leachate Quality : Major Ions (mg/L)

Date	Na	K	Ca	Mg	Fe	Al	SiO_2
13-07-98	1,000	56	63	11	0.3	0.37	6.2
16-07-98	570	31	26	5.4	0.06	0.25	6.2
21-07-98	450	25	19	3.5	<0.05	0.43	6.3
22-07-98	410	24	18	3.4	<0.05	0.37	6.0
27-07-98	410	27	30	6	<0.01	0.33	5.5
29-07-98	330	20	15	2.4	0.01	0.46	6.5

Table 5.18 - Leachate Quality : Trace Elements (mg/L)

Date	As	B	Ba	Mo	Se
07-07-97	0.009	2.6	0.09	0.28	0.6
18-07-97	0.008	3.1	0.12	0.36	0.02
25-07-97	<0.01	0.87	0.04	0.09	0.4
04-08-97	0.01	-	0.14	0.28	0.56
07-08-97	0.006	2.9	0.07	0.28	1.0
11-08-97	0.007	3.4	0.08	0.29	1.2
18-08-97	0.014	3.0	0.03	-	0.97
25-08-97	0.009	3.8	0.07	0.3	0.65
01-09-97	0.016	3.4	0.06	-	1.0
08-09-97	0.012	3.2	0.05	0.18	0.45
15-09-97	0.003	3.6	0.06	-	1.2
22-09-97	0.006	4.0	0.05	0.26	-
29-09-97	0.006	3.9	0.05	0.26	0.1
20-10-97	0.006	3.7	0.05	0.22	1.5
27-10-97	<0.01	4.6	<0.01	0.27	1.7
04-11-97	0.005		<0.01	0.13	2.0
10-11-97	0.006	4.1	0.04	-	1.6
17-11-97	0.006	4.4	0.05	-	1.6
24-11-97	0.005	5.2	0.02	0.14	0.53
01-12-97	0.005	4.9	0.04	0.14	1.1
08-12-97	0.005	4.9	0.03	0.14	0.03
23-12-97	0.006	4.9	0.03	0.13	2.0
27-01-98	<0.001	4.7	0.03	0.12	1.3
02-02-98	0.005	5.3	0.03	0.12	6.8
02-02-98	<0.001	-	0.04	0.06	0.02
23-02-98	0.004	6.2	0.04	0.12	1.9
02-03-98	0.004	6.0	0.03	0.10	1.8
10-03-98	0.003	6.1	0.03	0.07	0.27
17-03-98	0.004	6.6	0.03	0.10	0.074
23-03-98	0.003	7.9	<0.01	0.11	1.5
07-04-98	0.004	5.6	0.02	-	0.7
15-04-98	0.002	5.6	0.02	0.07	1.2

Table 5.18 (cont'd) - Leachate Quality : Trace Elements (mg/L)

Date	As	B	Ba	Mo	Se
04-05-98	0.002	-	0.04	0.12	0.12
18-05-98	<0.001	5.5	0.03	-	0.3
19-05-98	<0.001	5.5	0.03	-	0.32
25-05-98	<0.001	5.1	0.03	-	0.21
01-06-98	0.001	6.0	<0.01	0.03	0.16
15-06-98	0.003	4.3	0.02	0.06	0.218
17-06-98	0.004	5.4	0.02	-	0.25
22-06-98	0.003	4.9	0.03	0.05	0.27
29-06-98	<0.005	4.9	0.05	0.06	0.27
06-07-98	0.004	5.2	0.04	0.04	-
13-07-98	0.03	4.7	0.03	0.05	0.6
16-07-98	<0.001	6.0	0.01	0.04	0.61
21-07-98	0.003	4.6	<0.01	0.02	0.14
22-07-98	0.002	4.6	<0.01	0.01	0.12
27-07-98	0.003	4.2	0.01	0.01	0.1
29-07-98	<0.005	4.8	<0.01	<0.01	0.08

An important feature of the leachate quality data over time is the three spikes in salinity on days 211, 305 and 355 (dates 29-01-98, 04-05-98 and 22-06-98, respectively). There does not appear to be any increase in trace element concentrations. The salinity increase on these days is similar to the sample with higher salinity from the Dry Cell in November 1997.

The salinity on day 211 (29-01-98) can be explained by the prevailing climatic conditions to that point in time. The preceding month had seen hot and dry conditions and very low rainfall and no irrigation. This led to an overall decrease in the soil moisture content within the cell, thereby concentrating the salinity by a small fraction. Importantly, the vertical moisture content data were obtained from samples on day 209 (27-01-98), the week following the first irrigation for about a month. Comparing the Wet Cell moisture profile to that of the Dry Cell from day 209, the Wet Cell is distinctly higher in moisture, the result of the previous weeks' irrigation. This earlier event also generated a very small volume of leachate, with most water retained in storage. The irrigation event on day 211 was therefore able to flow freely through the ash profile.

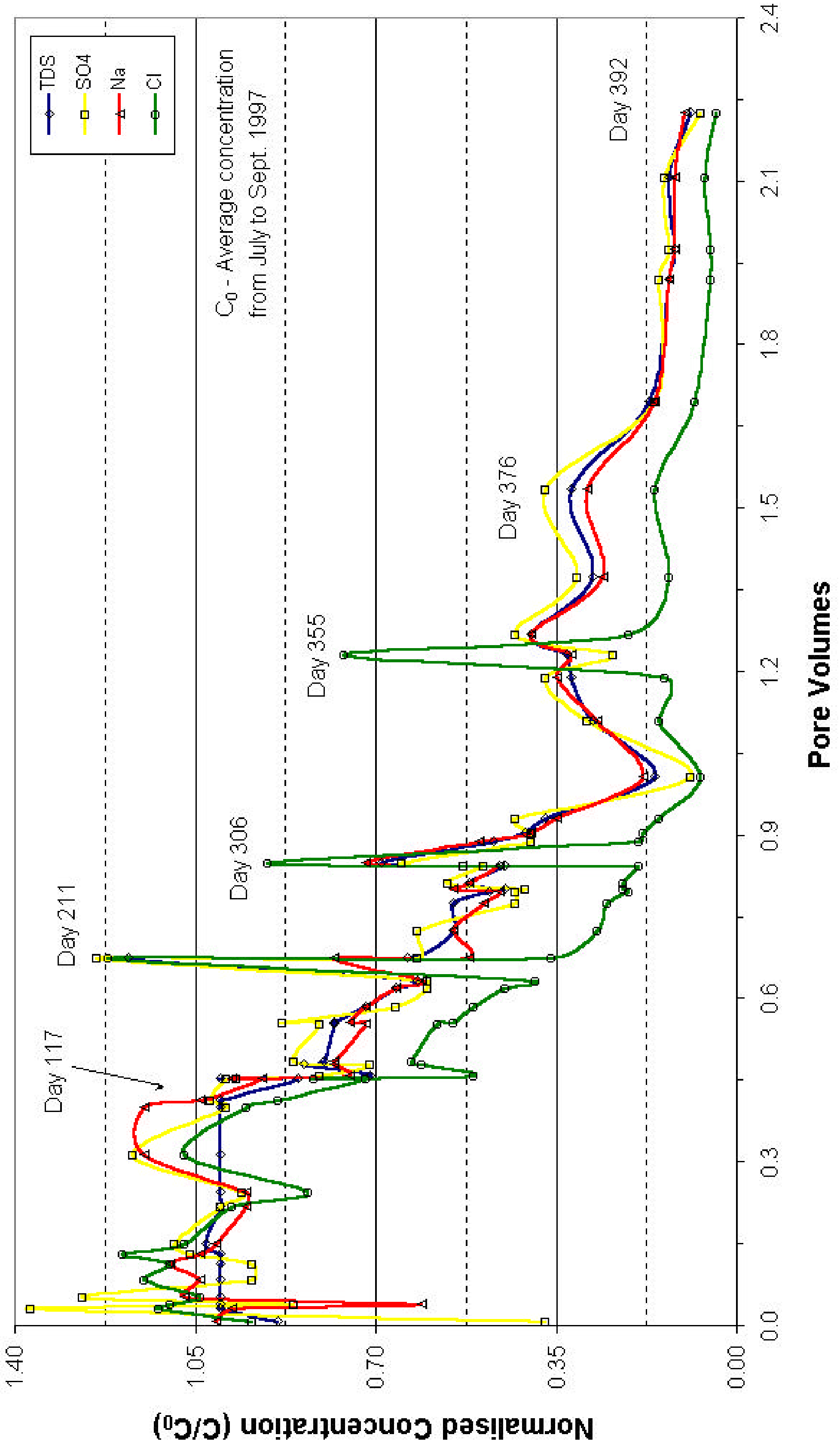


Figure 5.11 - Leachate Quality versus Pore Volume : Major Elements

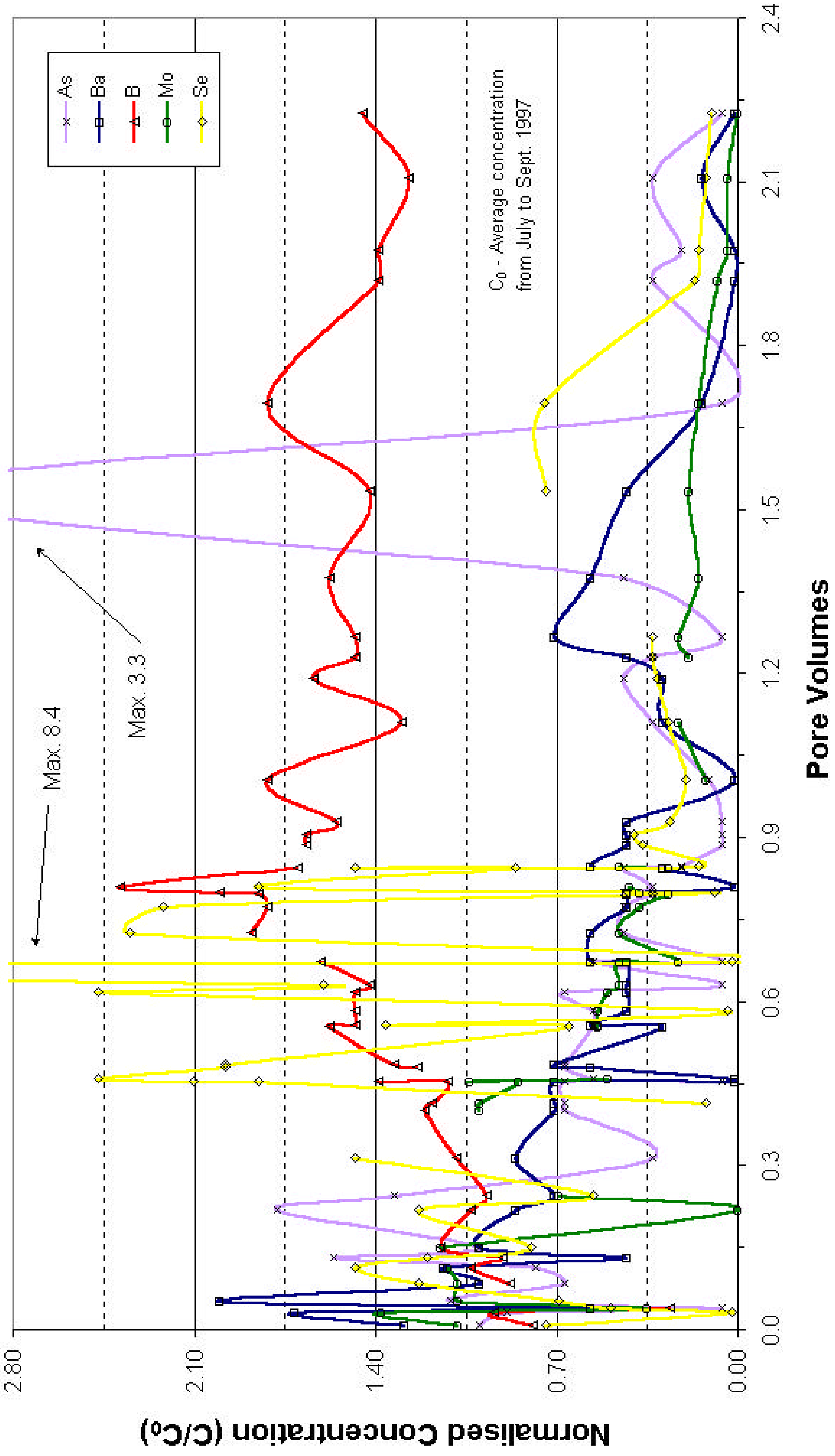


Figure 5.12 - Leachate Quality versus Pore Volume : Trace Elements

As the water flowed through the profile, however, it first displaced the higher salinity pore waters concentrated by previous evaporation and the leachate quickly reduced to a concentration representative of residual soluble minerals and salts. A further sample was taken from this event about 4 hours later, showing a signifcantly reduced salinity. It is unclear why a higher salinity was not recorded the previous week with the first irrigation after the months' break.

The higher salinity on day 306 also follows a period of lower rainfall and irrigation (nearly 3 weeks with no tank added) coupled with hot and dry climatic conditions, although not as extreme as around day 211. For day 355, however, the spike in salinity is restricted to Cl only compared to lower Na and SO_4. The month prior to this sample had abundant rainfall and irrigation with colder and more humid conditions. Thus evaporative concentration is not considered to be a viable mechanism for this sample spike. The laboratory analysis has a charge balance error of about 3.3%, compared to the average for the trial cells of around 3%, and hence such error is not considered realistic to explain the spike. Taking into account evaporative effects on leachate concentration appears important, although complex to discern with current data.

5.5.4 Ash Quality

The chemical quality of the leached ash has been determined regularly throughout the operation of the Wet Cell. Owing to the higher quantity of water passing through the Wet Cell, active leaching has occurred and a distinct change in the chemical quality of the ash is apparent. The results of 40 ash samples from the surface and at depth over time, including the samples taken from the 'wet' and 'dry' parts of the cell (as discussed earlier in Section 5.2.2), are presented in Tables 5.19 to 5.22.

Table 5.19 - Average Ash Quality : Major Elements (% dry basis)

Date	SO_4	Cl^1	Na	K	Ca	Mg	Fe	Al	A.I.	LOI
July 97	0.86	728	1.38	0.128	3.8	5.6	3.9	2.9	57	22
October 97	0.28	110	0.66	0.077	3.0	4.8	4.4	2.9	67	21
February 98	0.41	129	0.74	0.083	2.8	4.5	3.5	2.6	67	20
May 98	0.38	905^2	1.07	0.116	3.1	4.6	4.7	3.7	61	10
August 98	0.21	-	0.59	0.070	2.9	4.8	5.4	3.7	62	19

LOI - Loss On Ignition; A.I. - Acid Insoluble. ^{1} - Cl in mg/kg. ^{2} - average based on 1,800 & <10 mg/kg.

Table 5.20 - Average Ash Quality : Trace Elements (mg/kg) (dry basis)

Date	As	B	Ba	Cd	Cr	Co	Cu	Hg	Mo	Ni	Pb	Se	Sn	Zn
July 97	9.6	153	180	0.3	33	24	37	1.58	<5	43	12	<5	<5	74
Oct. 97	4.4	116	570	0.14	44	22	41	1.85	2.2	89	10	<5	<5	77
Feb. 98	11	171	400	<0.2	34	24	41	0.83	<5	40	12	<5	<5	85
May 98	8.5	121	455	0.12	36	29	37	1.20	3.9	39	9.2	5.3	3.3	75
Aug. 98	<5	128	607	<0.2	37	25	37	1.45	10[1]	40	11	<5	<5	93
EPAV			400	5	250	50		2.0	40	100			50	

[1] - Average of 3 samples only, excluding 11 results below detection limits.

Table 5.21 - Ash Quality : Major Elements (% dry basis)

Date	Site[1]	SO_4	Cl	Na	K	Ca	Mg	Fe	Al	AI	LOI
07-07-97	0 m SW	0.68	0.068	1.4	0.150	3.5	4.6	3.5	3.0	60	22.1
07-07-97	0 m NE	0.65	0.070	1.5	0.140	3.4	4.8	3.8	2.7	56	22.4
07-07-97	1.5 m C	1.00	0.076	1.4	0.110	5.0	8.2	4.6	3.2	49	23.7
07-07-97	3.0 m B	1.10	0.077	1.2	0.110	3.4	4.9	3.8	2.5	62	20.4
20-10-97	Wet	0.24	0.010	0.62	0.067	3.0	4.9	4.3	2.9	67	22
20-10-97	Dry	0.32	0.012	0.70	0.087	3.0	4.6	4.4	2.9	67	20
03-02-98	0.25 D	<0.05	0.012	0.69	0.082	3.0	4.8	3.5	2.7	67	25
03-02-98	0.11 D	0.42	0.010	0.88	0.090	3.1	5.3	4.1	2.8	67	20
03-02-98	1.92 D	0.46	0.010	0.82	0.085	2.6	3.9	3.6	2.4	72	17
03-02-98	2.58 D	0.50	0.025	1.40	0.130	3.5	5.4	4.7	3.3	67	23
03-02-98	0.30 W	<0.05	0.015	0.41	0.053	2.4	3.9	2.6	2.4	67	18
03-02-98	1.23 W	0.26	0.012	0.44	0.062	2.5	3.6	2.7	2.0	69	19
03-02-98	1.82 W	<0.05	0.007	0.65	0.076	3.3	5.3	4.2	2.7	65	21
03-02-98	2.71 W	<0.05	0.012	0.62	0.083	2.2	3.7	2.8	2.2	63	18
19-05-98	Dry Sth	0.56	0.180	1.60	0.160	3.4	5.1	4.6	4.2	55	11
19-05-98	Wet Nth	0.20	<0.001	0.54	0.072	2.7	4.1	4.7	3.2	67	9
07-08-98	Dry Sth	0.14	nd	0.56	0.065	2.4	3.7	5.8	3.6	66	19
07-08-98	0.35 DS	0.16	nd	0.81	0.076	2.6	4.2	4.9	3.7	67	18
07-08-98	0.65 DS	0.19	nd	0.58	0.073	3.1	5.5	5.5	3.9	58	20
07-08-98	0.95 DS	0.20	nd	0.65	0.075	2.5	4.2	5.0	3.3	64	14
07-08-98	1.50 DS	0.31	nd	0.57	0.056	3.2	5.2	6.4	3.3	59	19
07-08-98	2.00 DS	0.26	nd	0.66	0.083	2.9	4.7	5.0	3.2	64	19
07-08-98	2.55 DS	0.48	nd	0.59	0.081	3.5	6.9	6.4	4.7	56	18
07-08-98	Wet Nth	0.12	nd	0.59	0.072	2.1	3.7	5.5	3.8	65	17
07-08-98	0.30 WN	0.15	nd	0.54	0.069	3.0	4.6	5.0	3.9	64	20
07-08-98	0.60 WN	0.14	nd	0.46	0.059	2.6	4.5	4.9	3.6	64	15
07-08-98	0.95 WN	0.19	nd	0.60	0.058	3.1	5.3	5.4	3.7	59	23
07-08-98	1.40 WN	0.19	nd	0.59	0.065	3.2	5.0	5.4	3.8	61	21
07-08-98	2.10 WN	0.21	nd	0.56	0.066	3.2	5.3	5.7	3.4	61	19
07-08-98	2.70 WN	0.21	nd	0.46	0.08	2.7	4.8	5.3	4.1	65	18

LOI - Loss On Ignition; AI - Acid Insoluble; NE - North East corner; SW - South West corner. [1] - "279 Dry" is depth 279 cm. D - Dry area of cell (no ponding); W - Wet was ponded. nd - no data.

Table 5.22 - Ash Quality of the Wet Cell : Trace Elements (mg/kg) (dry basis)

Date	Site	As	B	Ba	Cd	Cr	Co	Cu
07-07-97	0 m SW	8.3	190	140	0.3	33	20	41
07-07-97	0 m NE	<5	120	200	<0.2	29	20	32
07-07-97	1.5 m C	9.4	130	170	<0.2	39	30	32
07-07-97	3.0 m B	11	170	210	<0.2	29	25	44
20-10-97	Wet	2.1	92	540	<0.1	38	20	41
20-10-97	Dry	6.7	140	600	0.14	50	24	40
03-02-98	0.25 D	8.5	170	490	<0.2	36	21	37
03-02-98	0.11 D	7.8	180	400	<0.2	31	28	46
03-02-98	1.92 D	8.9	170	380	<0.2	33	25	38
03-02-98	2.58 D	18	200	280	<0.2	31	26	40
03-02-98	0.30 W	<5	160	510	<0.2	35	20	49
03-02-98	1.23 W	<5	140	140	<0.2	31	23	38
03-02-98	1.82 W	<5	180	470	<0.2	30	23	38
03-02-98	2.71 W	<5	170	530	0.2	43	<5	45
19-05-98	Dry Sth	7	160	390	0.1	33	22	33
19-05-98	Wet Nth	10	82	520	0.13	39	35	40
07-08-98	Dry Sth	<5	94	610	<0.2	38	27	51
07-08-98	0.35 DS	<5	120	720	<0.2	39	24	34
07-08-98	0.65 DS	<5	160	700	<0.2	35	20	42
07-08-98	0.95 DS	<5	130	560	<0.2	28	21	34
07-08-98	1.50 DS	<5	190	640	<0.2	36	31	40
07-08-98	2.00 DS	<5	150	590	<0.2	30	23	33
07-08-98	2.55 DS	<5	150	480	<0.2	38	21	32
07-08-98	Wet Nth	<5	79	600	<0.2	41	27	46
07-08-98	0.30 WN	<5	96	640	<0.2	60	19	38
07-08-98	0.60 WN	<5	110	660	<0.2	36	30	40
07-08-98	0.95 WN	<5	140	600	<0.2	32	29	39
07-08-98	1.40 WN	<5	110	500	<0.2	27	32	31
07-08-98	2.10 WN	<5	120	590	<0.2	37	24	31
07-08-98	2.70 WN	<5	140	-	<0.2	37	25	33
EPAV (1993)		30		400	5	250	50	

B - Bottom; C - Centre; N - North; S - South.

Table 5.22 (cont'd) - Ash Quality of the Wet Cell : Trace Elements (mg/kg) (dry basis)

Date	Site	Hg	Mo	Ni	Pb	Se	Sn	Zn
07-07-97	0 m SW	1.7	<5	41	9.4	<5	<5	90
07-07-97	0 m NE	1.4	<5	44	15	<5	<5	56
07-07-97	1.5 m C	1.6	<5	43	10	<5	<5	60
07-07-97	3.0 m B	1.6	<5	42	13	<5	<5	92
20-10-97	Wet	2.0	1.4	37	9.4	<5	<5	76
20-10-97	Dry	1.7	3	140	11	<5	<5	78
03-02-98	0.25 D	0.5	14	40	11	<5	<5	75
03-02-98	0.11 D	0.89	<5	42	13	<5	<5	100
03-02-98	1.92 D	1.1	<5	40	11	<5	<5	75
03-02-98	2.58 D	0.82	<5	40	11	<5	<5	88
03-02-98	0.30 W	0.57	<5	36	13	<5	<5	81
03-02-98	1.23 W	0.69	<5	38	9	<5	<5	70
03-02-98	1.82 W	1.0	<5	40	13	<5	<5	96
03-02-98	2.71 W	1.1	<5	44	13	<5	<5	92
19-05-98	Dry Sth	1.0	3.7	37	7.5	7.5	4.7	60
19-05-98	Wet Nth	1.4	4.2	40	11	3	1.8	90
07-08-98	Dry Sth	1.7	<5	46	14	<5	<5	170
07-08-98	0.35 DS	1.2	<5	42	9.6	<5	<5	76
07-08-98	0.65 DS	2.4	<5	41	14	<5	<5	94
07-08-98	0.95 DS	1.2	<5	37	10	<5	<5	79
07-08-98	1.50 DS	1.4	<5	46	11	<5	<5	100
07-08-98	2.00 DS	1.3	<5	35	9.4	<5	<5	79
07-08-98	2.55 DS	1.4	<5	33	12	<5	<5	87
07-08-98	Wet Nth	1.4	<5	50	16	<5	<5	140
07-08-98	0.30 WN	1.3	19	38	12	<5	<5	88
07-08-98	0.60 WN	1.3	6.7	42	11	<5	<5	85
07-08-98	0.95 WN	1.6	<5	39	13	<5	<5	82
07-08-98	1.40 WN	1.6	<5	36	8.7	<5	<5	73
07-08-98	2.10 WN	1.3	5.1	37	7.8	<5	<5	72
07-08-98	2.70 WN	1.2	<5	37	12	<5	<5	83
EPAV (1993)		2.0	40	100			50	

B - Bottom; C - Centre; N - North; S - South.

5.5.5 Changes in Soluble Mass

To ascertain the extent of leaching for particular species, the total soluble mass was calculated before and after the one year of active leaching, on the basis of dry density of the ash and the concentration of the particular species. For the major species SO_4, Cl, Na and K, between 45% and 98% of their soluble mass was leached. For the less soluble species, Ca, Mg, Fe and Al, there appears to be no significant change in soluble mass.

By calculating the cumulative mass leached based on the concentration of a species in the leachate and the volume of leachate, an alternate mass leached can also be derived. The behaviour of B is interesting, as the concentration gradually increases before beginning to decrease by the end of the trial. This behaviour has the effect of causing the cumulative mass leached to be approximately linear, in comparison to the asymptotic curves for most major species (see Figure 5.13d). The results are presented in Tables 5.23 and 5.24 and Figure 5.13. The geochemistry of ash leachate and solubility controls by mineral phases will be discussed in Chapter 7.

Table 5.23 - Total Soluble Mass in Leached Ash and Leachate : Major Elements (kg)

		SO_4	Cl	Na	K	CO_3	Ca	Mg	Al	Fe	SiO_2[1]
Ash	Initial	332	28	533	49	-	1,468	2,163	1,120	1,506	22,000
	Final	81	0.4[2]	228	27	-	1,120	1,854	1,429	2,086	23,948
Leachate		424	32	211	8.4	10.8	9.6	1.7	0.058	0.013	0.83

[1] - Assuming the acid insoluble fraction is silica; [2] - Assuming final Cl of 10 mg/kg.

Table 5.24 - Total Soluble Mass in Leached Ash and Leachate : Trace Elements (g)

	As	B	Ba	Mo	Se
Initial	371	5,909	6,953	371[*]	317[*]
Final	193	4,944	23,445	276	193
Leachate	0.74	598	3.91	9.41	75.1

[*] - Assuming the average from Dry Cell ash.

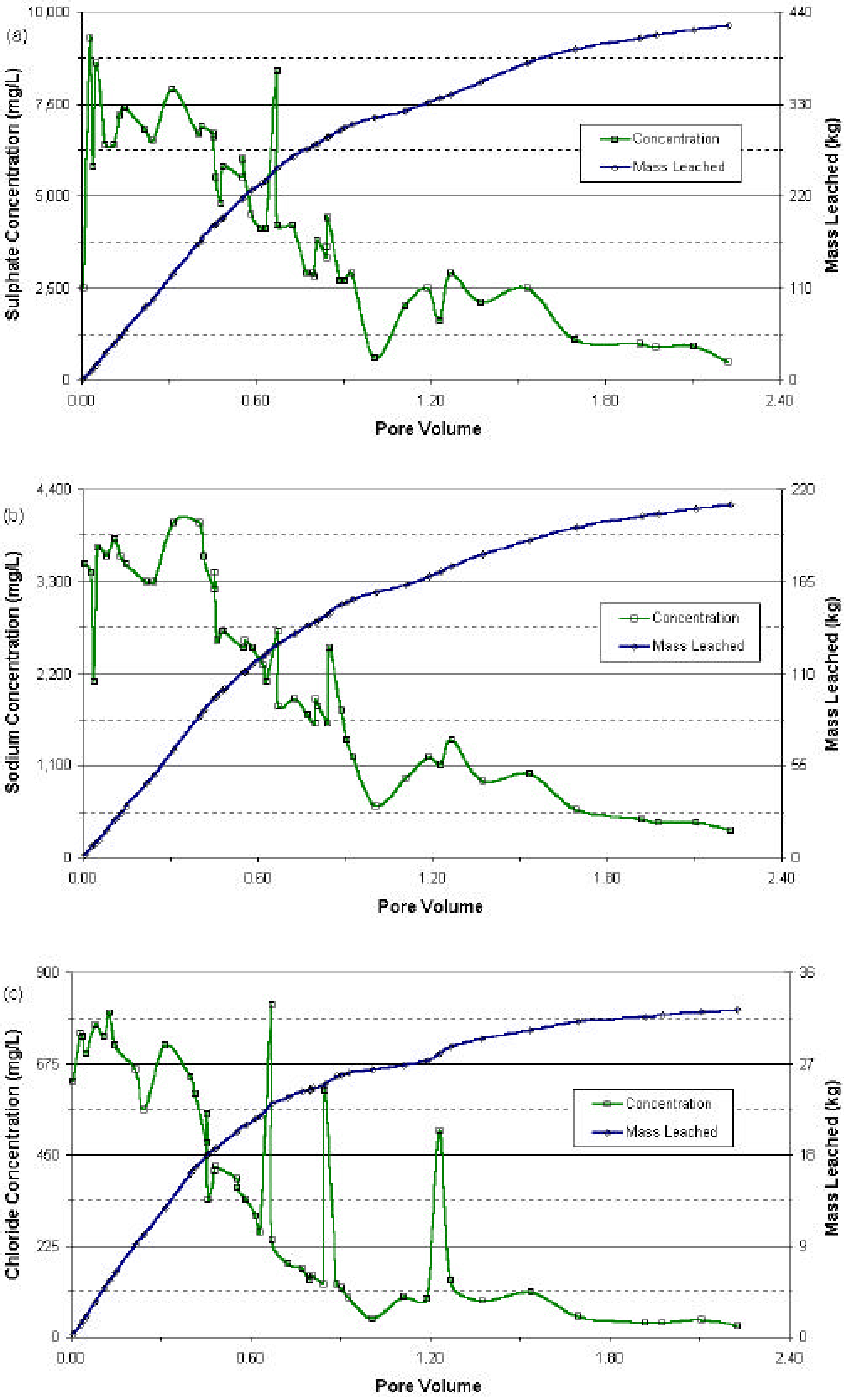


Figure 5.13 - Concentration and Mass Leached versus Pore Volume : (a) SO_4, (b) Na & (c) Cl

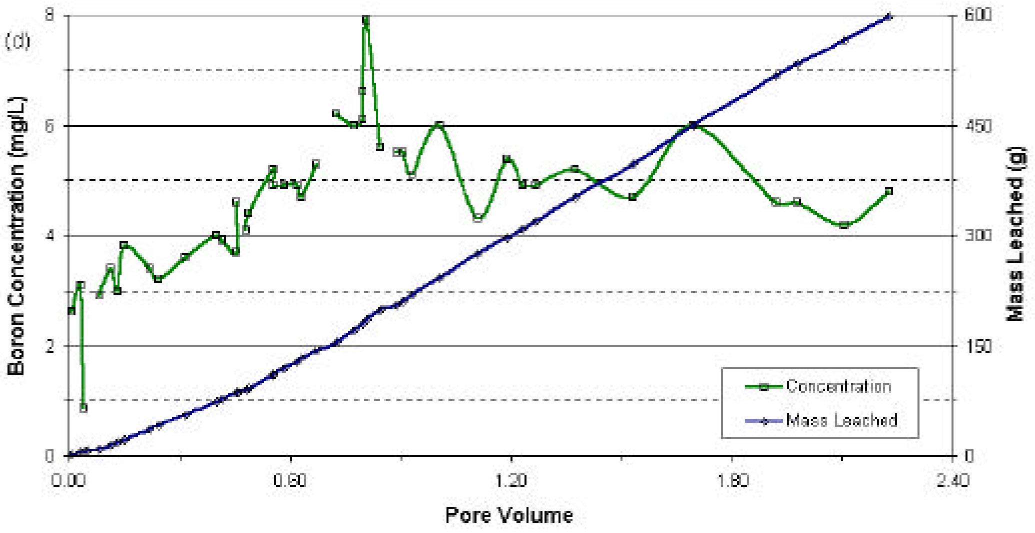


Figure 5.13 (cont'd) - Concentration and Leached Mass versus Pore Volume : (d) B

Calculation of the soluble mass leached allows comparison with the soluble mass available at the start and end of the trials; estimation of initial salt loadings due to surface washing of soluble salts; estimates of remaining salt loads; and behaviour of trace elements. A further use of these assessments is a check on the accuracy of ash and leachate analyses and soluble mass calculations. Thus it is possible to ascertain the long term potential leachate that may influence groundwater quality, if leachate was to migrate into the underlying aquifers.

These tables and figures demonstrate that leaching has occurred according to Farquhar (1989) and the discussion presented earlier in Chapter 2. That is, the leachate concentration drops rapidly from a high initial value and asymptotes towards a low and near steady state value. Conversely, the soluble mass leached from the ash increases rapidly and asymptotes towards a maximum value, close to the concentration present in the ash at the start of the trial. The major solutes, such as SO_4, Na and Cl, have mostly leached from the ash, and thus pose a very low potential to generate saline leachate.

5.5.6 Summary of the Wet Cell

The data obtained from the year-long operation of the Wet Cell has provided an excellent basis for assessing the behaviour of ash disposal sites from both a leachate generation (or physical flow) and a geochemical leachate behaviour perspective.

The ash held most rainfall and applied water within porous storage, again signifying the unsaturated behaviour of the ash under field conditions. For the majority of the trial, the volume and rate of leachate generated was related to climatic conditions (such as rainfall, temperature and relative humidity) and the time between irrigation events. Near the end of the trial, when the irrigation rate was approximately constant for several days at a time, the peak leachate outflow rate is close to the irrigation rate, suggesting near-saturated behaviour.

The leachate generated was of a moderate salinity, identical in chemical signature as the Dry Cell. It was dominated chiefly by Na and SO_4, with minor amounts of Cl, Ca, Mg and K. The trace elements detected in the leachate were As, Ba, B, Mo and Se. Most elements analysed for were very close to or below detection limits.

Although apparent to a different extent due to the higher volumes of inflow, the unsaturated and evaporative behaviour of the Wet Cell suggests that these processes are crucial in modelling and predicting moisture flow, leachate generation and geochemistry.

5.6 Summary of the Field Leaching Trial Cells

The results from the construction and operation of two large field leaching cells have been presented. The cells were operated over a period of about 14 months, in an unusually low rainfall year for the Latrobe Valley of 596 mm. Overall, the Wet and Dry Cells demonstrated :

- the importance of unsaturated flow behaviour through the ash;
- climate conditions and evaporation controlling the water balance and generation of leachate;
- initially leachate is moderately saline, consisting predominantly of Na, SO_4 and Cl and minor Ca, Mg, K, Al and Fe;
- the leachate concentration declined rapidly after about 0.4 pore volumes;
- the trace elements detected in the leachate were As, B, Ba, Mo, Se, with most other elements being below analytical detection limits;

These factors are critical, therefore, in assessing and modelling leaching processes occurring within ash disposal sites, potential rates of solute transport and associated impacts on groundwater quality. The unsaturated flow behaviour, however, requires further soil properties to allow more theoretically correct modelling. A laboratory leaching study using column experiments will now be presented in Chapter 6 to assess more rigourously the flow behaviour of ash.

Chapter 6

Laboratory Leachability Studies

An investigation of ash leachability under controlled conditions in a laboratory will be presented. Three 100 mm diameter leaching columns of varying heights were constructed, instrumented and monitored over a period of up to three months. They were monitored for inflow and outflow over time, detailed leachate chemistry, and the internal moisture content of the ash was electronically monitored through the use of TDR probes. The Soil Water Characteristic Curve was also determined through the use of a Tempe Cell.

6.1 Overview

The field leaching cells provided a case study of complex field behaviour with the congruent interaction of several processes to produce leachate, although this complexity has precluded any modelling of the results without further data on ash properties. The most critical issue identified from the results of the two field cells was the unsaturated and evaporative-driven moisture behaviour, with respect to Section 5.6. Further assessment of the data was therefore limited due to the unknown unsaturated hydraulic properties of the ash. Another issue involved was the residence time of leachate and pore waters.

It was assumed in the operation of the field work that the initial salinity of the leachate was independent of the height of the ash within the cells. This hypothesis, however, remained untested and not addressed in the available literature. The height of an ash disposal site is also critical in that the larger the height, the greater the pore volume per unit area. This leads to longer leaching times for disposal sites with deeper ash deposits compared to those with shallow deposits and lower pore volumes. Given the different shape of such leaching curves for varying site designs, an assessment of height versus pore volume was warranted to verify the modelling and parameters that are dimensionally independent (to be developed in Chapter 8).

To assess these issues concurrently, a total of four column leaching experiments were established. Three columns were filled with leached ash, while the fourth was filled with dry (unleached) precipitator ash available from earlier studies (bulk sample from May 7, 1996; see Section 4.3). The precipitator ash, being dry and unleached, was used to provide a comparison of leaching dynamics of leached versus unleached ash, and thus provide a further assessment of total soluble minerals arising from the various ash management streams at Loy Yang.

It was decided not to examine in detail the effects of evaporation, as this was beyond the time and resources available for this thesis. However, a limited study is incorporated into the operation of two of the leached ash columns.

A Tempe Cell was obtained to experimentally determine the Soil Water Characteristic Curve (SWCC) of the ash - the principal unsaturated hydraulic property required for detailed unsaturated flow modelling of ash disposal sites.

6.2 Column Design, Operation and Monitoring

Three different column heights were used - 300, 750 and 1,500 mm, with flow percolating downwards by gravity drainage. The precipitator ash column used a 300 mm height. All columns were made with perspex, had a 101 mm internal diameter and a 3 mm wall thickness. A 6 mm thick porous stone of 100 mm diameter was placed at both the top and bottom of each column, being held in place with silicon sealant. The porous stones were used to ensure even inflow distribution across the top of the column and uniform outflow (leachate) discharge at the base of the column. The bottom porous stone used a layer of Whatman's No. 57 filter paper (Catalog No. 1001 110) to prevent any blockage of the porous stone. All columns had top and bottom caps constructed and fitted to ensure minimal evaporative losses. A conceptual design is given in Figure 6.1.

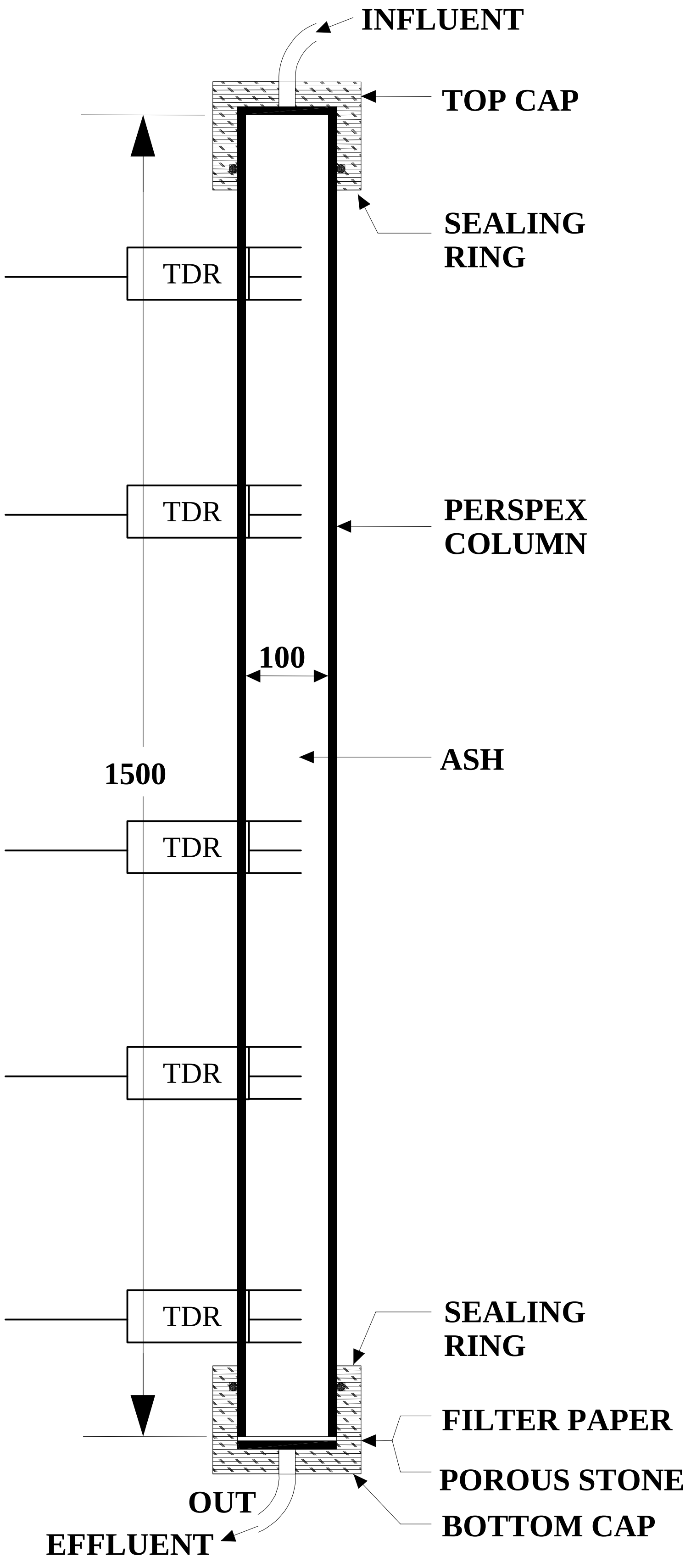


Figure 6.1 - Conceptual Design of Ash Leaching Columns (mm) (not to scale)

The inflow was delivered by a MasterFlex peristaltic pump (Model No. 7521-57) connected to a 6-roller pump head (Model No. 7519-15). Tygon flexible tubing used to deliver the flow to each column. Distilled water, courtesy of the Department of Chemistry, was used as the influent water. The inflow tubing was connected to the column cap and secured using silicon sealant. A 30 litre drum of distilled water was maintained next to the columns, and was placed on a 30 kg mass balance to enable calculation of the inflow rate and cumulative flow over time.

The outflow was directed, through a short tube from the base of the bottom cap, into a 2 litre collection flask. The orifices of the flasks were not sealed, however, they were covered with tape (except for a small hole for the leachate discharge tube) to minimise possible evaporative losses and leachate chemistry changes. The flask was regularly monitored for mass to determine the volume of leachate discharged over time, and hence allow calculation of leachate flow rate and cumulative leachate over time. The complete inflow and outflow data for all columns is given in Appendix 7.

The internal moisture content of the columns was monitored using stand alone Time Domain Reflectometry (TDR) probes connected to a datalogger and laptop computer. The probes were manufactured by Delta-T Devices, model ThetaProbe ML2 (Delta-T, 1998). This allows effective continuous and non-intrusive monitoring of the moisture content profile within each column and any response to changes in inflow and outflow. The TDR probes were inserted through specially drilled large holes in the side of each column, and silicon sealed after placement to prevent leakage or evaporation.

The ash in each column was given light compaction by a tamp rod to achieve a similar density as the field cells and ash disposal sites (based on previous laboratory and field investigations). The columns were operated in a room maintained at an approximately constant temperature of 16 ^{0}C, through the use of an air conditioner. The average wind speed in the room was determined to be approximately 0.2 m/s. The relative humidity varied slightly and was typically about 57%. The setup of the columns can be seen in Figure 6.2.

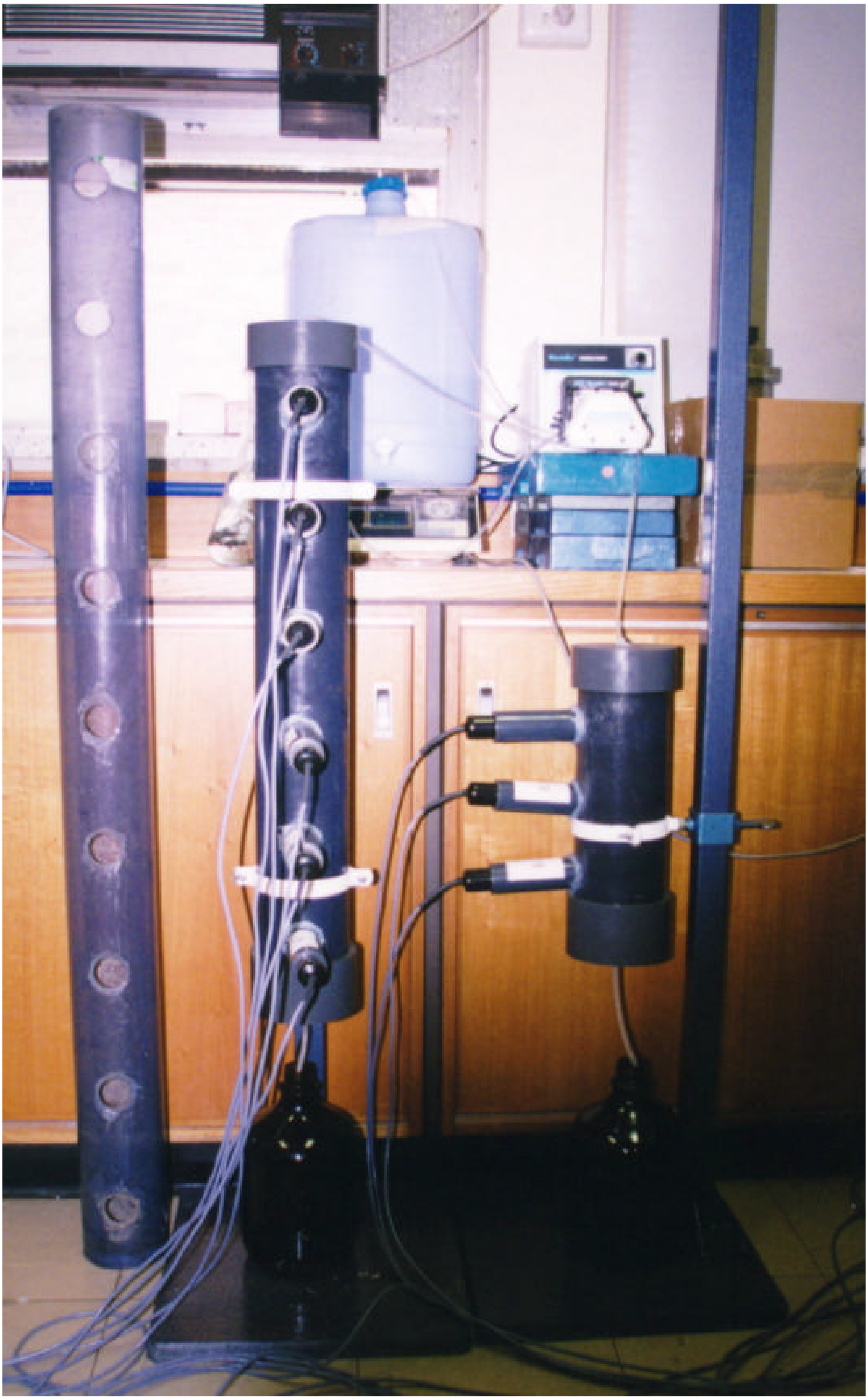


Figure 6.2 - Laboratory Setup of Ash Leaching Columns (Large, Medium & Small; L-R)

The ash from each column was sampled during construction for both moisture content and comprehensive chemical analysis. After operation of each column, the ash was removed and further samples obtained for moisture content and chemical analysis. All chemical testing of both ash samples and leachates was undertaken by WSL Consultants Pty Ltd, under contract to Loy Yang Power Pty Ltd (on behalf of Vic. Uni.).

6.3 Calibration of TDR Probes

6.3.1 Principles of Time Domain Reflectometry

The direct measurement of the moisture content of a soil can be achieved through the use of Time Domain Reflectometry (TDR). The technique functions on the basis that the apparent dielectric constant of a soil is directly proportional to its water content, given that the apparent dielectric constant (ε) for water is 81, soil 3 to 5 and air 1 (Selig & Mansukhani, 1975; Topp & Ferré, 2000). The release of an electromagnetic (EM) pulse by a TDR device into a soil generates a small voltage, proportional to the dielectric constant, which can be measured (Fang, 1997; O'Connor *et al.*, 2000). Since the majority of the electromagnetic response of a soil is controlled by the presence and amount of water (ie. - resistance to the EM pulse), it is possible, therefore, to correlate this generated voltage to the moisture content of a particular soil (Delta-T, 1998).

Early TDR devices were developed in the power and telecommunications industries, and were adapted to detect faults or water ingress in cables (O'Connor *et al.*, 2000). These involved a portable device, called the cable tester, which both generated the EM pulse and analysed the resulting voltage. For engineering applications, this approach is undesirable since it involves manually using the cable tester to obtain readings at the desired interval. A new type of TDR device has recently been developed by Delta-T Devices which incorporates both the EM pulse and the voltage meter into the TDR probe, with wiring connecting the probe to an electronic datalogger (Delta-T, 1998). This allows the probes to be placed permanently at a field site or in a laboratory configuration and logged continuously at a desired interval with minimal manual labour.

There are now a variety of configurations of TDR equipment available to suit the particular needs for soil moisture monitoring (O'Connoer *et al.*, 2000). The TDR probe adopted for use in the following laboratory work is the stand alone ThetaProbe ML2, manufactured by Delta-T Devices (Delta-T, 1998). The probe has an outer diameter of 40 mm, with the diameter of measurement approximately 26.5 mm (Delta-T, 1998).

The relationship between the voltage measured by the ThetaProbe and the square root of the apparent dielectric constant ($\sqrt{\varepsilon}$) of the soil can be represented by a polynomial (6-1a) or a linear (6-1b) equation, where V is voltage (Delta-T, 1998) :

$$\sqrt{\varepsilon} = 1.07 + 6.4V - 6.4V^2 + 4.7\,V^3 \qquad (R^2 = 0.998) \qquad \text{6-1a}$$

$$\sqrt{\varepsilon} = 1.1 + 4.44V \qquad (R^2 = 0.99) \qquad \text{6-1b}$$

The voltage measured by the ThetaProbe is converted to the apparent dielectric constant using either 6-1a or 6-1b, which is then related to the soil moisture content by the calibration curve. By obtaining voltage readings from soils of varying moisture content, it is possible to develop the calibration curve for a particular soil and the relationship between TDR voltage and soil moisture.

The relationship between soil moisture content and TDR probe voltage can be influenced by soil density, specific surface area (ie. - high clay or organic content), salinity, temperature and entrained air pockets (Whalley, 1993; White *et al.*, 1994; Rassam & Williams, 1997). An approximate relationship can be used for typical clayey or organic soils (Delta-T, 1998), although it is preferrable to develop a specific correlation to account for particular soils. Studies in the literature have used both volumetric water content (θ) versus the measured voltage (V) and θ versus calculated $\sqrt{\varepsilon}$ (eg. Rassam & Williams, 1997; Delta-T, 1998). Coal ash is not a typical soil, and thus a calibration study was performed for use in current and future laboratory and field work.

6.3.2 Calibration of TDR Probes to Ash

A total of 14 ash samples were prepared with different moisture contents and placed in 100 mm diameter soil cups. All ash samples were oven dried for 24 hours, and then varying levels of moisture added to achieve the desired range. The average dry density was relatively consistent at 723 kg/m^3, ranging from 628 to 805 kg/m^3 with a standard deviation of 51 kg/m^3. This is within the range found within the ash pond and disposal sites from previous research (cf. Kacavenda & McKinley, 1994). The gravimetric moisture content ranged from 0.0% to 81.4%. The soil data is given in Table 6.1. A ThetaProbe was placed in the centre of each cup and the average voltage of several measurements taken. This was converted to the apparent dielectric constant using equations 6-1a and 6-1b.

Table 6.1 - Soil Calibration Data for TDR Thetaprobes

Gravimetric Moisture Content	Volumetric Water Content (θ)	ThetaProbe Voltage (V)	$\sqrt{\varepsilon}$ Linear	$\sqrt{\varepsilon}$ Polynomial	Density (kg/m^3) Dry	Density (kg/m^3) Wet
0.0%	0.00	0.234	2.14	2.33	719.9	719.9
5.5%	0.04	0.320	2.52	2.68	757.5	799.4
8.6%	0.06	0.364	2.71	2.85	756.3	821.3
16.5%	0.12	0.575	3.65	3.60	744.1	866.7
18.9%	0.13	0.550	3.54	3.51	700.8	833.2
23.3%	0.17	0.764	4.49	4.37	738.5	910.7
27.5%	0.19	0.703	4.22	4.10	682.2	869.7
34.3%	0.23	0.830	4.79	4.70	682.4	916.8
45.9%	0.30	0.927	5.22	5.27	658.4	960.7
55.6%	0.35	0.912	5.15	5.17	628.1	977.6
59.5%	0.43	0.960	5.36	5.49	721.6	1150.7
41.4%	0.30	0.931	5.23	5.29	735.8	1040.5
77.6%	0.59	1.009	5.58	5.84	787.1	1397.7
81.4%	0.66	1.007	5.57	5.82	805.3	1460.6

The results are shown in Figures 6.3 and 6.4, with a 6th order polynomial regression line fitted to the experimental data (using the statistical regression feature available in Microsoft Excel 97). The graphs θ versus TDR voltage (V) and θ versus $\sqrt{\varepsilon}$ are included for comparison.

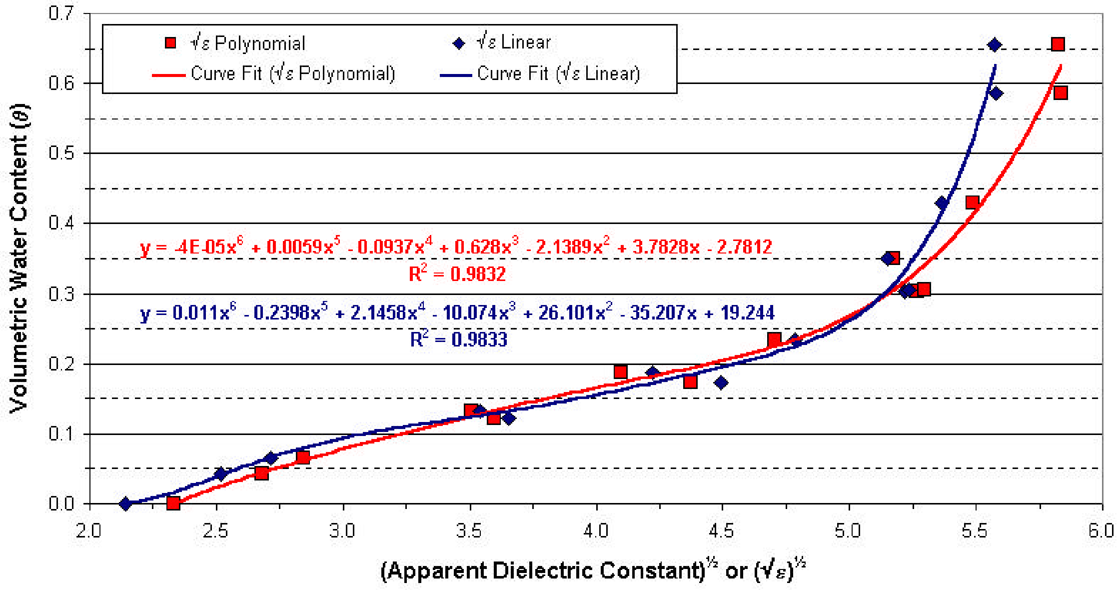


Figure 6.3 - Volumetric Water Content (θ) versus (Apparent Dielectric Constant or √ε)^{½}

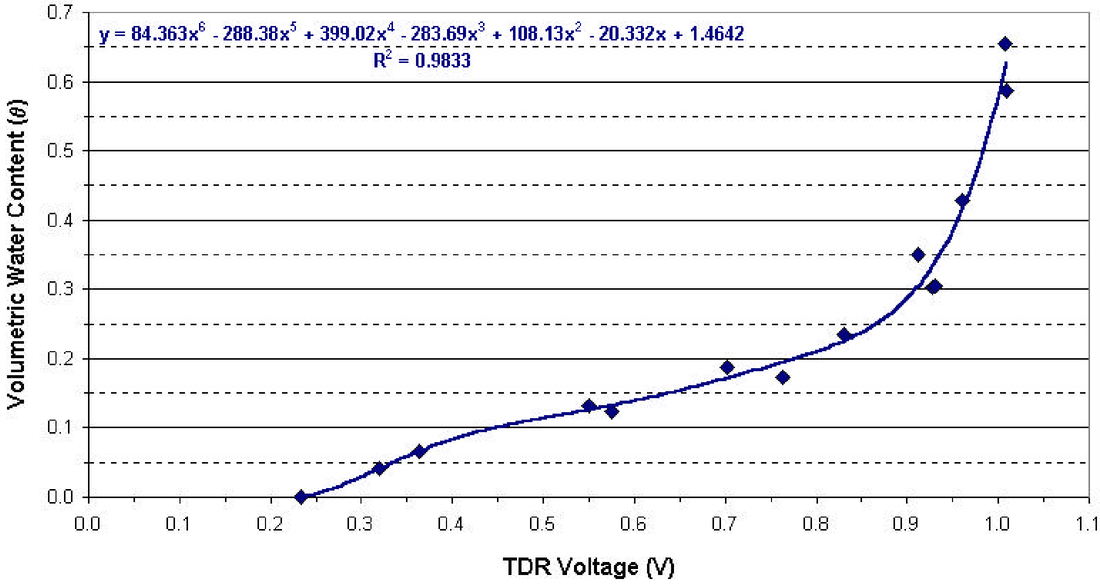


Figure 6.4 - Volumetric Water Content (θ) versus TDR Voltage (V)

The 3 different curves, using the linear or polynomial equation for √ε, give a reasonable approximation to the data, with R^2 values of 98.3%. The equation of θ versus V (6-2) will be used for column leaching tests, as this is a more convenient and direct method.

θ vs V $$\theta = 84.363(V)^6 - 288.38(V)^5 + 399.02(V)^4 - 283.69(V)^3 + 108.13(V)^2 - 20.332(V) + 1.4642 \qquad \text{6-2}$$

θ vs √ε (√ε - Linear, 6-1b) $$\theta = 0.011(\sqrt{\varepsilon})^6 - 0.2398(\sqrt{\varepsilon})^5 + 2.1458(\sqrt{\varepsilon})^4 - 10.074(\sqrt{\varepsilon})^3 + 26.101(\sqrt{\varepsilon})^2 - 35.207(\sqrt{\varepsilon}) + 19.244 \qquad \text{6-3a}$$

θ vs √ε (√ε - Polynomial, 6-1a) $$\theta = -4\text{x}10^{-5}(\sqrt{\varepsilon})^6 + 0.0059(\sqrt{\varepsilon})^5 - 0.0937(\sqrt{\varepsilon})^4 + 0.628(\sqrt{\varepsilon})^3 - 2.1389(\sqrt{\varepsilon})^2 + 3.7828(\sqrt{\varepsilon}) - 2.7812 \qquad \text{6-3b}$$

6.4 Influent Water Quality

All 3 samples of influent (distilled) water analysed had a salinity less than 10 mg/L with most trace elements below analytical detection limits. One sample showed trace concentrations of Cu at 0.08 mg/L and Al at 0.02 mg/L, marginally above analytical detection limits (0.01 mg/L).

6.5 Precipitator Ash Column

There were 2 samples from the precipitator ash which were chemically analysed, with the results in Tables 6.2 and 6.3. These results are similar to those from earlier research and presented in Section 4.3. The moisture content was low, at about 1%. This is expected due to the sample being stored in a dry area, within black plastic inside a closed storeroom (in a cupboard with no light).

Table 6.2 - Precipitator Ash Leaching Column : Major Elements (%, dry basis)

	SO_4	Cl	Na	K	Ca	Mg	Fe	Al	AI	LOI
1	19.0	2.4	11.0	0.29	9.1	8.3	1.3	4.6	20	11
2	15.0	2.3	11.0	0.30	9.5	8.3	1.2	4.6	20	13

Table 6.3 - Precipitator Ash Leaching Column : Trace Elements (mg/kg, dry basis)

	As	B	Ba	Cd	Cr	Co	Cu	Hg	Mo	Ni	Se	Sn	Sr	Zn
1	13	880	83	<0.2	13	<5	45	0.43	<5	19	38	<5	2,800	110
2	14	1,000	90	<0.2	13	<5	44	0.45	<5	18	39	<5	2,900	110

The precipitator ash column, despite 2 separate attempts, failed to operate acceptably. On each occasion, the inflow water was observed to flow progressively through the ash, until approaching the base of the column. After this point, the inflow failed to travel any further, and instead began back-flowing out of the top cap after a suitable back pressure developed to force the flow.

Investigations and deconstruction of the column on both occassions showed that the formation of a cement-like material dramatically reduced permeability of the ash. The cause, although not identified specifically, was likely due to the high Ca and SO_4 content of the ash leading to the precipitation of gypsum and possibly calcite.

Since this column was for comparitve purposes only and not intended for modelling of ash disposal sites, the column was abandoned. It is recommended that in the future a new series of ash samples be obtained and column leaching studies be conducted, to assess the different total soluble masses compared to leached ash.

6.6 Large Leached Ash Column

6.6.1 Overview

The Large column (1,500 mm) containing leached ash, operated from October 3, 1999, to December 9, 1999 - a total time of 67 days. The measured geotechnical properties are listed in Table 6.4. The dry density is similar to the field cells, although the moisture content is slightly lower. The gravimetric moisture content of the ash was uniform. There were a total of 9 TDR probes inserted equidistantly into the column. The top and bottom probes were 80 mm (to the centre of the TDR hole) from the column top/bottom, with all probes spaced at 160 mm between the centre.

Table 6.4 - Geotechnical Properties of the Large Column

Gravimetric Moisture	Density (kg/m^3)		Void Ratio	Porosity	Degree of Saturation	Volumetric Moisture
	Wet	Dry				
52.3%	893	586	2.99	75.0%	40.9%	30.7%

6.6.2 Cumulative Flows

The column was operated for an initial period of 16 days, at which time the inflow was temporarily stopped. The first day was operated with a higher inflow rate of about 32 mm/hr in order to expedite the initial saturation of the ash within the column (given the low initial volumetric water content). Once leachate was observed to begin flowing, the inflow rate was reduced to about 11 mm/hr to allow for more normal operation. The graph of inflow and outflow is given in Figure 6.5.

The discharge of leachate was initially observed to be sporadic, although after a few days this became more uniform drip-wise discharge, approximating the inflow rate. It can be observed that the cumulative inflow and outflow is approximately the same gradient, offset by a small difference. This difference is the amount of water required to bring the ash within the column to allow vertical percolation of moisture under gravity drainage. This remains the same for the remainder of the operation of the column.

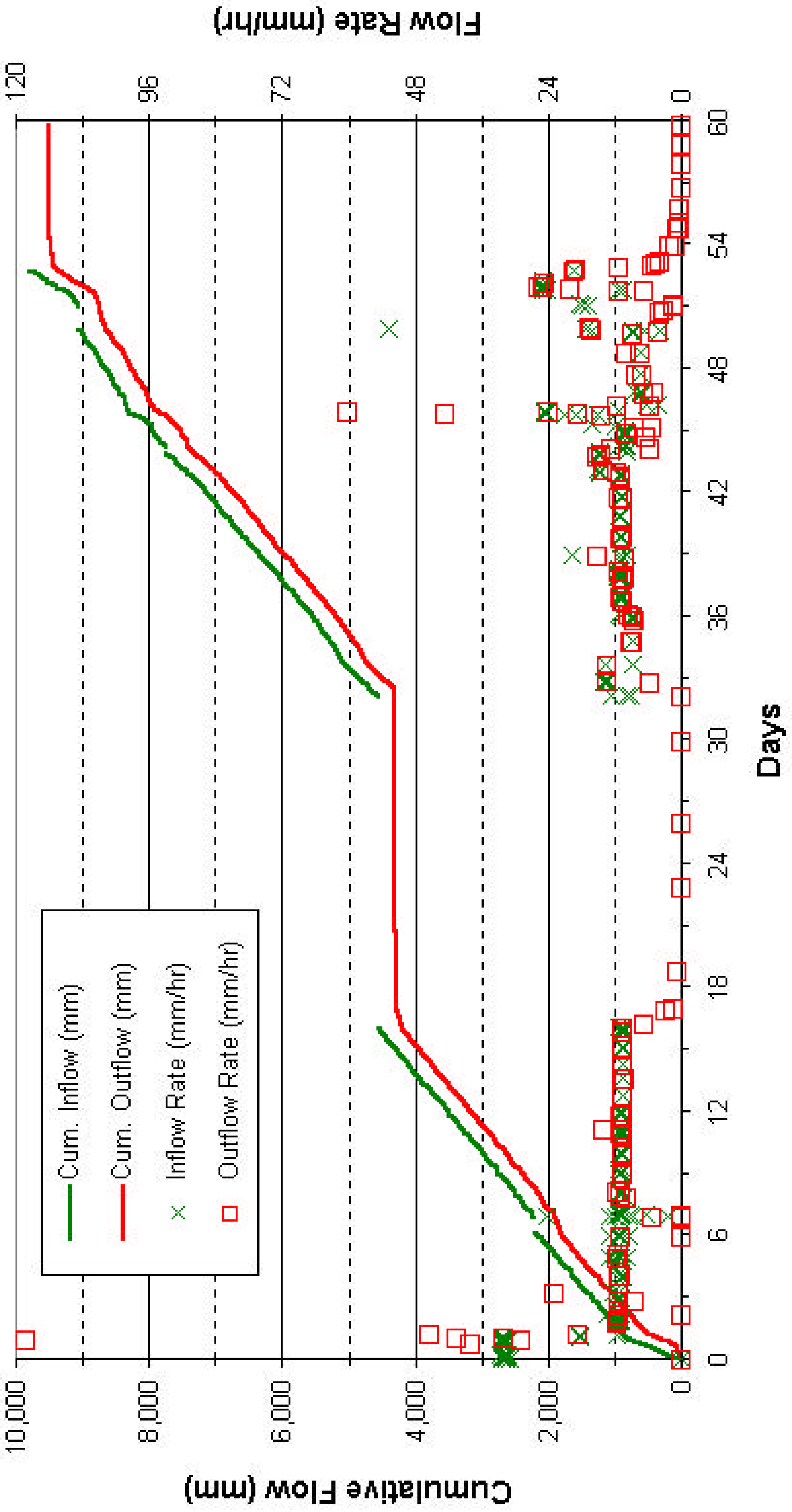


Figure 6.5 - Cumulative Flows of the Large Column

The inflow was stopped on day 16 to determine if the residence time of pore water within the ash has any effect on leachate chemistry, primarily salinity. As discussed in Chapter 2, the dissolution of most major minerals in coal ash is generally considered to be rapid, however, the results of the Dry Cell suggested that residence time may be important in some circumstances of low flow. This would primarily be due to diffusion occurring within the ash, transferring the solutes from inside the porous ash particles to the surface, where the solutes are easily available for advective leaching and removal (discharge) from the ash column.

The discharge of leachate continued for several days, although at a rapidly decreasing rate. This suggests that it would only take a small amount of water to induce flow again within the vertical profile, as the ash has satisfied its soil moisture deficit. The leachate flow rate, however, would primarily depend on the inflow rate. An analysis of the flow behaviour and hydraulic conductivity of all columns is presented later in this chapter.

After a further 16 days, the inflow was again started (day 32), and leachate was quick to begin discharge, less than 16 hours later. The exact time of leachate discharge is unclear since it occurred overnight between the monitoring times for the column. The TDR probe data is inconclusive as there is no significant repsonse in the measurements to suggest an increase in moisture in the column. Assuming the leachate flow rate of 13.5 mm/hr immediately after the first observed leachate discharge on day 32, it would have taken about 7 hours to reach the total volume of leachate collected, suggesting the outflow rate increased rapidly.

From about day 45, the inflow rate was varied, primarily to observe the response of the ash to different inflow rates, especially higher rates. The ash responded quite rapidly to changes in the inflow rate, with changes in the outflow (leachate) rate being observable generally within several hours. On day 52, the inflow was permanently stopped and the column allowed to continue to discharge leachate until dismantling. The outflow rate again showed a rapid reduction over time, albeit over a period of several days. A further discussion of water content response within the ash is given in a review of the TDR probe data, Section 6.6.5.

Overall, there was a total inflow of 9,781.8 mm (78.37 L) pumped into the Large column, with a total estimated discharge of 9,505.7 mm (76.16 L). The calculated pore volume is 1,117 mm (8.95 L), representing about 8.4 pore volumes of leaching.

6.6.3 Final Vertical Moisture Profile

During dismantling of the Large column, a series of ash samples were taken to obtain a vertical profile of moisture content, given in Table 6.5. This data shows a small increase in moisture content towards the base of the column, related to free drainage of excess pore water and corresponding well to that observed in the field trial cells and the current ash disposal site.

Table 6.5 - Final Profile of Moisture Content (Depth)

(cm)	Grav.	Vol.	(cm)	Grav.	Vol.	(cm)	Grav.	Vol.
0 TOP	89.1%	52.2%	54	85.9%	50.4%	112	91.4%	53.6%
6	82.0%	48.1%	65	83.8%	49.1%	120	96.6%	56.6%
15	80.4%	47.1%	73	87.5%	51.3%	128	99.3%	58.2%
22	80.4%	47.1%	80	83.2%	48.8%	138	100.5%	58.9%
30	67.3%	39.5%	89	93.2%	54.6%	145	94.4%	55.3%
39	84.3%	49.4%	96	94.9%	55.6%			
48	87.4%	51.2%	105	90.8%	53.2%			

Grav. - Gravimetric
Vol. - Volumetric

The average gravimetric moisture content is about 88.0%, or a volumetric water content of about 0.516 (68.8% degree of saturation). This gives a final moisture within the column equal to 767 mm, compared to the 457 mm initially present (40.9% saturation). The difference of 312 mm is very close to the deficit of 276 mm observed in the graph of cumulative flows (within ~12% error).

6.6.4 TDR Probes and Soil Moisture Monitoring

The continuous monitoring of soil moisture content by TDR probes appears to be less successful than hoped. The probes were able to demonstrate the initial saturation of the column, however, the apparent volumetric water content determined by TDR was 0.160 (calculated from 6-2), compared to the measured value of 0.306. If equations 6-3a and 6-3b are used with the linear and polynomial calibrations, the calculated volumetric water contents are 0.122 and 0.196, respectively. The various calculations suggest that the TDR probes underestimated the volumetric water content in the Large column. The probes had to be removed on day 53 (Nov. 25, 1999), as they were required for the joint operation of the Medium and Small columns. The full data set is shown in Figure 6.6, with initial data for days 0 to 20 and 0 to 2 in Figures 6.7 and 6.8, respectively.

The TDR data appears to display a small diurnal variation. The cause of this is unclear, since the laboratory was maintained at effectively constant temperature and the average wind speed provided by the fan did not vary. In addition, the column was sealed and so internal air pressure changes within the column should be minimal (since this may lead to small changes in the ratio of air and water volumes in the pore space). The magnitude of these changes are small compared to the changes in overall moisture content, however, further research to examine this behaviour is recommended.

The TDR data in Figure 6.5 displays good response to the initial wetting of the ash profile (days 0 to 2) and the first period of drainage from day 16. The probes at the top of the column (L1 - 80 mm and L3 - 250 mm) display decreasing water contents from this point, although little change is observed in probe L2 - 420 mm, in between L1 and L3. The data after this period, however, appears less than satisfactory. The missing data from days 19 to 26 is due to the need to test the TDR probes on the Medium and Small columns. This involved disconnecting the wiring from the installed TDR probes on the Large column and wiring the probes for the Medium and Small columns to the datalogger. It appears that after this point, despite the TDR probes on the Large column being connected identically, the data shows some bias toward a lower moisture value not consistent earlier data and the higher moisture content determined gravimetrically at the end of column’s operation. The causes of this are unclear.

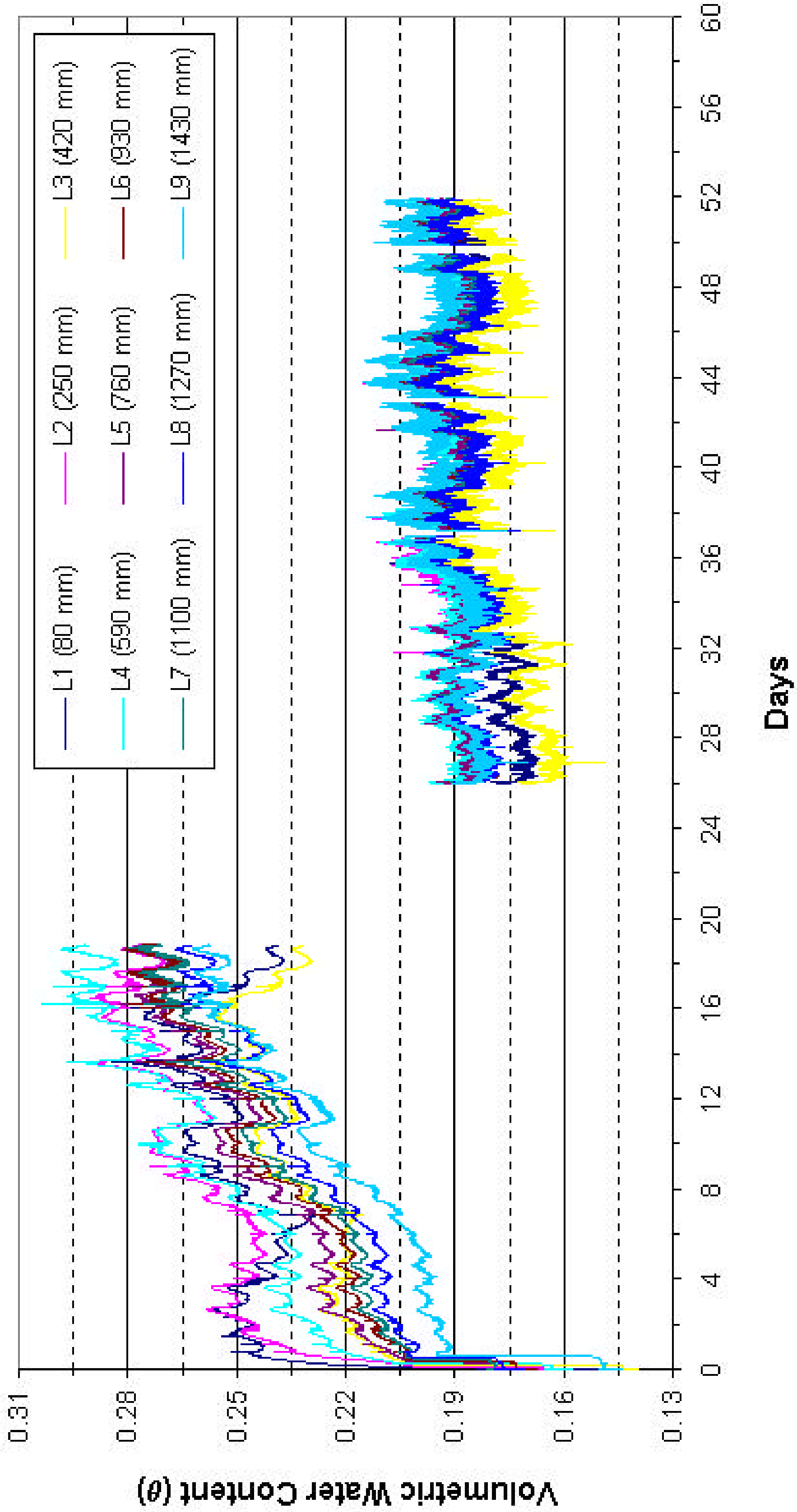


Figure 6.6 - Complete TDR Probe Data for Calculated Volumetric Water Content

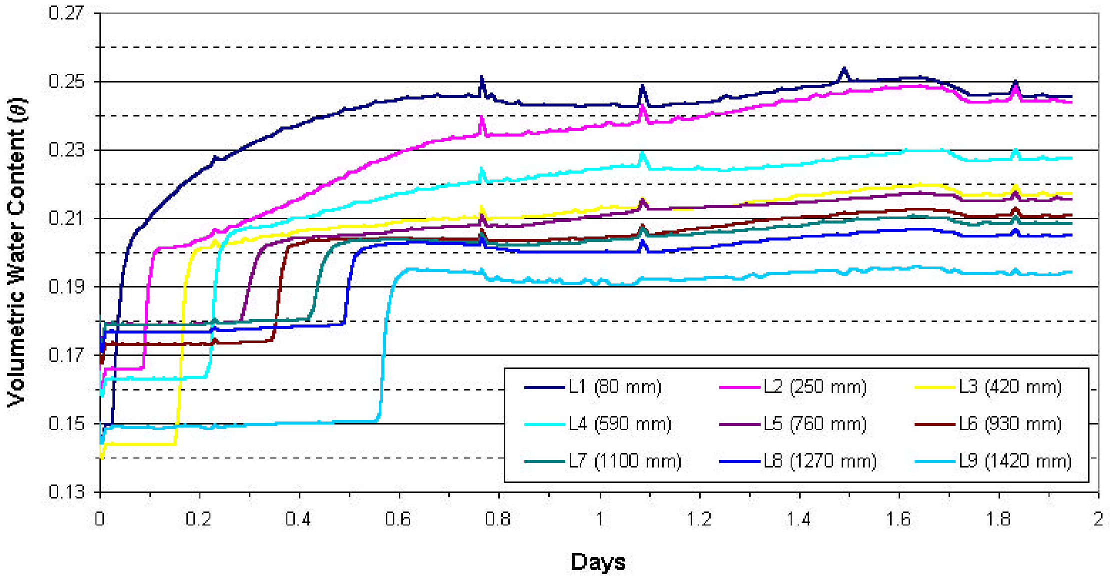


Figure 6.7 - TDR Probe Data for Calculated Volumetric Water Content : Days 0 to 2

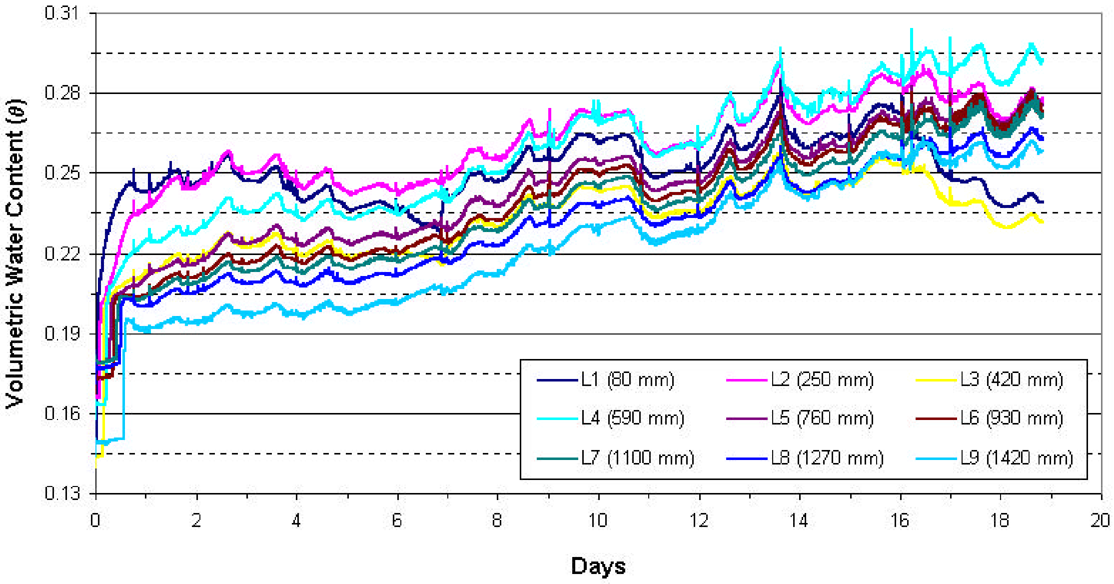


Figure 6.8 - TDR Probe Data for Calculated Volumetric Water Content : Days 0 to 20

6.6.5 Leachate Chemistry

The leachate emanating from the Large column was sampled regularly and chemically analysed for a comprehensive suite of major elements and trace elements. The results are given in Tables 6.6 and 6.7, and graphed as normalised concentrations relative to the first sample in Figures 6.9 and 6.10.

Table 6.6 - Leachate Quality : Major Ions (mg/L)

Days	Pore Vol.	pH	EC	TDS	SO_4	Cl	HCO_3	CO_3	F
0.930	0.207	-	3,000	28,000	18,000	1,800	180	64	-
1.802	0.595	-	1,300	10,000	5,300	380	150	72	-
4.047	1.136	-	370	3,000	2,100	27	130	100	-
7.880	1.878	-	19	1,400	920	5.0	84	110	-
10.822	2.554	9.4	130	810	460	2.0	84	92	0.9
14.294	3.352	9.4	82	530	260	2.0	72	76	1.0
32.794	3.932	9.1	97	660	320	3.3	140	60	<0.3
37.775	5.047	9.1	51	330	140	4.0	58	40	0.8
44.860	6.718	8.7	26	170	47	2.0	54	24	0.6
52.746	8.372	9.1	30	160	50	2.1	54	36	0.4

Note - EC in mS/m.

Days	Pore Vol.	Na	K	Ca	Mg	Fe	Al	SiO_2
0.930	0.207	9,500	320	270	330	1.20	0.08	5.0
1.802	0.595	3,000	140	88	100	0.27	0.05	5.9
4.047	1.136	1,000	47	21	24	0.04	0.03	6.1
7.880	1.878	440	28	13	12	0.03	<0.01	2.9
10.822	2.554	280	20	7.8	6.5	<0.01	0.07	4.8
14.294	3.352	200	17	4.9	4.6	<0.01	0.07	4.2
32.794	3.932	220	21	8.2	11	<0.01	0.26	5.3
37.775	5.047	100	15	3.2	4.8	<0.01	0.12	0.22
44.860	6.718	41	11	4.0	5.8	<0.01	0.10	0.22
52.746	8.372	34	14	9.8	11	0.55	0.28	3.7

Table 6.7 - Leachate Quality : Trace Elements (mg/L)

Pore Vol.	As	B	Ba	Cr	Cu	Mo	Se	Sr	Zn
0.207	0.130	4.9	0.04	0.02	0.02	0.77	8.5	25	0.02
0.595	0.071	5.1	0.04	<0.01	<0.01	0.22	2.5	6.4	<0.01
1.136	<0.001	5.3	0.05	0.02	<0.01	0.06	0.72	1.5	<0.01
1.878	<0.001	6.4	0.06	<0.01	<0.01	0.02	0.23	0.89	<0.01
2.554	<0.001	6.1	0.04	-	-	<0.01	0.086	0.56	-
3.352	<0.001	5.5	0.05	-	-	<0.01	0.049	0.42	-
3.932	<0.001	3.7	0.07	-	-	0.01	0.051	0.55	-
5.047	<0.001	2.5	0.05	-	-	<0.01	0.036	0.32	-
6.718	<0.001	5.5	0.07	-	-	<0.01	0.017	0.41	-
8.372	0.034	2.0	0.13	<0.01	<0.01	<0.01	<0.001	0.74	0.02

The following elements were consistently below analytical detection limits (mg/L) : Cd <0.001, Co <0.01, Hg <0.001, Ni <0.01 and Sn <0.01.

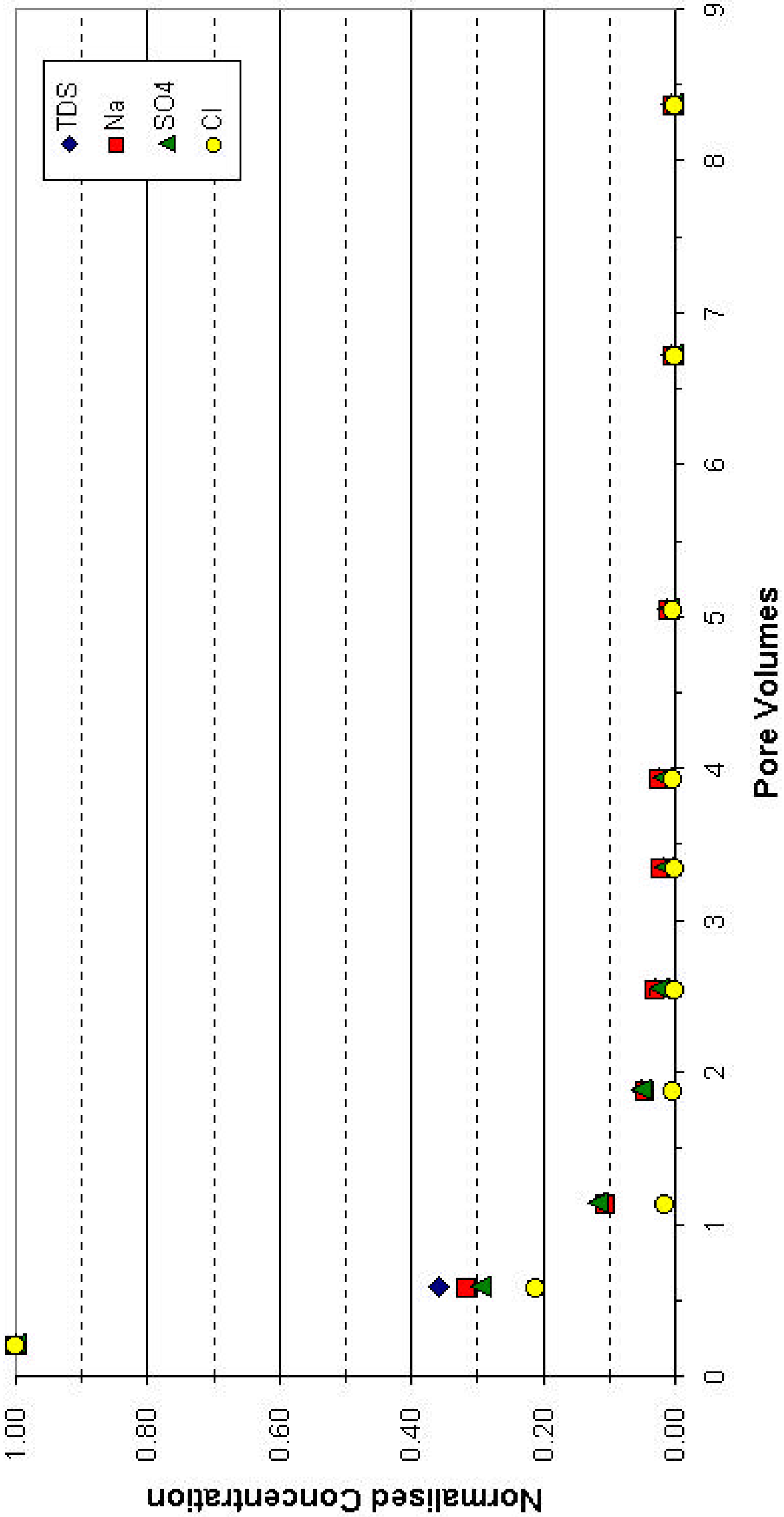


Figure 6.9 - Major Element Leaching Curves of the Large Column

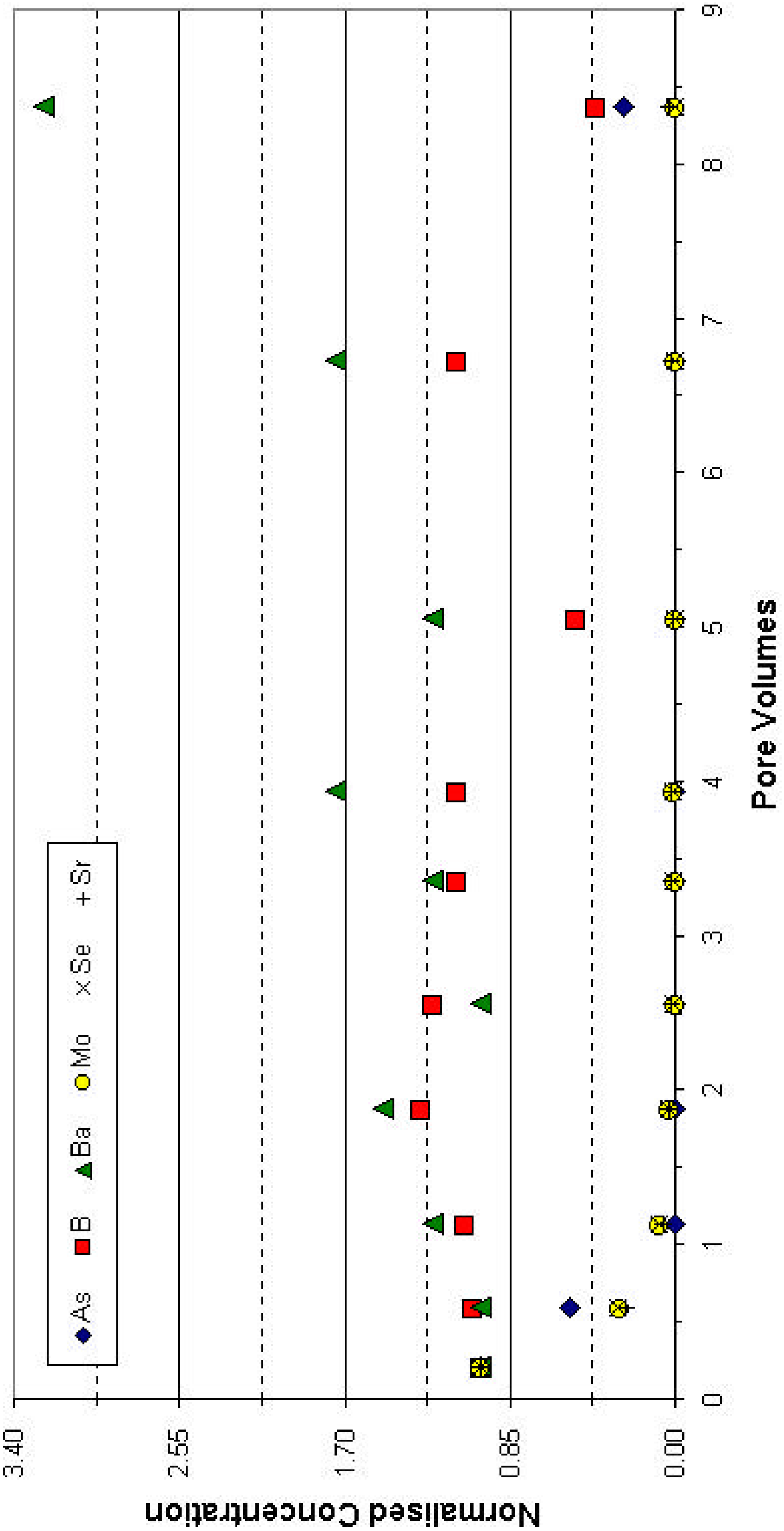


Figure 6.10 - Trace Element Leaching Curves of the Large Column

The leachate chemistry is initially highly saline, approximately that of seawater (cf. Langmuir, 1997), although with the same chemistry as the field cells and the ash pond - high Na, SO_4 and Cl. The decrease in concentrations is rapid - by about 1 pore volume of leaching, Na and SO_4 are 10% of their initial concentration, while Cl is at 1.5%.

Of particular note is the sample collected at 32.79 days - the first sample after 16 days of no inflow. This sample has a salinity of 660 mg/L, about 25% higher than the previous sample of 530 mg/L. This pattern is confirmed in the higher respective proportions of almost all major species in the leachate. Thus the residence time would appear to be important in characterising and modelling leachate behaviour.

6.6.6 Ash Quality

Samples of ash were obtained and analysed before and after operation of the column. These results are within previous data, and are given in Tables 6.8 and 6.9. The results are within those reported in previous work and within the results reported in the thesis. The SO_4 and Cl are almost completely leached, while Na decreased by about half and K is only partially leached, similar to B. The concentrations of the more soluble elements, such as SO_4, Na, K and B, appear to increase with depth in the column.

Table 6.8 - Large Ash Leaching Column : Major Elements (%, dry basis)

	SO_4	Cl$^{\#}$	F$^{\#}$	Na	K	Ca	Mg	Fe	Al	AI	LOI
I-1	0.57	430	-	1.00	0.083	2.8	3.5	2.6	2.0	60	16
I-2	0.54	430	-	0.81	0.071	2.6	2.9	2.1	1.6	51	16
P-T	0.015	13	<5	0.44	0.051	3.3	4.7	4.6	4.6	43	20
P-M	0.015	12	<5	0.49	0.063	3.3	4.3	3.9	3.6	43	20
P-B	0.024	16	<5	0.51	0.068	3.4	4.3	4.3	3.9	33	19

Notes : I - Initial; P - Post Leaching; Mid - Middle, Btm - Bottom. $^{\#}$ - mg/kg.

Table 6.9 - Large Ash Leaching Column : Trace Elements (mg/kg, dry basis)

	As	B	Ba	Cd	Cr	Co	Cu	Hg	Mo	Pb	Ni	Se	Sn	Sr	Zn
I-1	10	200	480	<0.2	26	17	41	0.52	<5	-	32	<5	<5	700	78
I-2	9	180	460	<0.2	21	12	27	0.83	<5	-	23	<5	<5	620	52
P-T	8	130	640	0.4	83	27	48	1.5	<5	16	54	7	<5	710	110
P-M	7	120	570	0.3	70	32	38	1.3	<5	10	47	7	<5	620	60
P-B	8	140	550	0.4	72	23	34	1.3	<5	10	47	7	<5	640	58

6.6.7 Changes in Soluble Mass

The changes in soluble mass within the Large ash column have been calculated in the same as way as the field leaching cells and presented in Tables 6.10 and 6.11, except no graphs have been produced due to the similarity of the laboratory leaching curves with the field research. Comparison of the calculated mass leached from analysis of the ash to that calculated from the mass contained in leachate shows a similar pattern to the field cells also. The majority of SO_4 and Cl has been leached, combined with a significant proportion of the Na and K. Minor amounts of Ca, Mg and SiO_2 were leached, with the variability in chemical analysis precluding any accurate assessment of changes in soluble mass. The amount of SO_4, Cl, Na and K calculated to have been leached based on the mass in the leachate is significantly higher than that by analysis of the ash. For trace elements, the estimates suggest that only minor amounts of the contained As, Sr, Mo and Ba are leached, while significant proportions of the B and Se are leached. The estimates of Se and B leached based on leachate mass and ash analysis are comparable, while those for As, Ba, Mo and Se are somewhat different. Thus it appears that a soluble mass approach for trace elements is not feasible, while for major elements this appears capable of capturing the essential behaviour.

Table 6.10 - Total Soluble Mass in Leached Ash and Leachate : Major Elements (g)

	SO_4	Cl	Na	K	Alk.^{1}	Ca	Mg	Al	Fe	SiO_2^{2}
Initial	38.8	3.01	63.3	5.38	-	189	224	126	164	3,882
Final	1.3	0.10	33.6	4.24	-	233	310	282	298	2,774
Leachate	114.4	8.37	62.0	3.3	11.0	1.85	2.2	<0.01	<0.01	0.23

^{1} - Sum of alkalinity due to HCO_3 and CO_3; ^{2} - Assuming the acid insoluble fraction is silica.

Table 6.11 - Total Soluble Mass in Leached Ash and Leachate : Trace Elements (mg)

	As	B	Ba	Mo	Se	Sr
Initial	66.5	1,329	3,287	35^1	35^1	4,616
Final	53.6	909	4,103	35^1	49	4,593
Leachate	1.01	339.8	4.71	4.23	48.45	156.6

^{1} - Assuming the average is the detection limit of 5 mg/kg.

6.7 Medium Leached Ash Column

6.7.1 Overview

The Medium column (750 mm) containing leached ash, operated from November 25 to December 28, 1999 - a total time of 33 days. The measured geotechnical properties are listed in Table 6.12. The dry density is similar to the Large column and field cells, although the moisture content is slightly lower. The moisture content of the ash was uniform. There were a total of 6 TDR probes inserted equidistantly into the column. The top and bottom probes were 70 mm (to the centre of the TDR hole) from the column top/bottom, with all probes spaced at 130 mm between the centre.

Table 6.12 - Geotechnical Properties of the Medium Column

Gravimetric Moisture	Density (kg/m^3)		Void Ratio	Porosity	Degree of Saturation	Volumetric Moisture
	Wet	Dry				
50.2%	954	635	2.69	72.9%	43.7%	31.9%

6.7.2 Cumulative Flows

The column was operated for an initial period of 6 days, at which time the inflow was temporarily stopped. The inflow rate was maintained at about 10.9 mm/hr (1.45 mL/min). There was no need to expedite the initial saturation of the ash with a higher inflow rate due to the smaller size of the Medium column. A full graph of inflow and outflow is given in Figure 6.11.

The first discharge of leachate was also observed to be slightly variable, similar to the Large Column. The discharge approached steady state quickly, however, with the outflow approximately equalling the inflow rate for the remainder of the trial. It can be observed that the curves of cumulative inflow and outflow have approximately the same gradient, offset by a small difference which remains constant for the remainder of the operation of the column.

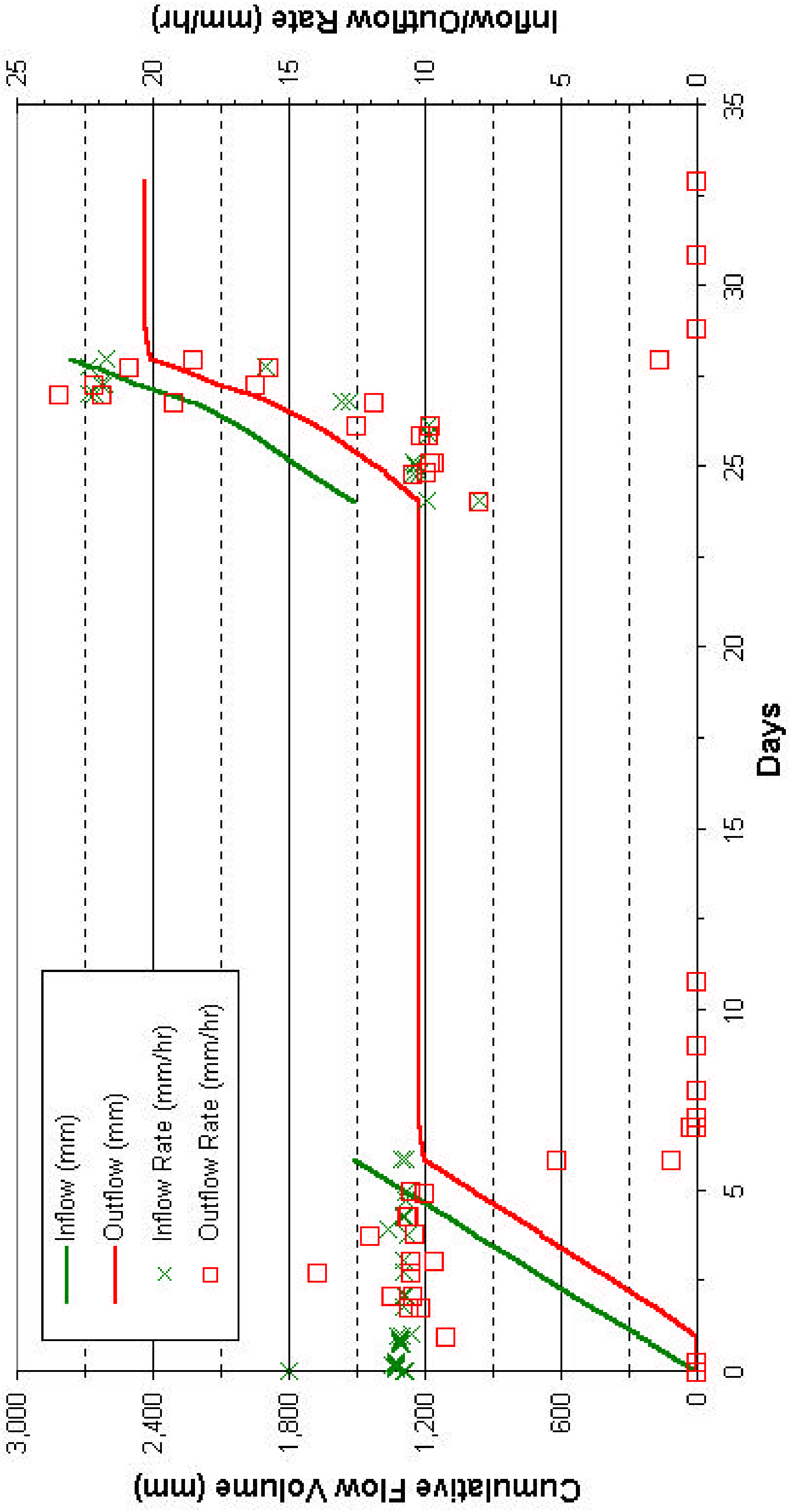


Figure 6.11 - Cumulative Flows of the Medium Column

On day 14, the top cap was removed from the column. This was to investigate the possible effects of evaporation on the moisture profile and the leachate chemistry. Initially, there appeared to be no change to the moisture profile (refer to the TDR data). About day 19 the overall moisture content began to decrease throughout the column, until stabilising around day 21. On the basis of the TDR data, the small changes observed in the soil moisture profile are consistent with the moderate temperature (~16 ^{0}C) and humidity (~57%) within the soils laboratory, leading to mild evaporative conditions. Time constraints did not allow any variation or testing of the effects of varying climatic conditions in the laboratory columns to be studied during this work.

The inflow was restarted about 18 days after the temporary stop (day 24), with the inflow rate maintained at about 10.9 mm/hr. At about day 26 the inflow rate was increased to 19.2 mm/hr to allow for more pore volumes to be reached and complete discharge of leachate before termination of the test on day 33. The inflow was stopped at the end of day 28, with the discharge of leachate taking about 5 days to complete.

Overall, there was a total inflow of 2,758.6 mm (22.10 litres) pumped into the Medium column, with a total estimated discharge of 2,435.4 mm (19.51 litres). Given the calculated pore volume of about 539 mm (4.32 litres), this represents about 4.5 pore volumes of leaching.

6.7.3 Final Moisture Vertical Profile

During dismantling of the Medium column, a series of ash samples were taken to obtain a vertical profile of moisture content, given in Table 6.13. This data shows a small increase in moisture content towards the base of the column, corresponding well to the behaviour observed in the field trial cells and the current ash disposal site.

Table 6.13 - Final Profile of the Moisture Content

(cm)	Gravimetric	Volumetric	(cm)	Gravimetric	Volumetric
0 TOP	90.9%	57.7%	31	91.6%	58.2%
7	94.3%	59.9%	44.5	79.7%	50.6%
13	90.1%	57.2%	57	94.8%	60.2%
19.5	90.9%	57.7%	69	113.3%	71.9%

The average moisture content is about 93.2%, or a volumetric water content of about 0.592 (81% degree of saturation). This gives a final moisture within the column equal to 438 mm, compared to the 323 mm initially present (43.7% saturation). The difference of 115 mm compares to the deficit of 324 mm observed in the graph of cumulative flows.

6.7.4 TDR Probes and Soil Moisture Monitoring

The monitoring of soil moisture content by the TDR probes appears to be more successful for the Medium column than the Large column. Similarly to the Large column, the probes were able to demonstrate the initial saturation of the column, however, the apparent volumetric water content determined by TDR was 0.142 (calculated from 6-2), compared to the measured value of 0.319. If equations 6-3a and 6-3b are used with their respective linear and polynomial calibration regressions, the calculated volumetric water contents are 0.118 and 0.126, respectively. As for the Large column, these calculations suggest that the TDR probes are underestimating the actual volumetric water content. The probes were removed on day 33 (Dec. 28, 1999), when the test was completed. The full data set is shown in Figure 6.12, with initial data for days 0 to 4 in Figures 6.13. The TDR data appears to display a larger diurnal variation than the Large column, although the environmental conditions in the laboratory were unchanged.

The TDR data displays good response to the initial wetting of the ash profile (days 0 to 4) and the first period of drainage from day 16. All probes display a slight decreasing trend in water content from this point. The data after this period (days 8 to 11) was not recorded properly by the datalogger and is missing. The initial data for days 11 to 13 is slightly higher than that previously measured, but within expected ranges. A further malfunction occurred on day 14, and the data for day 15 is higher again. After the data was downloaded from the datalogger, the TDR probes return to readings similar to those earlier from days 11 to 13 and earlier. The causes of this are unclear, but warrant a degree of caution in interpreting the datasets.

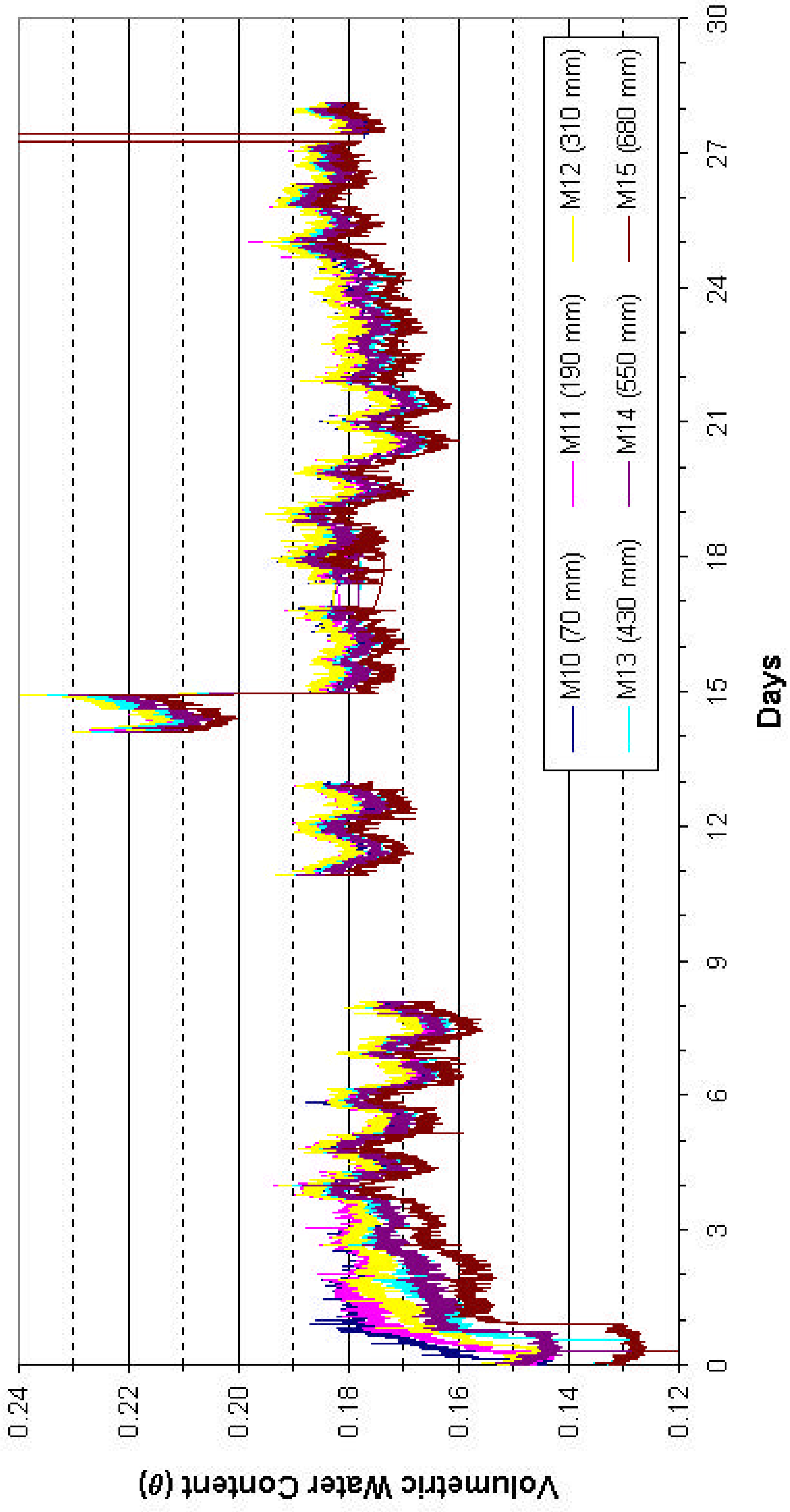


Figure 6.12 - Complete TDR Probe Data for Calculated Volumetric Water Content

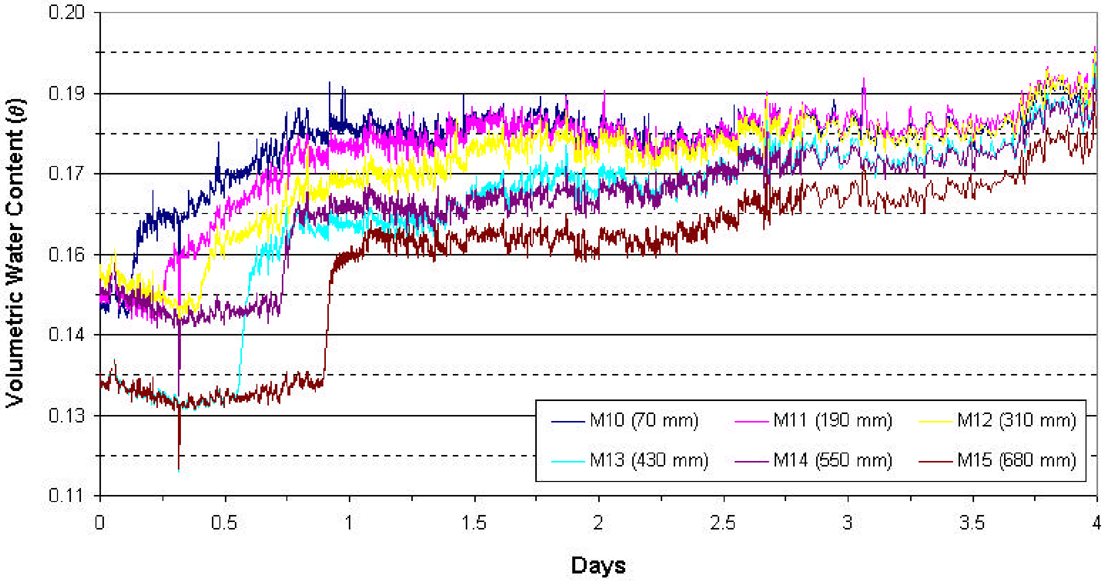


Figure 6.13 - TDR Probe Data for Calculated Volumetric Water Content : Days 0 to 4

6.7.5 Leachate Chemistry

The chemistry of leachate is again similar to that from previous research, being Na-SO_4-Cl dominated water with minor trace metal content. The initial salinity is slightly lower than the Large column, but still higher than the initial leachates from the Wet and Dry field cells. As expected, there is a rapid decline in salinity as inflow and leachate discharge increase. The first sample of leachate on day 24, after the 18 day break, shows an increase in salinity of about 29% with a similar increase in most major elements. The results are provided in Tables 6.14 and 6.15 and Figures 6.14 and 6.15.

The following elements were consistently below analytical detection limits (mg/L) : Cd <0.001, Co <0.01, Hg <0.001, Ni <0.01 and Sn <0.01.

It appears that As, Ba, Cr, Mo and Se all increase during the 18 day break in inflow, with Cu and Sr decreasing. The trend for B is unclear, since this was already increasing before the break. The trend for Ba after day 24 is a steady decline to a stable value of 0.04 mg/L. The geochemical controls on major and trace element solubility will be reviewed in more detail in Chapter 7.

Table 6.14 - Leachate Quality : Major Ions (mg/L)

Days	Pore Vol.	pH	EC	TDS	SO_4	Cl	HCO_3	CO_3	F
1.778	0.332	8.7	2,300	20,000	14,000	900	260	110	0.4
2.115	0.484	8.8	1,600	12,000	8,800	320	250	96	0.4
2.747	0.784	9.0	820	6,000	4,300	28	230	100	0.5
3.066	0.934	9.0	480	2,300	2,200	16	210	100	0.5
3.778	1.266	9.1	320	1,900	1,100	3	190	100	0.7
4.279	1.498	9.1	240	1,500	820	4	200	100	0.8
4.960	1.818	9.2	190	1,100	600	2	150	140	0.8
5.840	2.227	9.2	160	930	470	3	130	140	0.9
24.823	2.544	9.1	160	1,200	480	<1	250	130	0.7
25.106	2.669	9.2	140	900	430	<1	220	110	0.8
25.853	2.989	9.5	110	770	330	<1	170	130	0.8
26.799	3.480	9.3	110	570	230	1	110	110	1.0
27.967	4.463	9.3	68	370	130	1	78	92	1.1

Note - EC in mS/m.

Days	Pore Vol.	Na	K	Ca	Mg	Fe	Al	SiO_2
1.778	0.332	6,400	250	160	300	0.4	<0.01	5.2
2.115	0.484	3,700	150	88	150	<0.01	<0.01	5
2.747	0.784	1,900	88	36	63	<0.01	<0.01	4.6
3.066	0.934	1,100	53	14	25	<0.01	<0.01	5
3.778	1.266	730	38	7.3	13	<0.01	<0.01	4.9
4.279	1.498	500	28	4.8	7.7	<0.01	0.15	4.9
4.960	1.818	430	26	3.3	6.1	<0.01	<0.01	5
5.840	2.227	350	23	2.6	5	<0.01	0.11	4.9
24.823	2.544	360	30	7.5	13	0.04	0.03	5.2
25.106	2.669	300	25	5.4	9.4	0.03	0.02	5
25.853	2.989	230	22	4.4	7.6	0.02	0.02	5.3
26.799	3.480	180	23	2.9	4.9	<0.01	0.61	-
27.967	4.463	260	49	3.9	5.2	<0.01	0.50	-

Table 6.15 - Leachate Quality : Trace Elements (mg/L)

Pore Vol.	As	B	Ba	Cr	Cu	Mo	Se	Sr	Zn
1.778	0.14	5.5	0.04	<0.01	0.65	0.39	5.2	11	<0.01
2.115	0.068	5.1	0.03	<0.01	0.25	0.22	3.0	5.0	<0.01
2.747	<0.001	5.3	0.04	<0.01	0.25	0.11	1.5	2.3	<0.01
3.066	<0.001	5.3	0.04	<0.01	0.25	0.05	0.67	0.96	<0.01
3.778	<0.001	5.6	0.04			0.03	0.38	0.54	
4.279	<0.001	6.9	0.04			0.02	0.23	0.36	
4.960	<0.001	5.7	0.04			<0.01	0.18	0.29	
5.840	<0.001	6.3	0.04			<0.01	0.12	0.25	
24.823	0.015	6.7	0.08	0.05	<0.01	0.03	0.17	<0.01	<0.01
25.106	0.015	7.0	0.06			0.02	0.19	<0.01	
25.853	0.013	7.0	0.05			0.01	0.14	<0.01	
26.799	<0.001	5.4	0.04			<0.01	0.06	0.24	
27.967	<0.001	4.9	0.04			<0.01	0.031	0.19	

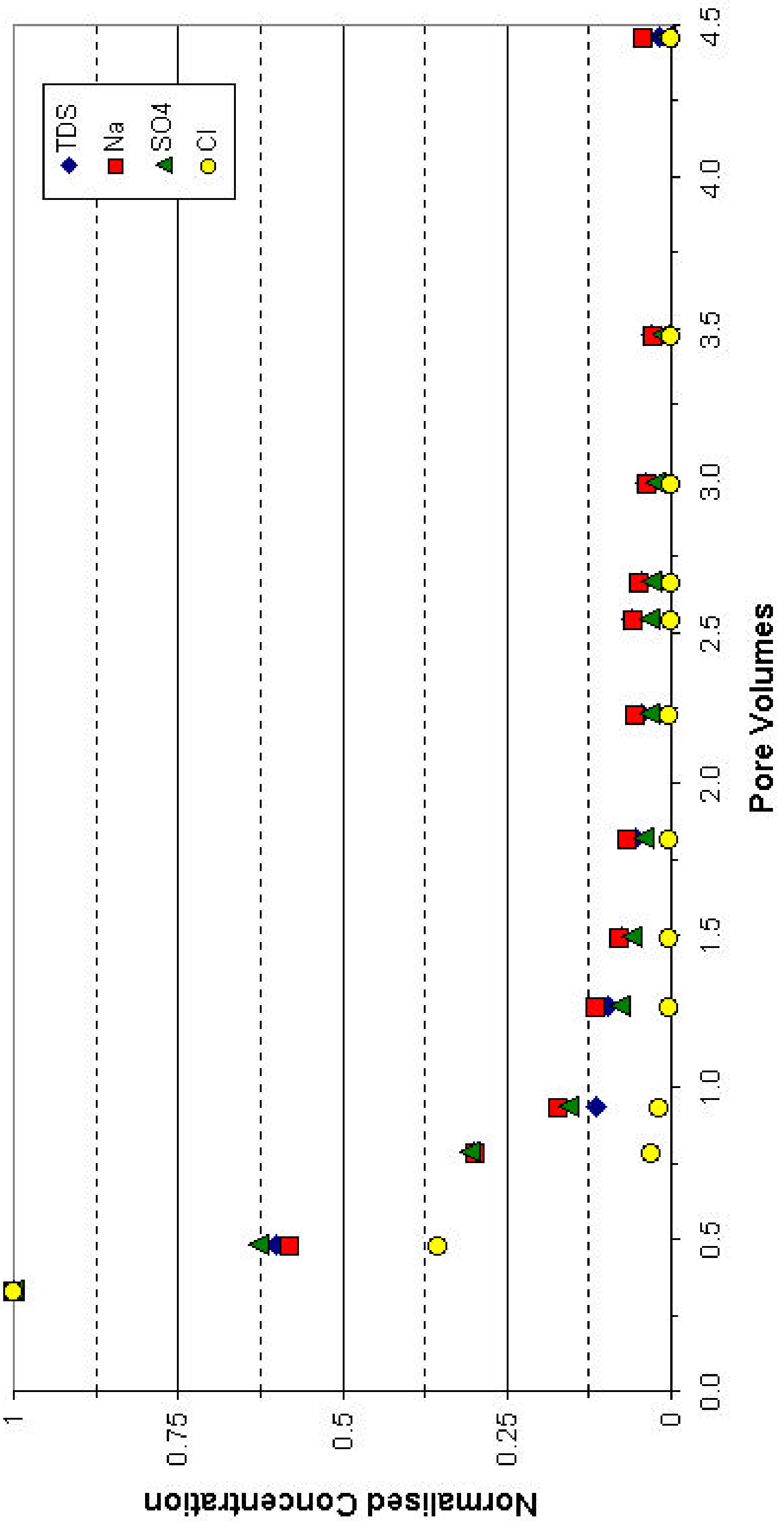


Figure 6.14 - Major Element Leaching Curves of the Medium Column

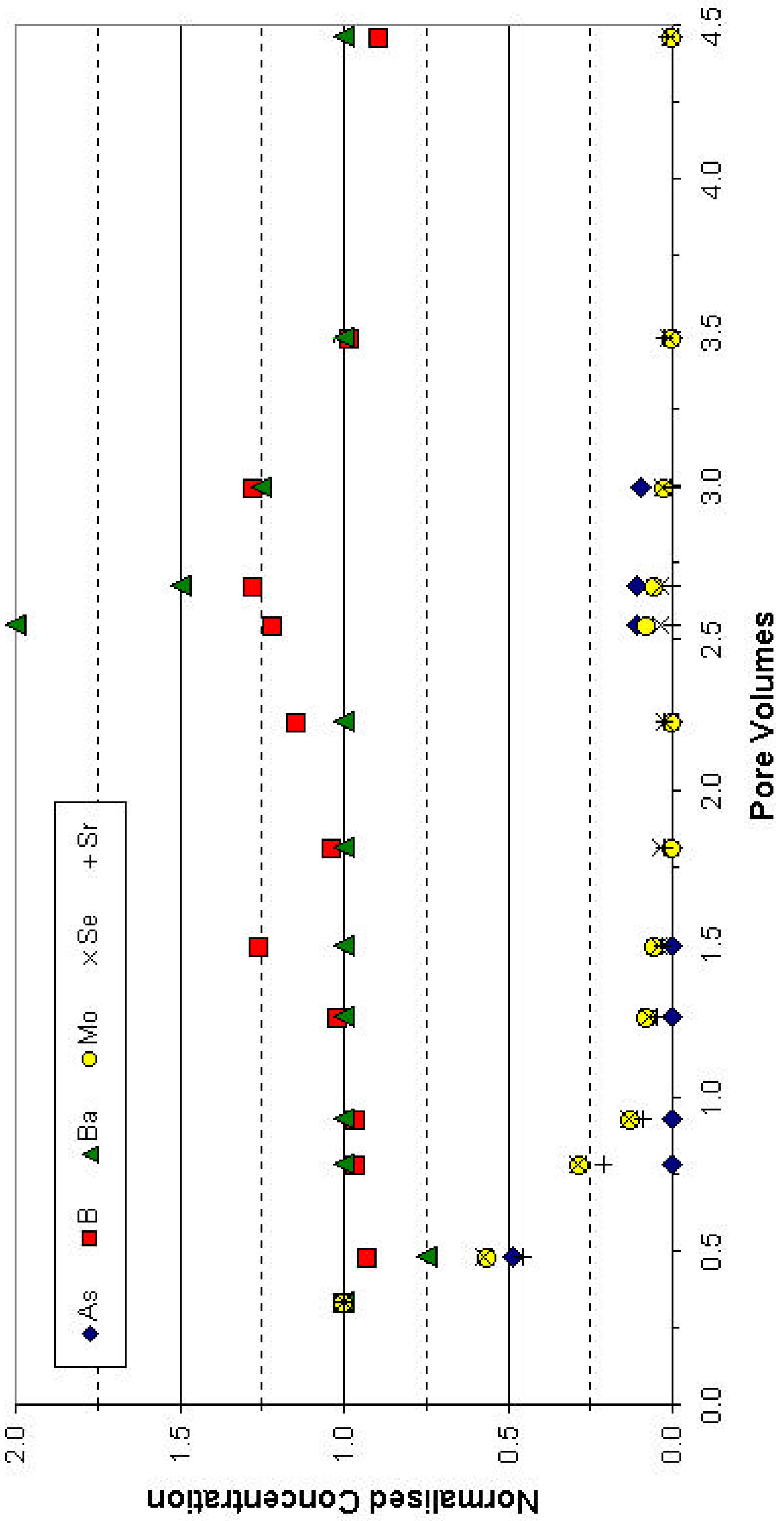


Figure 6.15 - Trace Element Leaching Curves of the Medium Column

6.7.6 Ash Quality

The results for the analysis of ash samples are within previous data and given in Tables 6.16 and 6.17. They are within those reported in previous work and within this thesis. They show the leaching of SO_4 and Cl, although Na and K concentrations appear not to change (or variability in the ash precludes any trend). The ony trace element that displays leaching is B, which appears to decrease by about half during the leaching. As for the Large coulmn, the concentrations of the more soluble elements, such as SO_4, Na, K and B, appear to increase with depth in the column.

Table 6.16 - Medium Ash Leaching Column : Major Elements (%, dry basis)

	SO_4	$Cl^{\#}$	$F^{\#}$	Na	K	Ca	Mg	Fe	Al	AI	LOI
I-1	0.38	250	-	0.69	0.07	2.2	2.6	4.6	1.3	48	14
I-2	0.30	300	-	0.82	0.069	2.7	3.3	4.6	1.2	51	14
P-T	0.005	<10	<5	0.77	0.11	7.5	9.6	4.8	3.9	38	6.6
P-M	0.012	<10	<5	0.91	0.19	5.9	8.9	4.2	3.8	44	4.2
P-B	0.025	<10	<5	1.00	0.18	7.1	9.6	3.7	3.7	46	5.1

Notes : I - Initial; P - Post Leaching; T - Top, M - Middle, B - Bottom. # - mg/kg.

Table 6.17 - Medium Ash Leaching Column : Trace Elements (mg/kg, dry basis)

	As	B	Ba	Cd	Cr	Co	Cu	Hg	Mo	Pb	Ni	Se	Sn	Sr	Zn
I-1	8	230	420	<0.2	26	17	36	0.8	<5	-	29	<5	<5	510	42
I-2	8	220	500	<0.2	38	33	31	0.83	<5	-	37	<5	<5	670	54
P-T	<5	96	610	<0.2	80	25	47	1.0	<5	10	58	<5	<5	800	51
P-M	6	130	560	<0.2	74	25	37	<0.1	<5	9	55	<5	<5	700	44
P-B	<5	130	500	<0.2	50	24	40	<0.1	<5	9	54	<5	<5	680	48

6.7.7 Changes in Soluble Mass

The changes in soluble mass within the Medium column are similar, as expected, to the Large column and Wet Cell. The calculations are shown in Tables 6.18 and 6.19. The majority of SO_4 and Cl has been leached as well as a notable proportion of the Na and K. Minor amounts of Ca, Mg and SiO_2 were leached, with the variability in chemical analysis precluding any accurate assessment of changes in soluble mass. For SO_4, Cl, Na and K, there is a significant difference between the estimates of mass leached based on leachate and ash analysis.

For trace elements, the estimates suggest that only minor amounts of the contained As, Sr, Mo and Ba have been leached, while significant proportions of the B and Se have been leached. The estimates for mass leached for all trace elements do not correlate, showing significant deviation.

Table 6.18 - Total Soluble Mass in Leached Ash and Leachate : Major Elements (g)

	SO_4	Cl	Na	K	Alk. [1]	Ca	Mg	Al	Fe	SiO_2 [2]
Initial	12.8	1.04	28.4	2.62	-	92.3	111	47.1	173	1,865
Final	0.53	<0.04	33.7	6.03	-	257	353	143	159	1,607
Leachate	46.3	1.96	22.9	1.15	5.49	0.48	0.87	<0.004	<0.001	0.081

[1] - Sum of alkalinity due to HCO_3 and CO_3; [2] - Assuming the acid insoluble fraction is silica.

Table 6.19 - Total Soluble Mass in Leached Ash and Leachate : Trace Elements (mg)

	As	B	Ba	Mo	Se	Sr
Initial	30.1	848	1,733	<19[1]	<19[1]	2,223
Final	20.1	447	2,097	<19[1]	<19[1]	2,738
Leachate	0.39	115.1	0.86	1.21	16.4	30.0

[1] - Assuming the average is the detection limit of 5 mg/kg.

6.8 Small Leached Ash Column

6.8.1 Overview

The Small column (300 mm) containing leached ash, operated from November 25, 1999, to December 28, 1999 - a total time of 33 days. The measured geotechnical properties are listed in Table 6.20. The dry density is similar to the field cells, although the moisture content is slightly lower. The moisture content of the ash was uniform. There were a total of 3 TDR probes inserted equidistantly into the column, at 70, 150 and 225 mm from the top (to the centre of the TDR hole), respectively.

Table 6.20 - Geotechnical Properties of the Small Column

Gravimetric Moisture	Density (kg/m^3)		Void Ratio	Porosity	Degree of Saturation	Volumetric Moisture
	Wet	Dry				
47.9%	907	613	2.82	73.8%	39.8%	29.4%

6.8.2 Cumulative Flows

The Small column was operated in tandem with the Medium coulmn, and thus both were treated the same. Inflow was for an initial period of 6 days at about 10.9 mm/hr (1.45 mL/min). The graph of inflow and outflow is given in Figure 6.16. The leachate discharge, initially observed to be slightly variable, approached steady state quickly, however, with the outflow approximately equalling the inflow rate for the remainder of the trial. The curves of cumulative inflow and outflow have approximately the same gradient, offset by the soil moisture deficit.

On day 14, the top cap was removed from the column to investigate the possible effects of evaporation on the moisture profile and the leachate chemistry. On the basis of the TDR data, and similar to the Medium column, there appeared to be no change to the moisture profile until day 19 when the overall moisture content began to decrease throughout the column, stabilising around day 21. The small changes observed in the soil moisture profile are consistent with the mild conditions in the soils laboratory. Time constraints prevented any investigation of varying the climatic conditions.

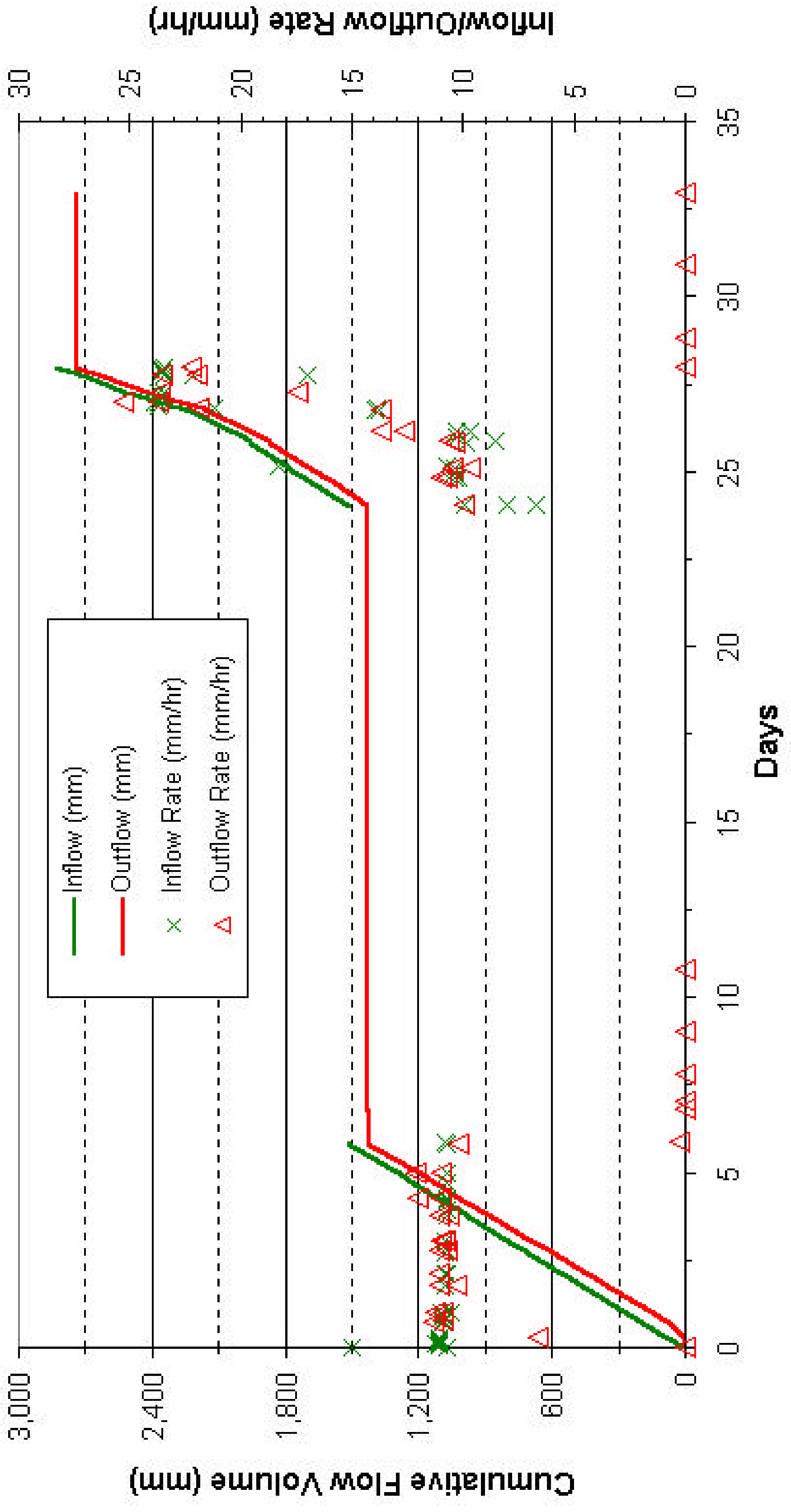


Figure 6.16 - Cumulative Flows of the Small Column

The inflow was restarted on day 24 and maintained at about 10.9 mm/hr. On day 26 the inflow rate was increased to 19.2 mm/hr to allow for a higher number of pore volumes to be reached and complete discharge of leachate before termination of the test on day 33. The inflow was stopped at the end of day 28, with the discharge of leachate taking about 5 days to complete.

Overall, there was a total inflow of 2,821.8 mm (22.61 litres) pumped into the Small column, with a total estimated discharge of 2,737.7 mm (21.93 litres). Given the calculated pore volume of about 221 mm (1.74 litres), this represents about 12.4 pore volumes of leaching.

6.8.3 Final Vertical Moisture Profile

A series of ash samples were taken during dismantling to obtain a vertical profile of moisture content, given in Table 6.21. This data shows a small increase in moisture content towards the base of the column, corresponding well to that observed in the field trial cells and the current ash disposal site.

Table 6.21 - Final Moisture Content Profile

(cm)	Gravimetric	Volumetric	(cm)	Gravimetric	Volumetric
0 TOP	93.7%	57.4%	17	88.8%	54.4%
7.5	87.6%	53.7%	26	121.8%	74.6%

The average moisture content is about 98.0%, or a volumetric water content of about 0.600 (81.3% degree of saturation). This gives a final moisture within the column equal to 198 mm, compared to the 97 mm initially present (29.4% saturation). The difference of 101 mm compares to the deficit of 84 mm observed in the graph of cumulative flows.

6.8.4 TDR Probes and Soil Moisture Monitoring

The monitoring of soil moisture content by the TDR probes appears to be more successful for the Small column than the Large column. The initial saturation of the column can be observed, however, the apparent volumetric water content determined by TDR was 0.083 (calculated from 6-2), compared to the measured value of 0.294. If equations 6-3a and 6-3b are used with their respective linear and polynomial calibration regressions, the calculated volumetric water contents are 0.062 and 0.061, respectively. As for the Large and Medium columns, these calculations suggest that the TDR probes underestimate the actual volumetric water content. The probes were removed on day 33 (Dec. 28, 1999), when the column test was completed. The full data set is shown in Figure 6.17, with initial data for days 0 to 4 in Figures 6.18. The TDR data appears to display a diurnal variation in between the Large and Medium columns. The top probe (S16) appears to malfunction from days 16 to 24. The cause of this is unknown, as it appeared to be performing satisfactorily during the operation of the column. About day 24, the probe returns to readings more typical of those expected based on earlier readings from S16 and probes below in the column. Possible causes of this are poor contact of the TDR probe with the ash inside the column or electronic malfunction. There was no visible indication of either of these possible causes.

The TDR data displays good response to the initial wetting of the ash profile (days 0 to 4) and the first period of drainage from day 16. All probes display a slight decreasing trend in water content from this point. The data after this period (days 8 to 11) was not recorded properly by the datalogger and is unfortunately missing. The initial data for days 11 to 13 is slightly higher than that previously measured, but within expected ranges. A further malfunction occurred on day 14, and the data for day 15 is higher again. After the data was downloaded, the TDR probes return to readings similar to those earlier from days 11 to 13 and earlier. The causes of this are unclear, but warrant a degree of caution in interpreting the datasets.

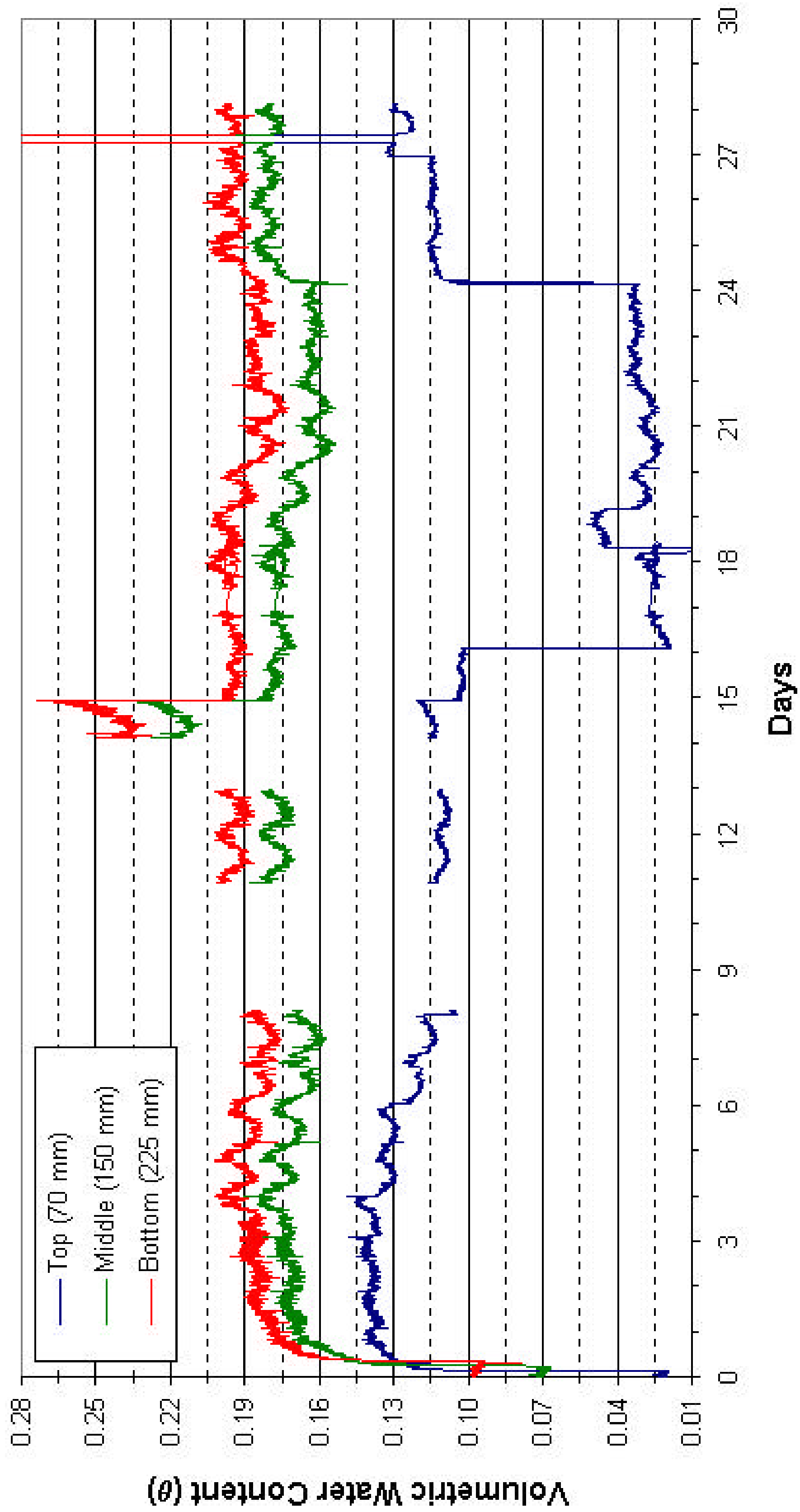


Figure 6.17 - Complete TDR Probe Data for Calculated Volumetric Water Content

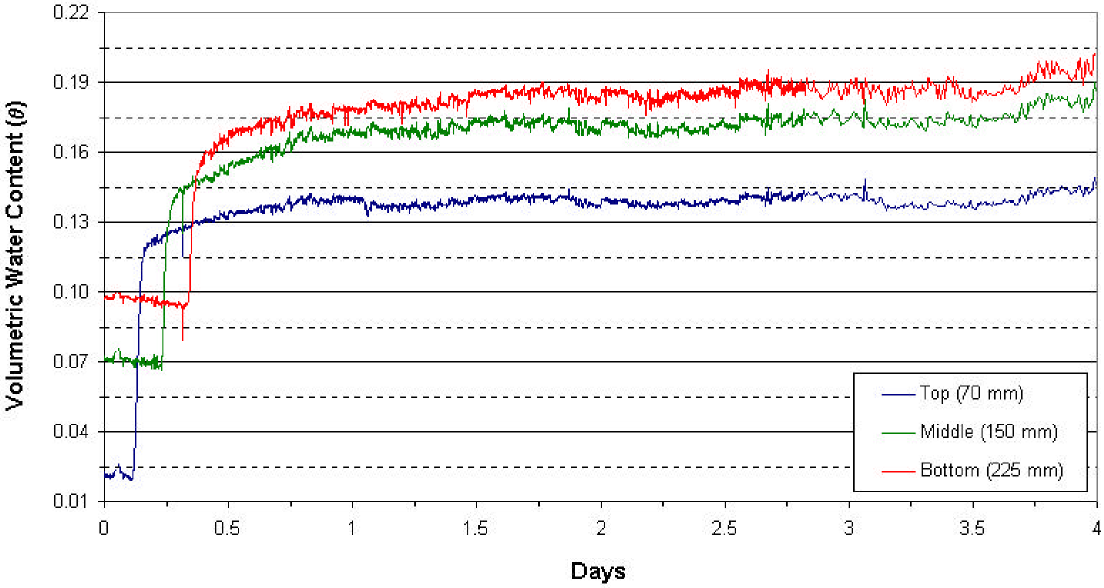


Figure 6.18 - TDR Probe Data for Calculated Volumetric Water Content : Days 0 to 4

6.8.5 Leachate Chemistry

The chemistry of the leachate emanating from the Small column was similar to previous columns and the field cells, dominated by Na-SO_4-Cl with minor Ca, K and Mg. The initial salinity is higher than both the Large and Medium columns and the field cells, which quickly falls to low concentrations as leaching progresses. The contentrations of trace elements are similar, although the initial values of Cu, Se, Sr and As are higher. The break in flow allows the salinity to increase by about 63%, nearly doubling the salinity. The concentrations of As, Se and Cr increase after this break but decrease after further leaching of the ash in the column. The full results are given in Tables 6.22 and 6.23 and graphed in Figures 6.19 and 6.20. The concentrations of B, initially stable, appear to be steadily decreasing towards the end of the leaching period of the column. Detailed analysis of geochemical controls will be presented in Chapter 7.

The following elements were consistently below analytical detection limits (mg/L) : Cd <0.001, Co <0.01, Hg <0.001, Ni <0.01 and Sn <0.01.

Table 6.22 - Leachate Quality : Major Ions (mg/L)

Days	Pore Vol.	pH	EC	TDS	SO_4	Cl	HCO_3	CO_3	F
0.783	0.350	8.6	3,400	31,000	21,000	1,300	270	160	<0.3
0.990	0.572	8.8	1,300	6,400	4,200	190	290	96	0.3
1.790	1.431	9.0	440	2,900	2,000	30	210	130	0.5
2.108	1.778	9.1	220	1,300	810	8	160	120	0.6
2.738	2.464	9.2	160	910	480	5	160	100	0.8
3.058	2.817	9.2	120	720	330	3	140	96	0.9
3.769	3.586	9.3	99	570	240	2	76	130	1.0
4.951	4.869	9.3	65	380	140	4	64	100	1.0
5.833	5.824	9.3	52	270	97	2	68	72	0.9
24.808	6.595	9.1	61	440	120	4	150	60	0.6
25.098	6.901	9.1	46	290	85	3	110	40	0.6
25.843	7.671	9.1	38	250	64	2	88	48	0.5
27.960	11.239	9.0	23	100	23	1	46	20	0.4

Note - EC in mS/m.

Days	Pore Vol.	Na	K	Ca	Mg	Fe	Al	SiO_2
0.783	0.350	8,900	380	300	490	1.3	0.33	5.0
0.990	0.572	2,900	140	95	120	0.71	0.26	6.2
1.790	1.431	1,000	49	14	22	<0.01	<0.01	4.6
2.108	1.778	480	26	4.4	7.4	<0.01	<0.01	4.4
2.738	2.464	350	21	2.9	5.4	<0.01	0.47	4.4
3.058	2.817	270	17	2.2	4.4	<0.01	0.24	5.3
3.769	3.586	210	15	1.9	3.8	<0.01	0.07	4.5
4.951	4.869	140	13	1.6	3.1	<0.01	<0.01	4.6
5.833	5.824	110	12	1.6	3.0	<0.01	0.09	4.5
24.808	6.595	120	16	6.2	10	0.02	<0.01	5.0
25.098	6.901	83	12	4.3	7.4	0.01	<0.01	4.7
25.843	7.671	65	11	3.8	6.7	<0.01	<0.01	4.7
27.960	11.239	14	8	4.8	8.9		0.39	

Table 6.23 - Leachate Quality : Trace Elements (mg/L)

Pore Vol.	As	B	Ba	Cr	Cu	Mo	Se	Sr	Zn
0.350	0.20	5.1	0.04	<0.01	0.65	0.53	8.0	15	0.05
0.572	0.14	5.0	0.04	<0.01	0.25	0.20	2.7	5.6	0.03
1.431	<0.001	5.1	0.04	<0.01	<0.01	0.05	0.66	1.2	<0.01
1.778	<0.001	5.3	0.04	<0.01	<0.01	0.02	0.22	0.4	<0.01
2.464	<0.001	5.2	0.04	<0.01	<0.01	0.01	<0.001	0.29	<0.01
2.817	<0.001	5.3	0.04			<0.01	0.098	0.25	
3.586	<0.001	4.9	0.04			<0.01	<0.001	0.23	
4.869	<0.001	4.1	0.04			<0.01	<0.001	0.20	
5.824	<0.001	3.6	0.04			<0.01	<0.001	0.19	
6.595	<0.001	3.4	<0.01	0.03	<0.01	0.01	0.068	<0.01	<0.01
6.901	0.007	3.5	<0.01			<0.01	0.050	<0.01	
7.671	0.006	3.1	<0.01			<0.01	0.038	<0.01	
11.239	<0.001	1.7	0.04			<0.01	0.010	0.47	

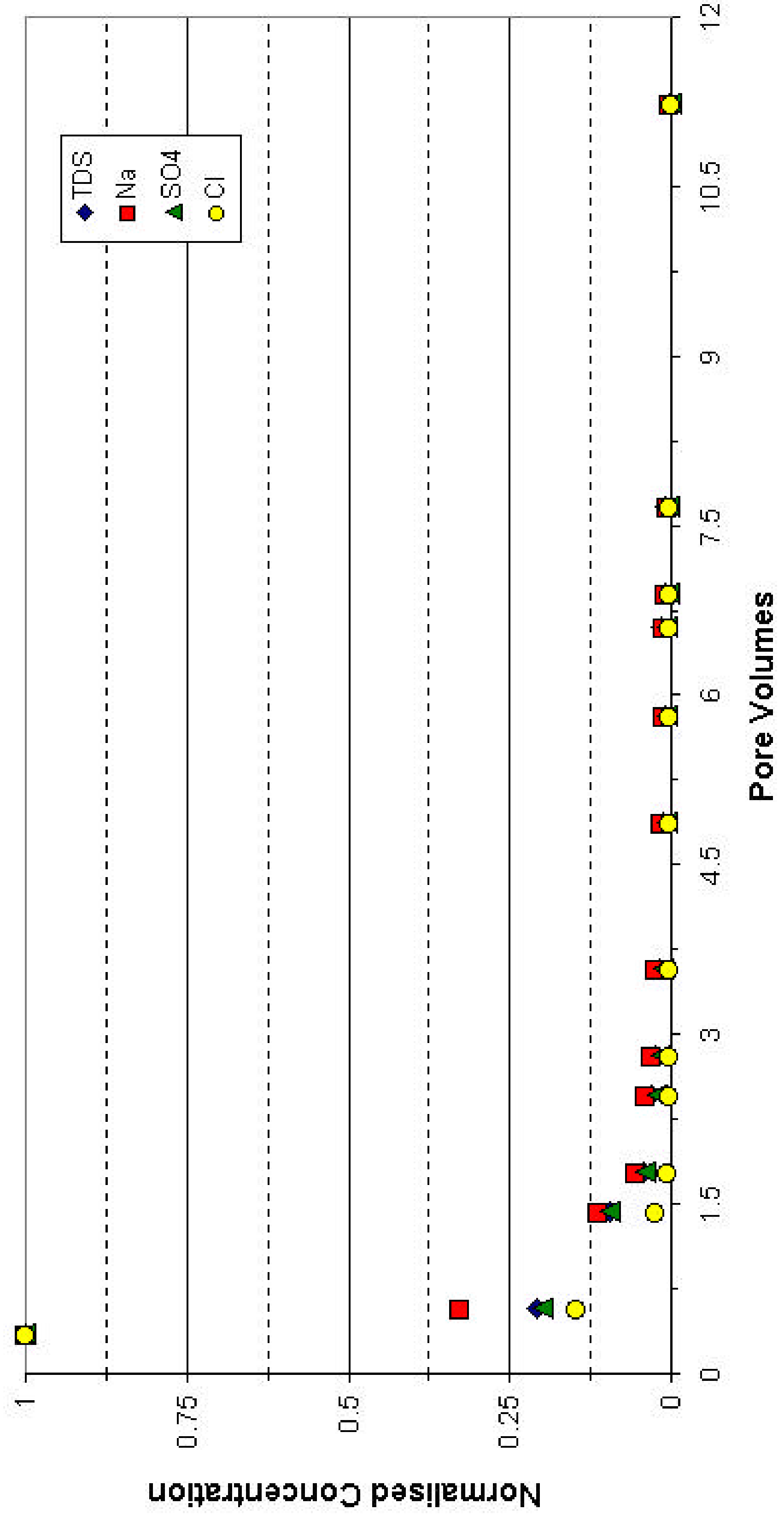


Figure 6.19 - Major Element Leaching Curves of the Small Column

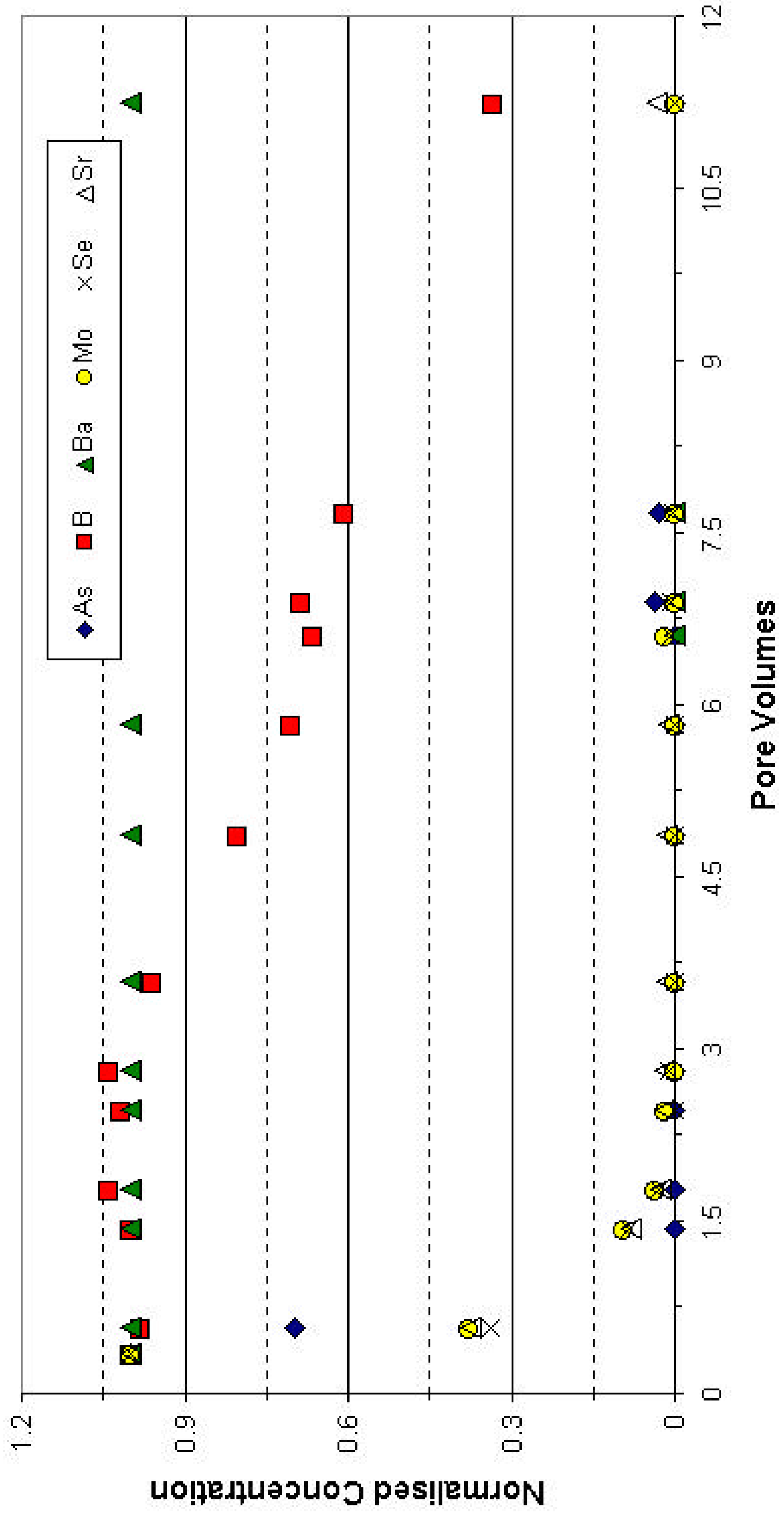


Figure 6.20 - Trace Element Leaching Curves of the Small Column

6.8.6 Ash Quality

The analysis of ash samples are within previous work in this thesis and given in Tables 6.24 and 6.25. They demonstrate the strong leaching of SO_4 and Cl, although Na and K concentrations appear not to change (or variability in the ash precludes any trend). There appears to be a moderate leaching effect for B and As. The concentrations of the more soluble elements, such as SO_4, Na, K and B, appear to increase with depth in the column

Table 6.24 - Small Ash Leaching Column : Major Elements (%, dry basis)

	SO_4	$Cl^{\#}$	$F^{\#}$	Na	K	Ca	Mg	Fe	Al	AI	LOI
I-1	0.35	350	-	0.75	0.061	2.7	3.3	3.6	2.1	45	6.3
P-T	0.007	<10	<5	0.97	0.14	6.4	8.7	3.9	3.6	47	6.3
P-B	0.010	<10	<5	0.99	0.19	6.7	9.0	4.5	3.9	42	1.7

Notes : I - Initial; P - Post Leaching; T - Top, B - Bottom. $^{\#}$ - mg/kg.

Table 6.25 - Small Ash Leaching Column : Trace Elements (mg/kg, dry basis)

	As	B	Ba	Cd	Cr	Co	Cu	Hg	Mo	Pb	Ni	Se	Sn	Sr	Zn
I-1	11	290	570	<0.2	54	22	40	0.88	8	-	39	<5	<5	650	68
P-T	6	11	560	<0.2	67	28	39	1.7	<5	11	55	<5	<5	730	58
P-B	<5	130	570	<0.2	87	28	38	1.4	<5	9	74	<5	<5	780	49

6.8.7 Changes in Soluble Mass

The changes in soluble mass within the Small column are similar, as expected, to the Large and Medium columns and the Wet Cell. The calculations are given in Tables 6.26 and 6.27 and demonstrate the leaching of SO_4 and Cl, differences in Na and K estimates and the large variability in trace element changes.

Table 6.26 - Total Soluble Mass in Leached Ash and Leachate : Major Elements (g)

	SO_4	Cl	Na	K	Alk. [1]	Ca	Mg	Al	Fe	SiO_2 [2]
Initial	5.67	0.57	12.2	0.99	-	44	54	34	58	729
Final	0.14	<0.016	15.9	2.67	-	106	144	61	68	721
Leachate	28.9	1.46	14.8	0.79	4.19	0.45	0.71	<0.01	<0.01	0.088

[1] - Sum of alkalinity due to HCO_3 and CO_3; [2] - Assuming the acid insoluble fraction is silica.

Table 6.27 - Total Soluble Mass in Leached Ash and Leachate : Trace Elements (mg)

	As	B	Ba	Mo	Se	Sr
Initial	17.8	470	924	13	8.1[1]	1,054
Final	8.9	114	916	8.1[1]	8.1[1]	1,224
Leachate	0.4	83.4	0.62	0.79	11.5	24.6

[1] - Assuming the average is the detection limit of 5 mg/kg.

6.9 Soil Water Characteristic Curve for Leached Ash

One of the most fundamental properties for unsaturated soil mechanics is the Soil Water Characteristic Curve (SWCC). The property is required for moisture flow modelling and a variety of methods are available to mathematically describe the SWCC for such purposes. The SWCC of the leached ash was determined using the Tempe Cell method (see Fredlund & Rahardjo, 1993). The Tempe Cells were custom made by the Unsaturated Soils Group from the Dept. of Civil Engineering at the University of Saskatchewan, Canada. The ceramics (porous stones) used in the cells were capable of withstanding 3-bars of applied air pressure, equivalent to 300 kPa soil suction. The air pressure was maintained through a regulated compressed air system and monitored through custom made gauges accurate to within 0.5 kPa. Due to the length of time it takes to fully complete a SWCC using a Tempe Cell, only 1 test was completed. The results are given in Table 6.28 and shown in Figure 6.21.

Table 6.28 - Soil Water Characteristic Curve for Leached Ash : Tempe Cell Method

Suction (kPa)	Vol. Water Content (θ)	Suction (kPa)	Vol. Water Content (θ)
3	0.696	60	0.561
8.5	0.664	100	0.508
15	0.645	150	0.461
25	0.623	210	0.393
40	0.596	290	0.292

The Air Entry Value (AEV) for the ash appears to be about 40 kPa. This represents the point at which the pores begin to desaturate and allow the ingress of air. This AEV is expected for a fine grained soil such as leached ash.

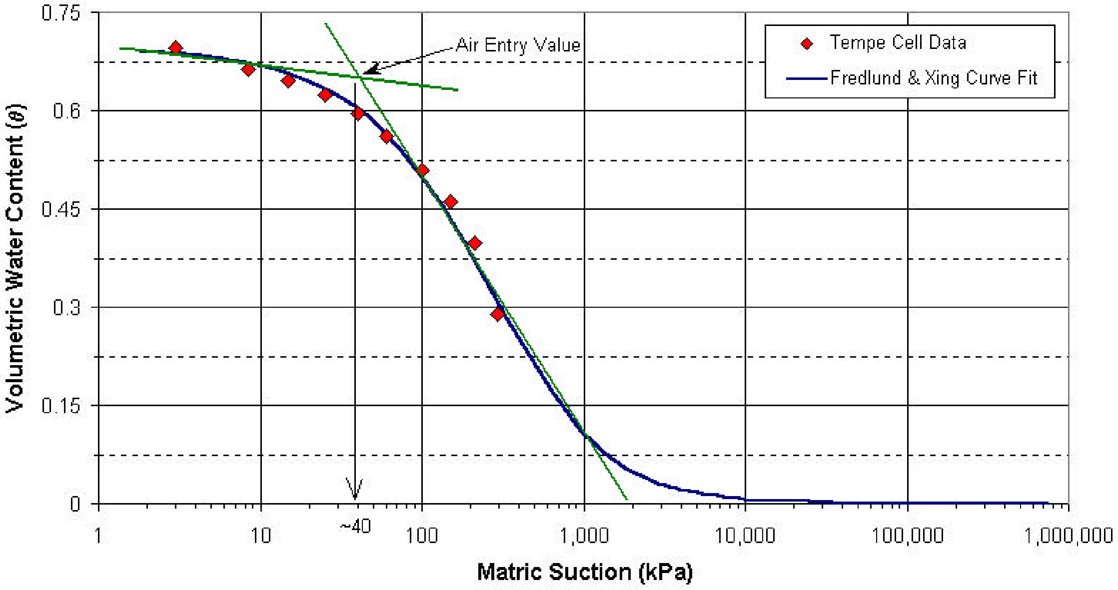


Figure 6.21 - Soil Water Characteristic Curve for Leached Ash

A semi-analytical curve fitting procedure proposed by Fredlund & Xing (1994) was used to estimate the SWCC (equations are given below). This method uses three parameters to mathematically describe the SWCC, which can then be used in unsaturated flow models or to estimate the unsaturated hydraulic conductivity function versus moisture content. The Fredlund & Xing (1994) method is included in the SoilCover unsaturated flow model, developed at the University of Saskatchewan (Wilson, 1990; Wilson *et al.*, 1994). The SoilCover model will be discussed in more detail in the Chapter 8, and was used to fit the SWCC data above. The SWCC parameters for the curve fit in Figure 6.21 are a - 403.57, n - 0.96 and m - 3.66.

$$\theta\,(\psi, a, n, m) = C(\psi)\,\frac{\theta_S}{\left\{\ln\left[e + (\psi / a)^n\right]\right\}^m} \qquad \text{6-4a}$$

where

$$C(\psi) = 1 - \frac{\ln\left(1 + (\psi / \psi_r)\right)}{\ln\left[1 + (1{,}000{,}000 / \psi_r)\right]} \qquad \text{6-4b}$$

ψ - matric suction in the ash, θ_S - residual saturation,

ψ_r - matric suction in the ash at residual saturation, e - exponential function.

6.10 Analysis and Summary of the Three Columns

6.10.1 Unsaturated Hydraulic Conductivity

The cumulative inflow and outflow graphs for all three leached ash columns all show similar gradients. No investigation or testing of the unsaturated hydraulic conductivity of the leached ash has been possible, however, the similar gradients allows an analysis to be undertaken. The flow of water in porous media is governed by Darcy's Law (see equation 3-2), which is valid for both saturated and unsaturated media. For unsaturated media, the hydraulic conductivity, K, is dependent on the moisture content of the porous medium. The situation in the three columns represents essentially steady state conditions since there is no change of inflow and outflow over time The porous media does not necessarily need to reach full saturation for this to occur, provided that there is connectivity (or continuity) in the pore space to allow full hydrostatic pressures to develop (cf. Fredlund & Rahardjo, 1993). This can be interpreted as the hydraulic gradient being near unity, representing gravity drainage conditions. The hydraulic conductivity is therefore effectively dependent on the inflow (or outflow) rate. Mathematically this becomes (eg. Freeze & Cherry, 1979; Fredlund & Rahardjo, 1993) :

$$v_z = K\frac{\partial h}{\partial z} \cong K \qquad \text{where} \quad \frac{\partial h}{\partial z} \cong 1 \qquad \text{6-5}$$

By analysing the different columns and their respective flow gradients at steady state, it is possible to derive an approximate hydraulic conductivity for the water content at which the columns were operated. The calculations are based on the outflow rate, since this represents the actual flow rate from the column for the given inflow rate. The results are given in Tables 6.29 and 6.30.

Table 6.29 - Estimates of Hydraulic Conductivity in Leaching Columns

	Large	Medium	Small
Flow Rate (mm/hr)	6.96 - 36.93	10.40 - 24.46	9.7 - 19.70
K (10^{-6} m/s)	1.93 - 10.26	2.89 - 6.24	2.69 - 5.48
Degree of Saturation (final)	68%	81%	81%
θ (final)	0.516	0.592	0.600

Table 6.30 - Hydraulic Conductivity Estimates Over Time

Large Column		
Time (days)	Outflow (mm/hr)	K (10^{-6} m/s)
0-1.02	36.93	10.26
1.2-16.02	10.49	2.91
32.1-44.9	10.93	3.04
46.2-49.9	6.96	1.93
51.8-52.2	24.02	6.67

Medium Column		
Time (days)	Outflow (mm/hr)	K (10^{-6} m/s)
0.74-5.83	11.029	3.06
24.06-25.85	10.397	2.89
26.79-27.96	22.464	6.24
Small Column		
Time (days)	Outflow (mm/hr)	K (10^{-6} m/s)
0.97-4.96	10.671	2.96
24.06-26.16	9.701	2.69
26.8-27.96	19.737	5.48

It is assumed in the calculations in Table 6.30 that steady state conditions have been established over the time interval for each estimate, which given the uniform gradients for the inflow and outflow curves, appears reasonable. Although these estimates are empirical, they demonstrate the high permeability of the ash with a high volumetric water content. The unsaturated K values range from 1.93 to 10.26 x 10^{-6} m/s, compared to the estimated saturated K value of about 3.5 x 10^{-6} m/s (see Section 2.2.5). The variation can be attributed to the different inflow rates and the respective change in the outflow rate. This suggests a small change in volumetric water content in response to different inflows, with a small subsequent change in K. After the inflow ceases, however, the fine-grained nature of the ash is effective in limiting further drainage of pore waters, indicating a rapid decrease in the hydraulic conductivity function as the volumetric water content falls.

Fredlund *et al.* (1994) proposed a new method to mathematically predict the unsaturated hydraulic conductivity function of a soil based on the fitted parameters for a SWCC. This method has been included in the SoilCover model, and the predicted curve for the ash is shown in Figure 6.22. The Relative Hydraulic Conductivity is the unsaturated K divided by the saturated K, for a given matric suction. Importantly, the predicted hydraulic conductivity function shows that up to the AEV (~40 kPa), the conductivity is within one order of magnitude of the saturated value, suggesting high permeability until the pore space begins to desaturate. This is consistent with the observed behaviour of the columns and the field cells, and is important for flow modelling.

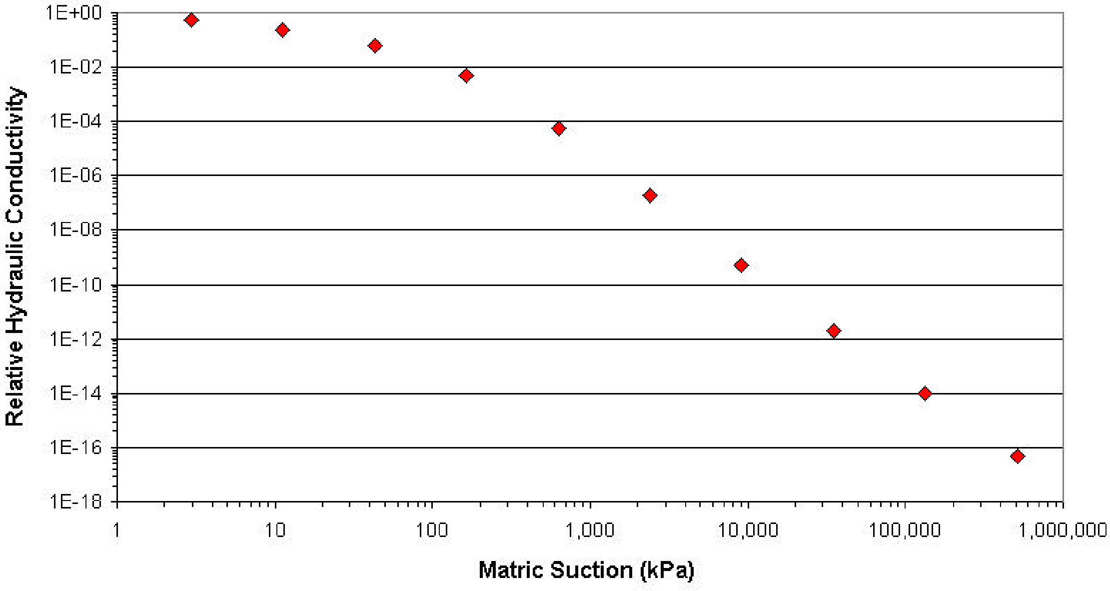


Figure 6.22 - Predicted Unsaturated Hydraulic Conductivity Function Relative to Saturated Conductivity - Fredlund *et al.* (1994) Method

6.10.2 Application of TDR Probes for Soil Moisture

The use of the TDR probes has proven less successful than expected. The probes appear to systematically underestimate the moisture content of the leached ash, although in general, the TDR probes are able to establish trends and relative changes over time. The causes of this are unclear. The results from TDR probes can be affected by several factors, including salinity (or more correctly, electrical conductivity), probe contact with the soil (such as air gaps) and soil mineralogy (particularly the presence of reactive clays and/or organic content) (Evett, 2000). A major advantage of the application of TDR monitoring in the leaching columns was that probe contact was tight and was not altered during the tests, however the salinity and residual char content may have contributed to the poor TDR results. It may be possible to correct the TDR results for these factors, given sufficient laboratory investigation, although this is clearly beyond the scope of this thesis. It is recommended that further research be undertaken to assess the performance of TDR probes in determining the soil moisture content of ash.

6.10.3 Vertical Profile of Soluble Salts

It was noted for each of the three columns that there appeared to be an increase in the concentrations of the soluble salts at the base of the columns. For example, the concentration of SO_4 in the Small column was initially 0.35%, compared to 0.007% near the top and 0.010% near the bottom after about 12.4 pore volumes of leaching. Similar observations were made for Na, K, Cl, and to a lesser extent, B. The vertical profile of these same soluble species in the Wet Cell (see Tables 5.21 and 5.22) also demonstrates this behaviour. This can be explained as the dissolution of the respective mineral near the top of the ash profile and transport by advection to the base. As leaching progresses, the soluble salts accumulate near the base of the ash profile until all species have been effectively leached.

6.10.4 Moisture Retention Within Columns

A clear feature of the cumulative water volumes for the three leaching columns is the consistent separation between inflow and outflow for each column. Korfiatis *et al.* (1984) reported similar behaviour for their municpal waste leaching columns, except in their case the gradients were not uniform and moisture was increasing within the waste profile in the column. Walsh & Kinman (1979) and Walsh *et al.* (1981) reported similar results from a field trial of a municipal waste cell. The explanation given in all papers was based on unsaturated flow behaviour. The moisture at the top of the waste profile reaches field capacity, the saturation point above which downward gravity drainage occurs, and excess moisture is then able to drain vertically down, until the field capacity is reached throughout the waste profile. The different gradients of the inflow and outflow curves they monitored, therefore, represented conditions that were not yet at equilibrium. In comparison, the Small, Medium and Large columns, with equal gradients, would appear to be in equilibrium between inflow and outflow and that steady state conditions were prevailing during their operation.

6.10.5 Summary

This chapter has presented the results from three laboratory leaching columns of varying heights, monitoring of soil moisture content using TDR probes and the measured Soil Water Characteristic Curve (SWCC) of the ash. The columns have demonstrated similar leaching curves for major soluble species (SO_4, Cl, Na) to the field cells reported in the previous chapter. The initial salinity was somewhat higher than the field cells, although there was no clear pattern relating the salinity to column or ash height. One important feature of the columns was the break in inflow applied to test the importance of pore water residence time. All three columns demonstrated higher salinity on the first flush of leachate after their respective breaks. Most trace elements leached appeared higher in the initial leachate but typically decreased after further leaching. The behaviour of Ba and B, however, was stable over the period of leaching, with B in particular tending to trend downwards in concentration if enough pore volumes of leaching were reached. A comparison of the various leaching curves and a mathematical model for this process will be developed in Chapter 8, while Chapter 7 will analyse the geochemical controls on leachate chemistry. The use of TDR probes to measure soil moisture content requires further testing and validation.

Chapter 7

Geochemistry of Ash Leachate

The geochemistry of ash leachate generated in the field and the laboratory leaching columns is analysed and discussed. The apparent controls of soluble species are investigated through geochemical modelling and plots of speciation data. A brief risk assessment of trace element geochemistry is presented. This analysis forms the basis for later solute transport modelling of ash leaching studies undertaken.

7.1 Overview and Approach

On the basis of the literature review presented earlier in Chapter 2, the major solutes in ash leachate will be predominantly controlled by dissolution and/or precipitation of the minerals containing these elements. These reactions are generally considered to be reversible and approach equilibrium rapidly (Fetter, 1993; Langmuir, 1997). The important geochemical parameters in determining the solubility of a particular species in a given solution are the pH (acidic or alkaline), redox state (oxidising or reducing) and ionic strength (Knox *et al.*, 1993). The controls on trace elements may also include sorption processes on oxide, oxyhydroxide or other surfaces.

Ideally, a detailed mineralogical study would identify the dominant primary and secondary (weathered) minerals present within the ash, their respective quantities, and would analyse and predict leachate chemistry through geochemical and mineral equilibrium modelling of column and batch tests (see Eighmy *et al.*, 1995).

Frequently, controlling mineral phases are not identified in ash, suggesting that dissolution and reprecipitation are the mechanisms that form the controlling solids (Eighmy *et al.*, 1995). The mineral phases of ash are difficult to determine from chemical analyses of either the coal or the ash, mainly due to the eight elements which form oxides or mixed oxides, namely Al, Fe, Ca, Mg, Na, K, Ti and Si (Cashion & Brown, 1996).

The comprehensive approach of Eighmy *et al.* (1995) was to undertake a detailed qualitative and quantitative assessment of ash mineralogy and morphology, and thereby to compare predicted leachate chemistry using geochemical modelling with MINTQEA2 (Allison *et al.*, 1991) with that from sequential batch leaching tests. Although Eighmy *et al.* (1995) were successful in demonstrating the different mineralogical controls on leachate chemistry, they recognised the need for further mineralogical analyses to establish a more comprehensive database of ash mineralogy, and therefore controls on leachate chemistry. This approach was acknowledged as quite expensive and time consuming, and not readily transferrable to studies of heterogeneous field disposal sites.

The transport of ash via slurrying and disposal in a saturated ash pond leads to active leaching, with dissolution and reprecipitation changing the mineralogical nature of the ash. Thus it is difficult to adequately identify, before, during and after disposal, the various solubility-controlling minerals and an alternative approach is required to assess geochemical controls.

One popular approach, used by several workers (eg. Roy & Griffin, 1984; Mattigod *et al.*, 1990; Eary *et al.*, 1990; Fruchter *et al.*, 1990; and others), is to use a geochemical model to calculate the speciation of soluble species with a given water chemistry. This speciation data is then plotted, as log [activity], against the solubility curves for different minerals thought to be present. This allows an assessment of the possible controlling mineral assemblages within the ash.

This approach is based on the assumption that equilibrium has been reached between the leachate solution and thermodynamically stable or meta-stable mineral phases (Langmuir, 1997). This implies the following assumptions : (i) the dissolved concentration of a particular species can be measured directly or calculated from total solution composition data; (ii) sufficient contact time has occurred between the solid and solution phases for the system to reach steady state; and (iii) the solid phases of interest are present in the soil in their thermodynamic standard states (Langmuir, 1997). This is generally known as a ‘batch’ approach to geochemistry and ignores possible kinetic effects, since individual leachate samples are assumed to be at equilibrium.

Given the wide variability of ash within the Latrobe Valley, it was considered more appropriate for this study to analyse the resulting leachate chemistry as it might influence environmental outcomes and management, rather than a detailed study of ash composition. Thus the above approach of plotting speciation data derived from geochemical modelling has been adopted. This allows an assessment of the controlling processes affecting different major solutes and trace elements, and therefore the appropriate methodology for solute transport modelling. It is not intended to be a detailed treatise, however, and is only for the purpose of verifying assumptions and approaches for solute transport modelling.

The geochemical model PHREEQC Version 1.1 (Parkhurst, 1995) has been used to assess the geochemical speciation of all ash leachates monitored in the field and laboratory leaching studies. This version of PHREEQC contains the WATEQ4F thermodynamic database (Parkhurst, 1995). The PHREEQC model is adequate for modelling of water chemistries up to the salinity of seawater (Parkhurst, 1995), compared to the majority of ash leachates which are of moderate to low salinity. The three laboratory columns and two field cells are maintained as separate data sets in the analysis, to allow the assessment of possible scale effects in the leaching. The data from the first three months of the Wet Cell have been separated as a data set, since this phase represents the primary dissolution and leaching phase of the ash. Only the trace elements already included in the PHREEQC database have been included in leachate geochemical modelling - namely Ba, B and Sr. A brief discussion of As, B, Mo and Se geochemistry is presented later in this chapter. The various minerals used in this analysis and their dissolution/solubility equations are compiled in Table 1. The PHREEQC analyses have been performed at an assumed temperature of 16 ^{0}C, on the basis of average temperature during the field work (see Appendix 4). Unless stated otherwise, all thermodynamic data is quoted at standard temperature (25 ^{0}C) and pressure (1 atm).

Table 7.1 - Mineral Dissolution and Solubility Equations (Parkhurst, 1995)

Mineral	Formula	Dissolution Equation	Equation
Gypsum	$CaSO_4.2H_2O$	$\log [Ca^{2+}] + \log [SO_4^{2-}] = -4.58$	7-1
Anhydrite	$CaSO_4$	$\log [Ca^{2+}] + \log [SO_4^{2-}] = -4.36$	7-2
Thenardite	Na_2SO_4	$2 \log [Na^{+}] + \log [SO_4^{2-}] = -0.179$	7-3
Barite	$BaSO_4$	$\log [Ba^{2+}] + \log [SO_4^{2-}] = -9.97$	7-4
Celestite	$SrSO_4$	$\log [Sr^{2+}] + \log [SO_4^{2-}] = --6.63$	7-5
Aragonite	$CaCO_3$	$\log [Ca^{2+}] + \log [CO_3^{2-}] = -8.336$	7-6
Calcite	$CaCO_3$	$\log [Ca^{2+}] + \log [CO_3^{2-}] = -8.48$	7-7
Siderite	$FeCO_3$	$\log [Fe^{2+}] + \log [CO_3^{2-}] = -10.45$	7-9
Witherite	$BaCO_3$	$\log [Ba^{2+}] + \log [CO_3^{2-}] = -8.562$	7-10
Strontianite	$SrCO_3$	$\log [Sr^{2+}] + \log [CO_3^{2-}] = -9.271$	7-11
Quartz	SiO_2	$\log [H_4SiO_4] = -3.98$	7-12
Silica $_{(am)}$	$SiO_{2\ (am)}$	$\log [H_4SiO_4] = -2.71$	7-13
Ferrihydrite	$Fe(OH)_3$	$\log [Fe^{3+}] +3\ pH = 4.891$	7-14
Gibbsite	$Al(OH)_3$	$\log [Al^{3+}] +3\ pH = 8.11$	7-15
$Al(OH)_{3\ (am)}$	$Al(OH)_3$	$\log [Al^{3+}] +3\ pH = 10.8$	7-16

Note - all values quoted at standard temperature (25 ^{0}C) and pressure (1 atm); [X] is the activity of species 'X' in solution as modelled by PHREEQC.

7.2 General Controls and Geochemical Conditions

The ash leachates generated in the field and the laboratory were generally mildly to strongly oxidising. The redox state of the field cells indicated an initial range around +45 to +160 mV, increasing rapidly to a stable value of around +300 mV. This environment is considered to be related to the entry of air into the unsaturated ash profile in the field. In the Wet Cell, the decrease in oxidising conditions to around +170 mV in July to August 1998 is most likely due to the lower rates of air entry through the ash profile as the degree of saturation increased with the high volume of water being irrigated.

The highly alkaline nature (pH >9) of many ash leachates is primarily due to the basic nature of the contained major minerals, such as calcium oxide (CaO or lime) and magnesium oxides (Mattigod *et al.*, 1990). The lack of acid-generating minerals (eg. pyrite, FeS_2) and high proportion of alkaline minerals gives the ash a substantial buffering capacity.

The leachate data for the Wet Cell has been analysed using the PHREEQC model and the calculated saturation indices for typical minerals likely to be present in the ash (see Table 7.1) are given in Table 7.2. Given the unsaturated nature of the ash and the observation of the redox state of the leachate related to the entry of air into the porous ash profile, a comparison of the influence of carbon dioxide (CO_2) on leachate chemistry has been included. The averaged leachate data (refer to Tables 5.15 and 5.16), has been equilibrated to atmospheric CO_2 at a pressure of 0.000316 (or $10^{-3.5}$) atm (Langmuir, 1997). By comparison to individual samples, the averaged data provides acceptable representation of the evolving chemistry of the ash leachate.

Table 7.2 - Saturation Indices of Wet Cell Leachate
With Respect to Likely Solubility-Controlling Mineral Phases

	July-Sept 97		December 97		March 98 *		June 98		July 98 *	
Formula	-	CO_2	-	CO_2	-	CO_2	-	CO_2	-	CO_2
Gypsum	-0.49	-0.49	-0.70	-0.69	-0.75	-0.75	-1.12	-1.12	-1.75	-1.75
Anhydrite	-0.71	-0.70	-0.91	-0.91	-0.97	-0.97	-1.34	-1.34	-1.97	-1.97
Barite	0.85	0.85	0.45	0.45	-0.02	-0.02	0.24	0.24	-0.21	-0.21
Aragonite	0.39	-0.38	0.37	-0.40	-0.29	-0.42	0.02	-0.81	-0.68	-1.06
Calcite	0.53	-0.24	0.51	-0.25	-0.15	-0.27	0.17	-0.66	-0.54	-0.91
Dolomite	0.69	-0.85	0.57	-0.96	-0.87	-1.12	0.08	-1.58	-1.55	-2.29
Siderite	-6.98	-7.55	-7.55	-7.77	-5.53	-5.65	nd	nd	-9.32	-8.04
Witherite	-3.44	-4.21	-3.65	-4.42	-4.73	-4.85	-3.78	-4.61	-4.31	-4.68
Gibbsite	0.71	1.80	0.03	1.20	1.52	1.67	-0.47	0.67	-0.27	1.71
$Al(OH)_{3\ (am)}$	-1.98	-0.89	-2.66	-1.49	-1.17	-1.02	-3.16	-2.02	-2.96	-0.98
Ferrihydrite	1.24	1.63	1.25	1.69	2.20	2.22	nd	nd	-0.14	0.85
$SiO_{2\ (am)}$	-1.19	-1.08	-1.19	-1.06	-1.13	-1.12	-1.30	-1.19	-1.68	-1.26
Quartz	0.08	0.19	0.08	0.21	0.14	0.14	-0.03	0.08	-0.41	0.01

Note - CO_2 column is SI after equilibration to pCO_2 of $10^{-3.5}$ atm; nd - no data.
* - Assuming a concentration of Ba at the detection limit of 0.01 mg/L.

The principal effect of equilibration to $CO_{2\ (atm)}$ is that the solubilities of major calcium- and carbonate-bearing minerals (eg. calcite and dolomite) increase due to the carbonate complexes formed (Langmuir, 1997). For example, in July 1998, the CO_2 equilibrated saturation index (SI) for calcite is -0.91; indicating undersaturation and the potential to dissolve further calcite. Without CO_2, the SI is -0.54, indicating a higher degree of saturation and lower potential to dissolve calcite. This behaviour of decreasing carbonate mineral saturation after equilibration to atmospheric CO_2 is also observed with other carbonate minerals aragonite (a calcite polymorph) and dolomite.

There appears to be only minor changes in the saturation indices for sulfate minerals, such as gypsum, thenardite and barite, due to the presence of atmospheric CO_2. In comparison, the saturation indices for aluminium and iron hydroxides and silica (quartz and amorphous silica) appear to be increased by CO_2; suggesting a decrease in the solubility of these minerals in the leachate.

The PHREEQC modelling presented in the following sections is based on analysis of individual leachate samples and plotting speciation data as outlined. The appropriateness of mixing laboratory column and field data will be examined in each section, where opportune, and summarised at the end of this chapter. Further analysis of scale effects is presented in Chapter 8.

7.3 Geochemical Controls on Major Elements

7.3.1 Sulfate Minerals and Leachate Chemistry

Many sulfate minerals are highly soluble in natural waters (Fetter, 1993; Appelo & Postma, 1994). The controls on the solubility of sulfate minerals in ash leachates have been investigated. Possible minerals that may control these species in the leachate solution are gypsum, anhydrite and thenardite. All of these minerals have been identified in ash from the Latrobe Valley previously (cf. Section 2.2.3), and hence may contribute to the concentration of their contsituents in ash leachate. Sulfate minerals are often the most ubiquitous in coal ash (Golden, 1983; EPRI, 1993). The behaviour of Ba and Sr sulfates in solution will be discussed later in Section 7.6.

The log activity plots of Ca versus SO_4 and for Na versus SO_4 are given in Figures 7.1 and 7.2, respectively, including the solubility equation number (from Table 7.1) for gypsum, anhydrite and thenardite.

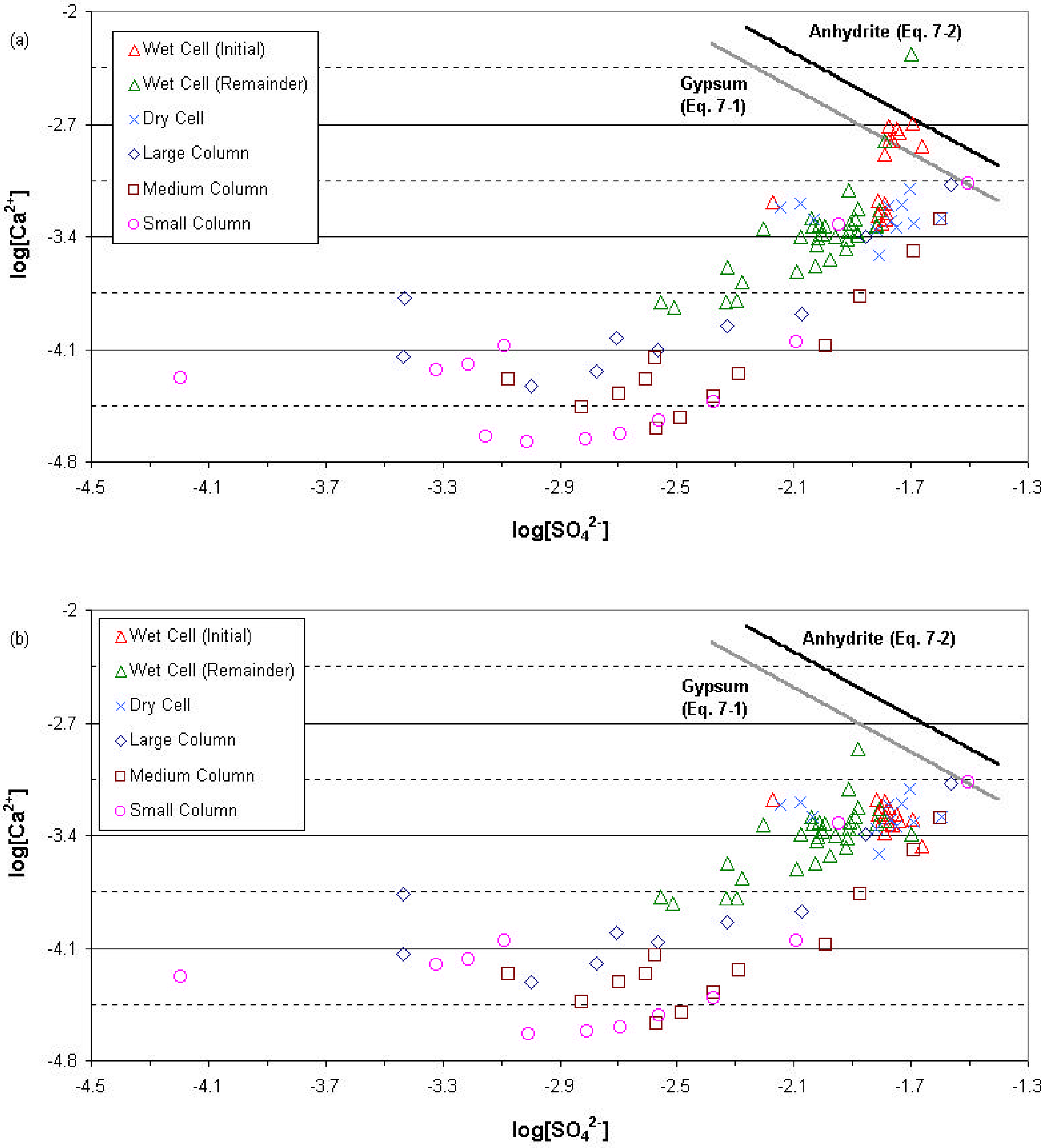


Figure 7.1 - Log Activity Plot of Ca vs SO_4 : (a) No CO_2 & (b) CO_2 Equilibrated

Before equilibration to CO_2, the initial leachate data from the Wet Cell, shows near saturation with respect to gypsum. The Dry Cell and Medium column data are slightly undersaturated, but still close to the initial Wet Cell data. The initial leachate samples from the Small and Large columns also plot on the gypsum solubility line. It is not clear if the lack of gypsum equilibration indicates insufficient residence times, although this is a possibility.

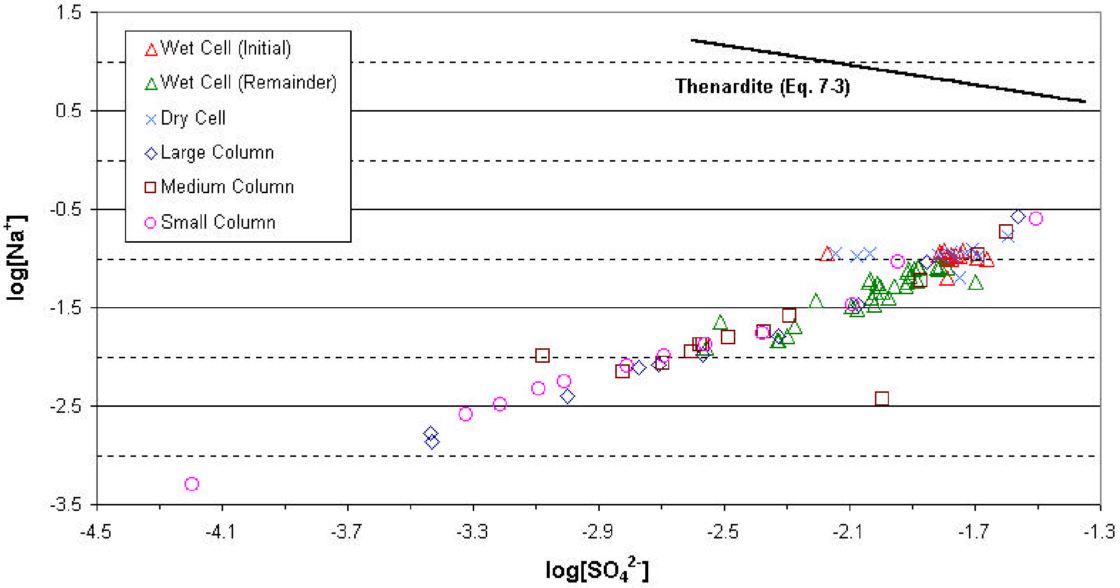


Figure 7.2 - Log Activity Plot of Na vs SO_4 (CO_2 Equilibrated)

The effect of atmospheric CO_2 on Ca and SO_4 activities is apparent, though not significant, indicating a higher solubility of sulfate minerals due to increased carbonate in solution. This is most likely due to the common ion effect, whereby two minerals of different solubility with a common element leads to the precipitation of the least soluble mineral. In the ash, this would be due to competition between the Ca derived from the dissolution of gypsum ($CaSO_4.2H_2O$) versus calcite ($CaCO_3$), with calcite being the least soluble of the two. The reaction can be represented as (Langmuir, 1997) :

$$CaSO_4.2H_2O + 2HCO_3^- \Leftrightarrow CaCO_3 + SO_4^{2-} + 2H_2O + CO_2 \qquad 7\text{-}17$$

During active leaching, the lower Ca and SO_4 concentrations in the leachate cause a shift to the left in Figures 7.1a and 7.1b. It appears that as leaching progresses, SO_4 becomes limited in availability compared to abundant Ca, as the data approaches an asymptote for near-constant Ca concentrations, independent of SO_4 concentrations. This is consistent with the Wet Cell and laboratory column data which shows that SO_4 concentrations decrease substantially after 2 to 3 pore volumes of active leaching.

The log activity plot of Na versus SO_4 data in Figure 7.2 shows that the leachate is consistently undersaturated with respect to thenardite solubility. This is expected, since thenardite is highly soluble, and does not appear to be affected by the presence of carbonates in solution (such as CO_2) in the leachate. The data clearly shows the effect of leaching over time for the Wet Cell and laboratory data. That is, as leaching removes the thenardite from the ash, the respective concentrations of Na and SO_4 in the leachate decreases. The concentration of Na continues to decrease as SO_4 declines, suggesting as the main soluble mineral containing Na, or limited secondary sources of Na (eg. halite). This is consistent with the calculated mineral compositions of various Latrobe Valley ashes, especially Loy Yang ash, given in Table 2.2.

As outlined earlier in Section 2.4 of the literature review, leaching generally proceeds according to an exponential decay function and rapidly approaches a steady state value (see Figure 2.8). For Na and SO_4, in which the dissolution and leaching process is rapid, this approach is more than adequate to capture the above behaviour. This is consistent with the approach and findings of several workers, most notably Farquhar (1989), Eighmy *et al.* (1995), Lu (1996) and others (see next chapter). For the purposes of solute transport modelling of these species in the leachate, it would appear reasonable to assume that both Na and SO_4 can be treated as independent of pH, redox conditions and the concentrations of other species such as Ca.

The behaviour of Ca, however, is more complex and reliant upon leachate chemistry and controlling mineral phases present in the ash, such as calcite (see next section). Thus it would not be reasonable to model Ca leaching over time without incorporating these processes. This is beyond the scope of this thesis, and hence cannot be further addressed. The generally low concentrations of Ca in the various leachates are not environmentally sensitive and thus no further assessment is needed on Ca (except in conjunction with carbonate chemistry).

7.3.2 Carbonate Minerals and Leachate Chemistry

Most carbonate minerals are only sparingly soluble in natural waters (Appelo & Postma, 1994; Langmuir, 1997). The controls on the solubility of various carbonate minerals in ash leachates have been investigated. The dominant carbonate minerals that may control carbon species, Ca and Mg in leachate are calcite, aragonite (a high density calcite polymorph) and dolomite - $CaMg(CO_3)_2$. Aragonite may contribute to some extent due to more favourable precipitation kinetics in saline solutions (Langmuir, 1997), however, it has not been documented in ash either in the Latrobe Valley or other literature. Calcite has been identified in ash from the Latrobe Valley previously (see Section 2.2.3), and as shown earlier in Section 3.10, the exposure of ash pond water to atmospheric CO_2, in conjunction with high Ca concentrations and a sufficiently high pH, is an important process for precipitating calcite in the ash. The presence of dolomite has not been documented in Latrobe Valley ash, and is thus not expected to exert any dominant control on leachate chemistry.

As expected, the presence or absence of atmospheric CO_2 exerts a significant influence on carbonate / calcite geochemistry in the leachate. The log activity plots of Ca versus CO_3 are presented in Figure 7.3.

In general, both plots show that the various leachates are near to slightly over-saturated with respect to calcite, with a general trend close to the solubility curve for calcite, especially for the CO_2-equilibrated plot. There appears to be some degree of separation between the laboratory and field data in Figure 7.3a, which is more clearly defined in Figure 7.3b. The field data appears higher in Ca activities compared to the laboratory columns which appear higher in CO_3 activities. The columns, with their top and bottom caps, were not as freely exposed to atmospheric CO_2 as the field sites were, and hence the wider variation with respect to calcite solubility in Figure 7.3b can be expected due to less calcite precipitation than in the field.

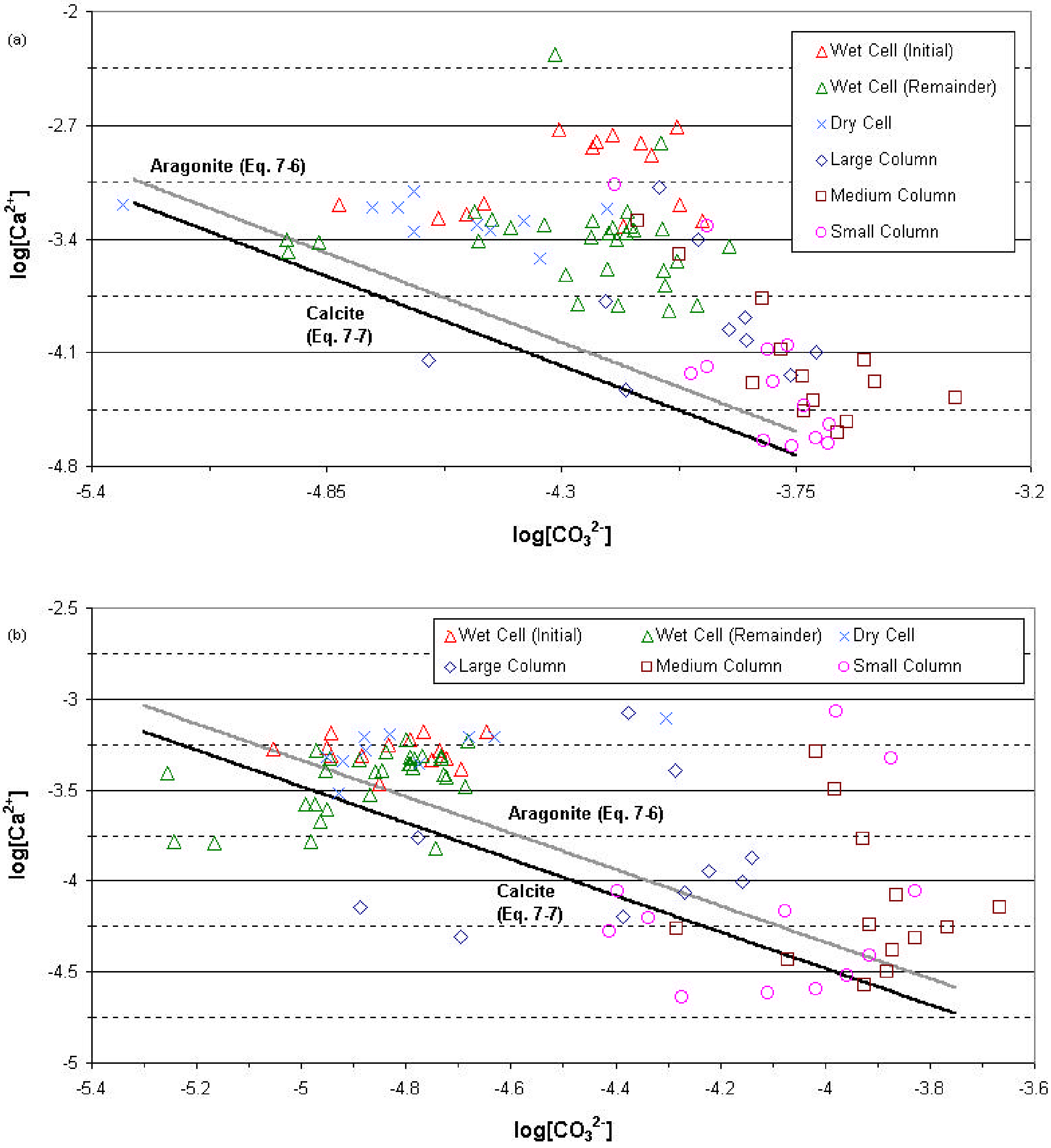


Figure 7.3 - Log Activity Plot of Ca vs CO_3 : (a) No CO_2 & (b) CO_2 Equilibrated

7.3.3 Chloride

The concentrations of Cl in the various leachates are generally not of concern, initially about 670 mg/L in the Wet Cell and decreasing to around 30 mg/L after completion of the trial. The Cl in ash is considered to be present as halite, formed during combustion of the coal in the boilers (cf. Section 2.2.3). Halite is a highly soluble mineral which would leach rapidly and be removed after the addition of water to the ash within the Loy Yang power station.

The ash analyses within the power station, ash pond delta, the column leaching experiments and the Wet Cell all confirm that Cl is the solute to leach most rapidly from ash. Thus it is reasonable to assume that Cl can be modelled on the basis of an initial soluble mass and the approach discussed earlier (cf. Section 7.3.1; see next chapter).

7.4 Metal Oxides and Hydroxides

The ash contains appreciable quantities of Al and Fe, chiefly as oxides and hydroxides. The main Al mineral appears to be alumina, Al_2O_3, which tends to be higher in Loy Yang compared to other Latrobe Valley power stations (cf. Black *et al.*, 1992; Section 2.2.3). Although not identified as a mineral phase in ash (most likely due to mineral speciation analyses being performed on fresh, unleached ash samples and not field leached samples from an ash pond), it is likely that aluminium hydroxides, such as gibbsite - $Al(OH)_3$, or its amorphous form - $Al(OH)_{3\ (a)}$, are also important in controlling aluminium in ash leachates due to hydration and extended leaching in the Loy Yang Ash Pond (see Langmuir, 1997). The dominant Fe minerals appear to be hematite, Fe_2O_3, and magnetite, Fe_3O_4 (cf. Black *et al.*, 1992; Section 2.2.3). The speciation of Al and Fe oxides in the ash is often hampered by the presence of several mixed oxide phase (Macphee *et al.*, 1994; Cashion & Brown, 1996). Analagous to Al, it is likely that Fe activities in the leachate are also controlled by iron hydroxides. The log activity plots of Al versus pH and Fe versus pH are presented in Figures 7.4 and 7.5.

Exposure to atmospheric CO_2 exerts a significant influence on both Al and Fe speciation in the leachate. Before equilibration to CO_2, the data plots very close to the solubility for crystalline gibbsite at a high pH (above 8.5), while below this pH the graph suggests that amorphous $Al(OH)_3$ becomes more important in controlling solubility. The plot for Fe shows similar behaviour with respect to amorphous iron hydroxide ($Fe(OH)_{3\ (a)}$), although Fe activities are over-saturated by one to two orders of magnitude (the Fe concentrations in the leachate were generally low and close to analytical detection limits). This behaviour of Al and Fe is consistent with the data reported by other workers Fruchter *et al.* (1990) and Mattigod *et al.* (1990).

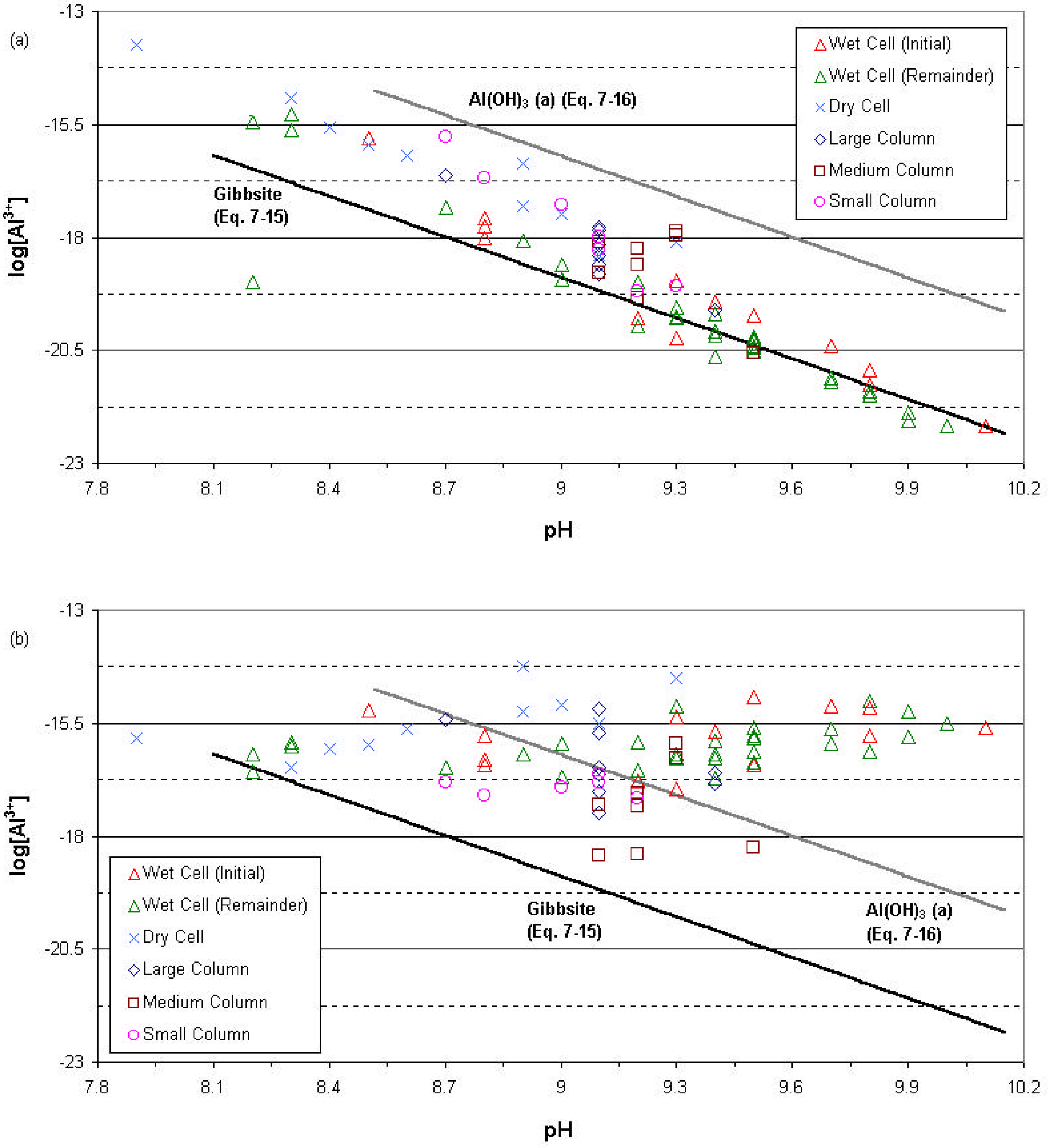


Figure 7.4 - Log Activity Plot of Al^{3+} vs pH : (a) No CO_2 & (b) CO_2 Equilibrated

After equilibration to atmospheric CO_2, the activity data for both Al^{3+} and Fe^{3+} modelled by PHREEQC, as shown in Figures 7.4b and 7.5b, approaches their respective constant values, independent of pH, and no longer appears in equilibrium with either gibbsite or amorphous $Al(OH)_3$ or amorphous $Fe(OH)_3$, respectively. The exact cause of this is unclear, since the addition of low concentrations of CO_2 into the leachate chemistries introduces a weak acid. Given the lack of mineral speciation data for Fe and Al, it is not possible to ascertain the mechanism for this.

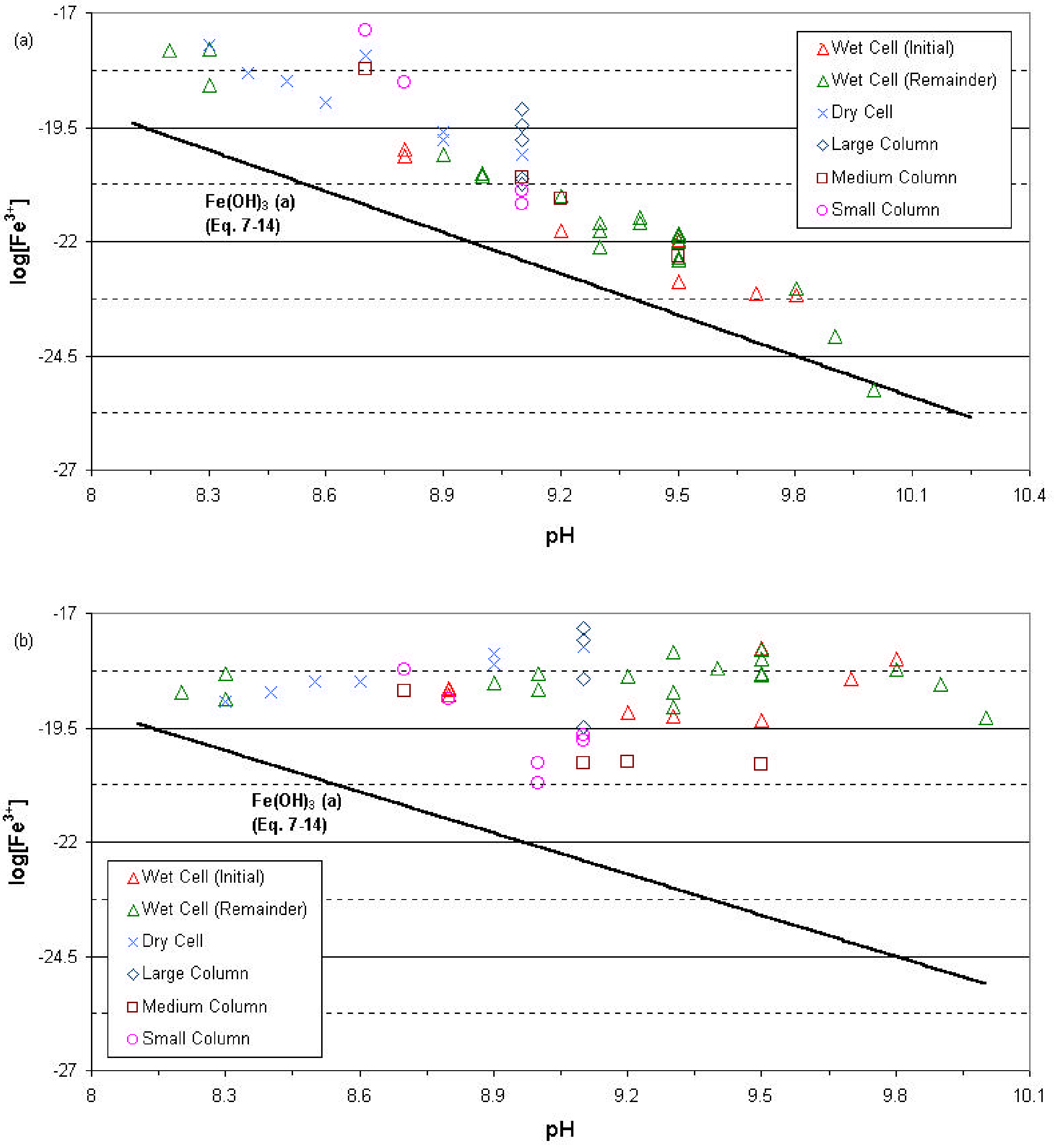


Figure 7.5 - Log Activity Plot of Fe^{3+} vs pH : (a) No CO_2 & (b) CO_2 Equilibrated

For solute transport modelling, it would be necessary to incorporate this pH- and CO_2-dependent behaviour of both Fe and Al (assuming a near-surface disposal site with access to atmospheric CO_2). This could be achieved through the use of a coupled solute transport and geochemical model, however, this is beyond the bounds of this thesis and the practicalities of assessing and modelling heterogeneous ash disposal sites. Given their low concentrations in ash leachate, Fe and Al are not of environmental concern but should be continually monitored to allow further research into their geochemistry.

7.5 Silica

There are a number of probable silica (SiO_2) and mixed aluminosilicate phases in the ash (see Sections 2.2.3 and 2.3.1), however, it is this large variation and the difficulty in determining the exact phases and their respective quantities which precludes a more thorough analysis. Hence only a brief examination of SiO_2 in leachate will be presented. A log activity plot of silicic acid (H_4SiO_4 or $Si(OH)_4$) versus pH is given in Figure 7.6, with the solubility curves for quartz (crystalline SiO_2) and amorphous silica included. Their solubility is effectively independent of pH (Parkhurst, 1995; Langmuir, 1997).

The data in both the non-CO_2 and CO_2 equilibrated graphs (Figures 7.6a and 7.6b) plots close to the line for quartz, suggesting that this phase may be controlling dissolved SiO_2 in the leachate. This would most likely be a dissolution mechanism only with no reprecipitation, due to the high temperature of formation of quartz (Langmuir, 1997). Fruchter *et al.* (1990) demonstrated that wairakite ($CaAl_2Si_4O_{12}.2H_2O$) may be the controlling silicate mineral phase in their Montour fly ash from Pennsylvania. Roy & Griffin (1984) confirmed the control of SiO_2 in leachate by both amorphous silica, quartz and mullite ($3Al_2O_3.2SiO_2$) at various times during leaching.

There appears to be a significant effect of CO_2 equilibration at higher pH (above about 9.4), although the mechanism is not clear. The lack of aluminosilicate mineral speciation in Latrobe Valley ash, however, prevents further analysis of controlling silica phases in the ash. Given the low concentrations in leachate and low environmental sensitivity of silica, it will not be inlcuded in solute transport modelling.

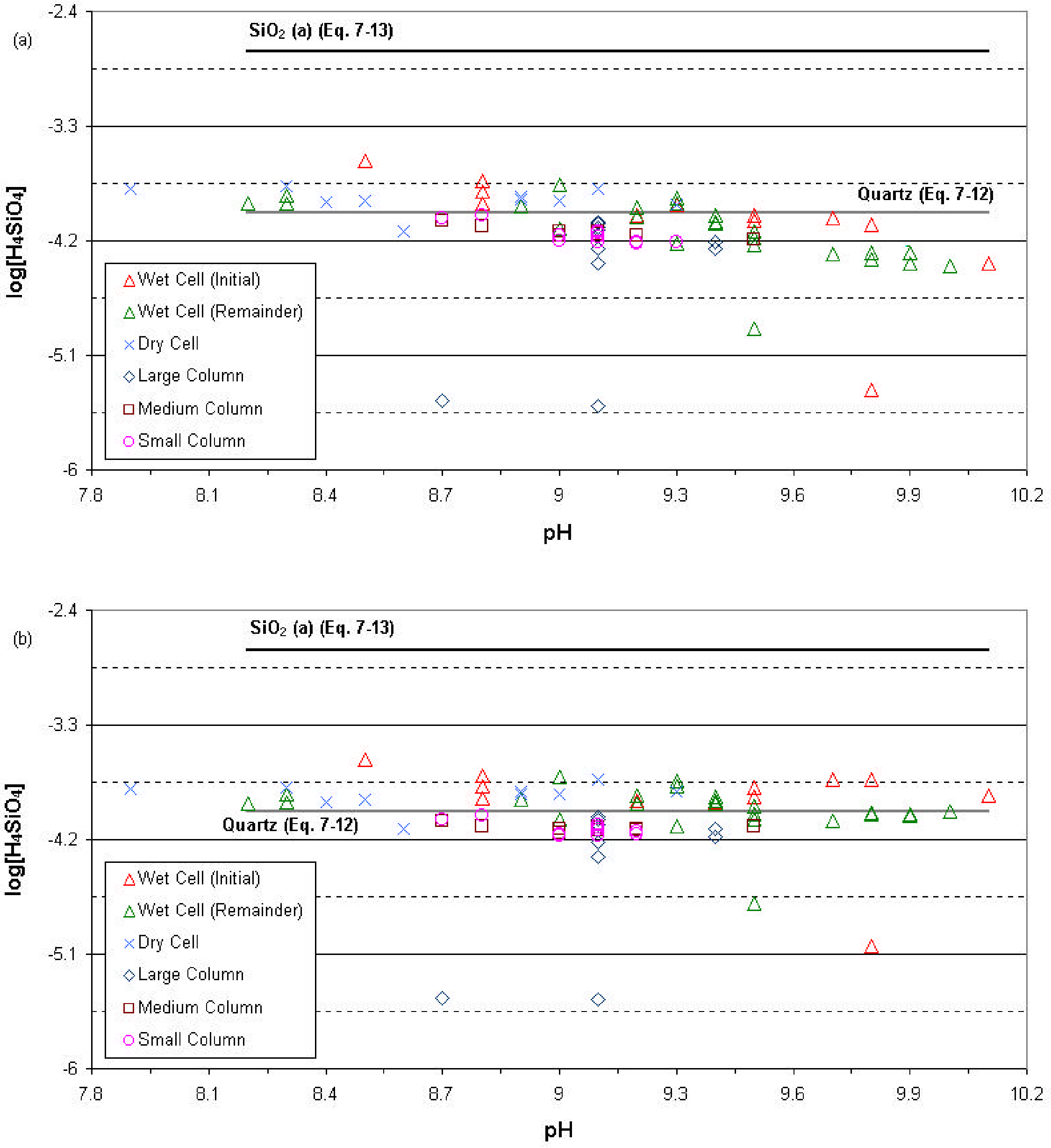


Figure 7.6 - Log Activity Plot of H_4SiO_4 vs pH : (a) No CO_2 & (b) CO_2 Equilibrated

7.6 Barium and Strontium Sulfates and Carbonates

The behaviour and geochemical controls on Ba and Sr are related but complex, and are therefore considered together. Both elements can exist as pure sulfate minerals and may also exist as Ba/Sr co-precipitates (McBride, 1994). The principal sulfate minerals are barite ($BaSO_4$) and celestite ($SrSO_4$). The solubility product of barite is low at $10^{-9.97}$, while celestite, in contrast, is sparingly soluble with a solubility product of $10^{-6.63}$ (Parkhurst, 1995; Langmuir, 1997). The principal carbonate minerals are witherite ($BaCO_3$) and strontianite ($SrCO_3$), both have quite low solubility products of $10^{-8.562}$ and $10^{-10.45}$, respectively (Parkhurst, 1995; Langmuir, 1997).

The log activity plot for Ba versus SO_4 is given in Figure 7.7. There is negligible effect from CO_2 on Ba activities, and hence this plot has not been included. The plot shows that Ba concentrations are up to one order of magnitude higher than those predicted by equilibrium dissolution from barite, consistent with the findings of other researchers (Ainsworth & Rai, 1987; Fruchter *et al.*, 1988; Eary *et al.*, 1990). The laboratory and field data appear as a cluster in the bottom right corner of the plot, where higher SO_4 activities prevail, with the laboratory columns progressively shifting toward the upper left as sulfate minerals are leached from the ash. This also leads to near-equilibrium with barite for the leachate from the three columns.

The log activity plots for Sr versus SO_4 are given in Figure 7.8. For Sr, there are no analyses from the field trials, and thus only the laboratory leaching columns can be plotted. The initial samples plot very close to equilibrium with celestite, however, as leaching progresses they move sharply to the left, showing significant undersaturation with respect to celestite by one order of magnitude. This is analogous to the behaviour of Ca and SO_4 shown earlier in Section 7.3.1 (see Figure 7.1) and is consistent with the results of Ainsworth & Rai (1987) and Eary *et al.* (1990). The data appears to suggest that Sr becomes independent of SO_4 concentrations after leaching progresses, since an asymptote develops for Sr with respect to SO_4. The presence of atmospheric CO_2 appears to have a minor influence on modelled Sr activities (discussed later in conjunction with carbonate chemistry).

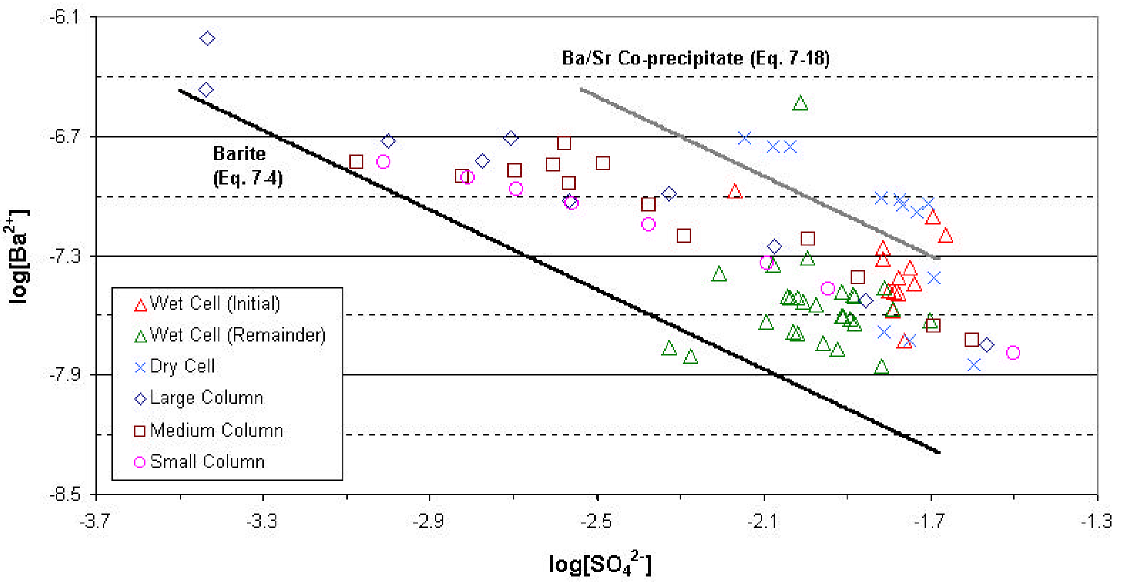


Figure 7.7 - Log Activity Plot of Ba vs SO_4 (CO_2 Equilibrated)

A common phenomenon in ash leachate geochemistry is for Ba and Sr to form a mixed mineral phase or co-precipitate, giving barite-celestite or $(Ba,Sr)SO_4$. (Eary *et al.*, 1990; Fruchter *et al.*, 1990; Felmy *et al.*, 1993). Due to the higher solubility of celestite, this leads to an effective increase in Ba solubility and a decrease in Sr solubility. The solubility of the co-precipitate is generally estimated based on the molar proportions of Ba and Sr present (cf. Eary *et al.*, 1990; Felmy *et al.*, 1993; Appelo & Postma, 1994).

The average concentrations of Ba and Sr in ash are approximately 304 and 635 mg/kg, respectively, based on the average of all ash analyses from laboratory and field work. This gives a Ba:Sr molar ratio of about 1:3.27, or a $SrSO_4$ mole fraction of about 0.766. In comparison, Eary *et al.* (1990) found a 1:1 ratio in good agreement with experimental and field data. On the basis of a Ba:Sr molar ratio of about 1:3.27, a mixed phase dissolution equation can be derived for the laboratory and field data as an intermediate of barite and celestite, being closer to celestite than barite (cf. Fruchter *et al.*, 1990; Appelo & Postma, 1994) :

$$\log [Ba^{2+} \text{ or } Sr^{2+}] + \log [SO_4^{2-}] = -7.41 \qquad \text{Ba/Sr co-precipitate} \qquad 7\text{-}18$$

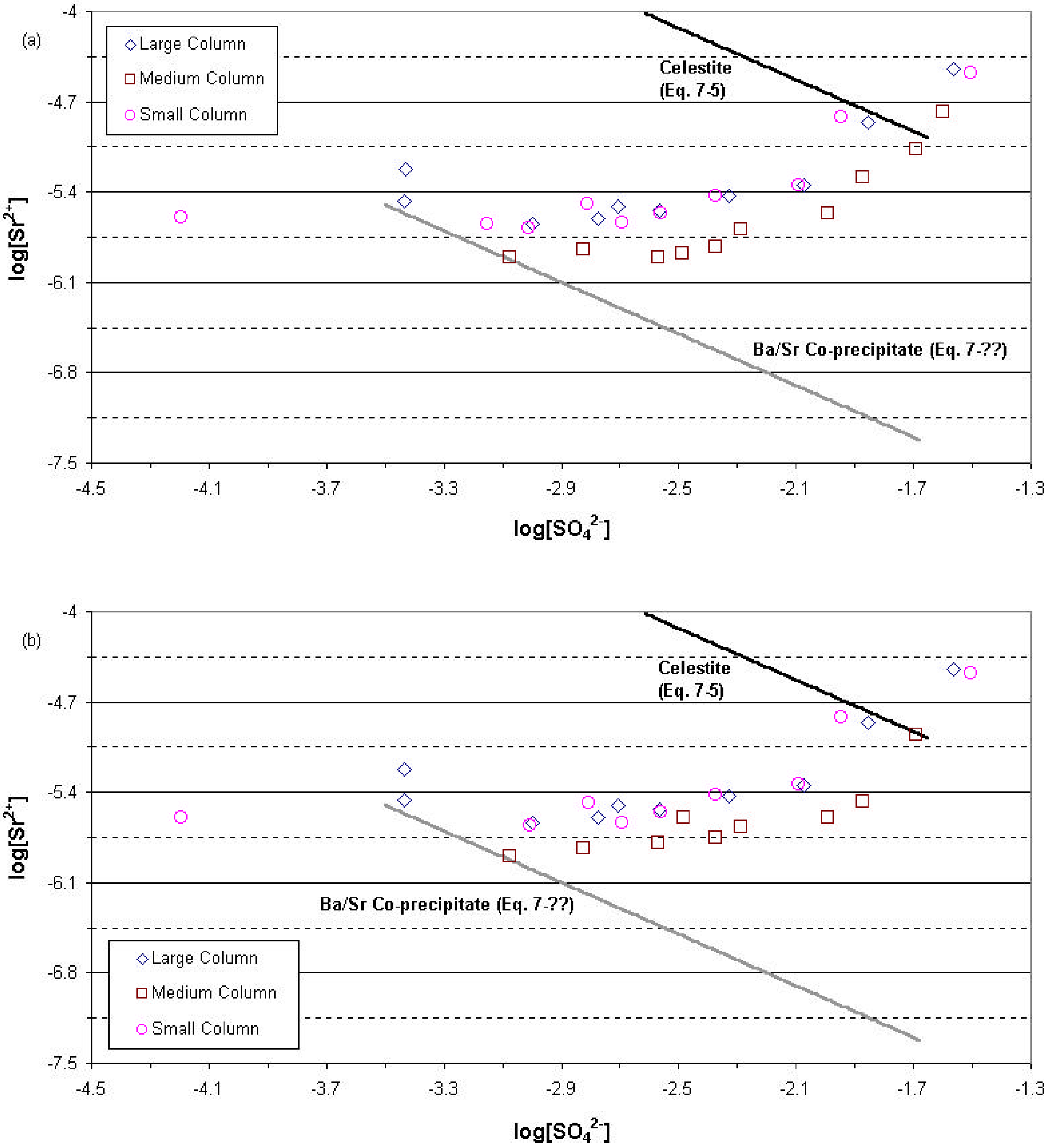


Figure 7.8 - Log Activity Plot of Sr vs SO_4: (a) No CO_2 & (b) CO_2 Equilibrated

Further investigations of the co-precipitation controls on Ba and Sr sulfates are hampered by several difficulties (Felmy *et al.*, 1993). Firstly, the approach to equilibrium appears to be slow; secondly, the composition of the solid phase of the surface of the co-precipitate is relatively unstudied; and finally, the low concentrations of Ba and Sr are often problematic to determine analytically, increasing uncertainty in geochemical behaviour. A plot of Sr versus Ba is given in Figure 7.9.

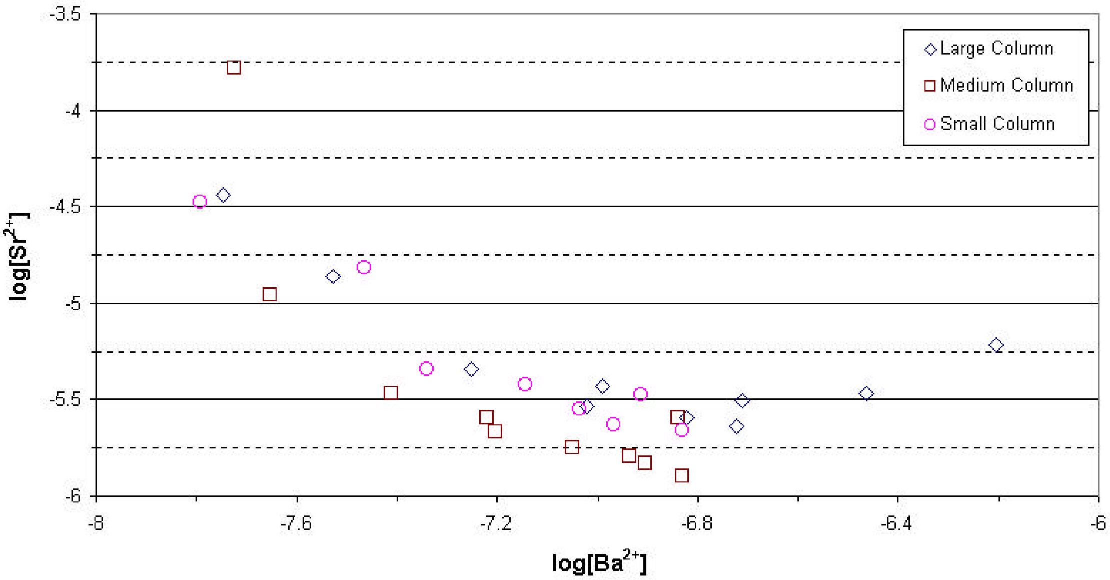


Figure 7.9 - Log Activity Plot of Sr vs Ba (CO_2 Equilibrated)

Thus, after significant leaching, the concentrations of Sr appear to approach a constant value, independent of Ba which increases slightly in the laboratory leaching columns. This indicates that the possible sulfate phases present in the ash have little influence on Ba and Sr concentrations in leachate. In other words, Sr in particular would therefore be dominantly controlled by carbonate mineral phases. This is in good agreement with Eary *et al.* (1990). The influence of carbonates further complicates the behaviour of Ba and Sr in ash leachate. After the leaching of the more soluble sulfate minerals from the ash, it is possible that carbonate species exert more control Ba and Sr concentrations in ash leachates and pore waters in the long term; especially under strongly alkaline conditions (Eary *et al.*, 1990; Bagchi, 1990). The plots of Ba versus CO_3 and Sr versus CO_3 are given in Figures 7.10 and 7.11, respectively.

The Ba plots show undersaturation with respect to witherite, and a significant effect from the presence of CO_2. The degree of scatter in the data, especially after CO_2 equilibration, precludes any accurate assessment of whether Ba is controlled by witherite, although it does appear to be slight at best. Before CO_2, the laboratory and field data do not appear distinct, however, the presence of CO_2 clearly separates the different data sets, similar to that observed for Ca versus CO_3 (Section 7.3.2). This is presumably due to the lack of CO_2 available to the columns.

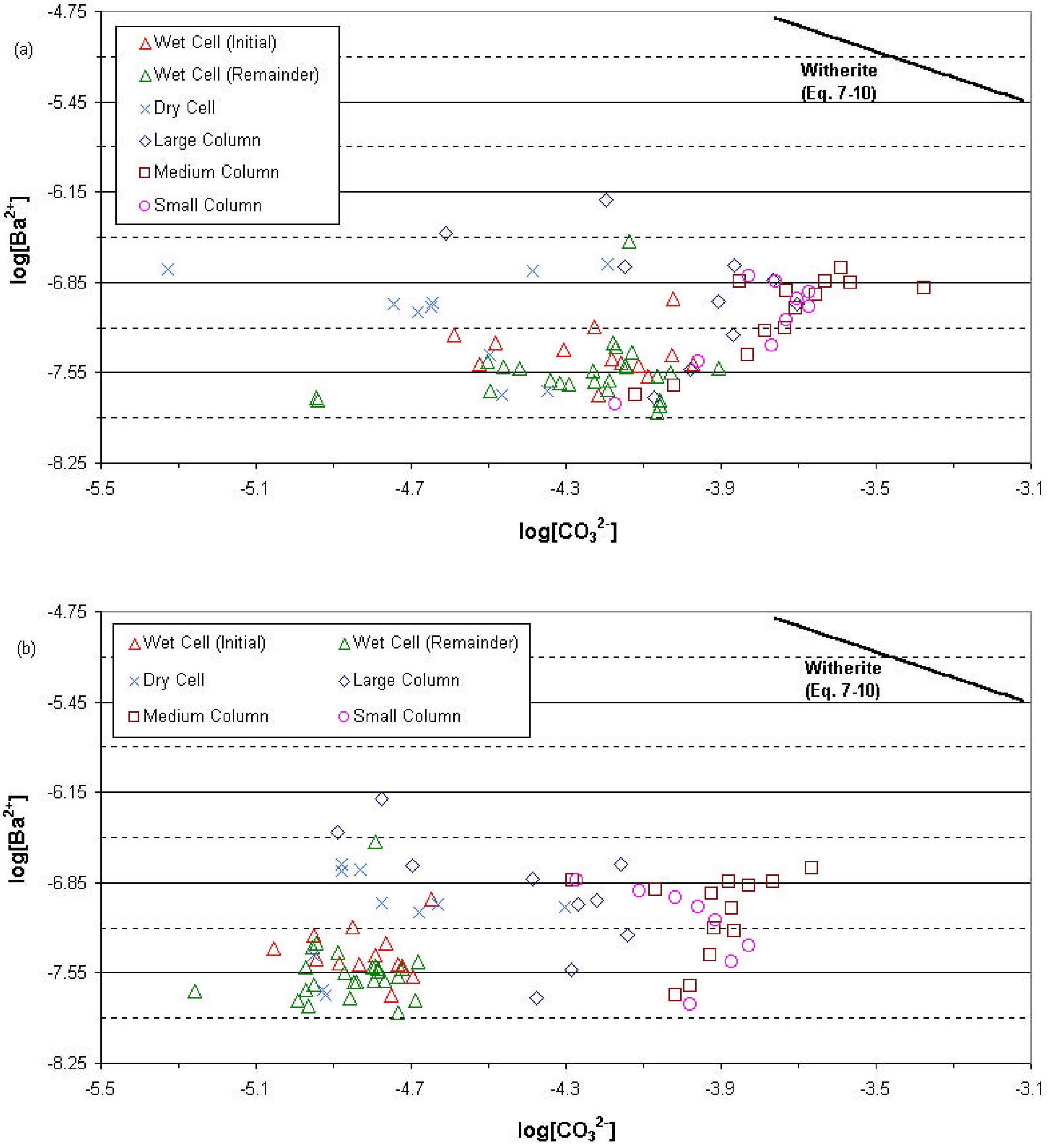


Figure 7.10 - Log Activity Plot of Ba vs CO_3 : (a) No CO_2 & (b) CO_2 Equilibrated

The behaviour of Sr, in comparison to Ba, is more defined. The initial data shows oversaturation with respect to strontianite by about one order of magnitude, although with respect to witherite (included for comparison), the data is quite close. After equilibration to CO_2, the data plots more closely to equilibrium with strontianite, although the degree of scatter increases. The lack of CO_2 for the laboratory columns and the apparent dependence of Sr on CO_2 would suggest that CO_2 is therefore important in considering the leachate chemistry of Sr.

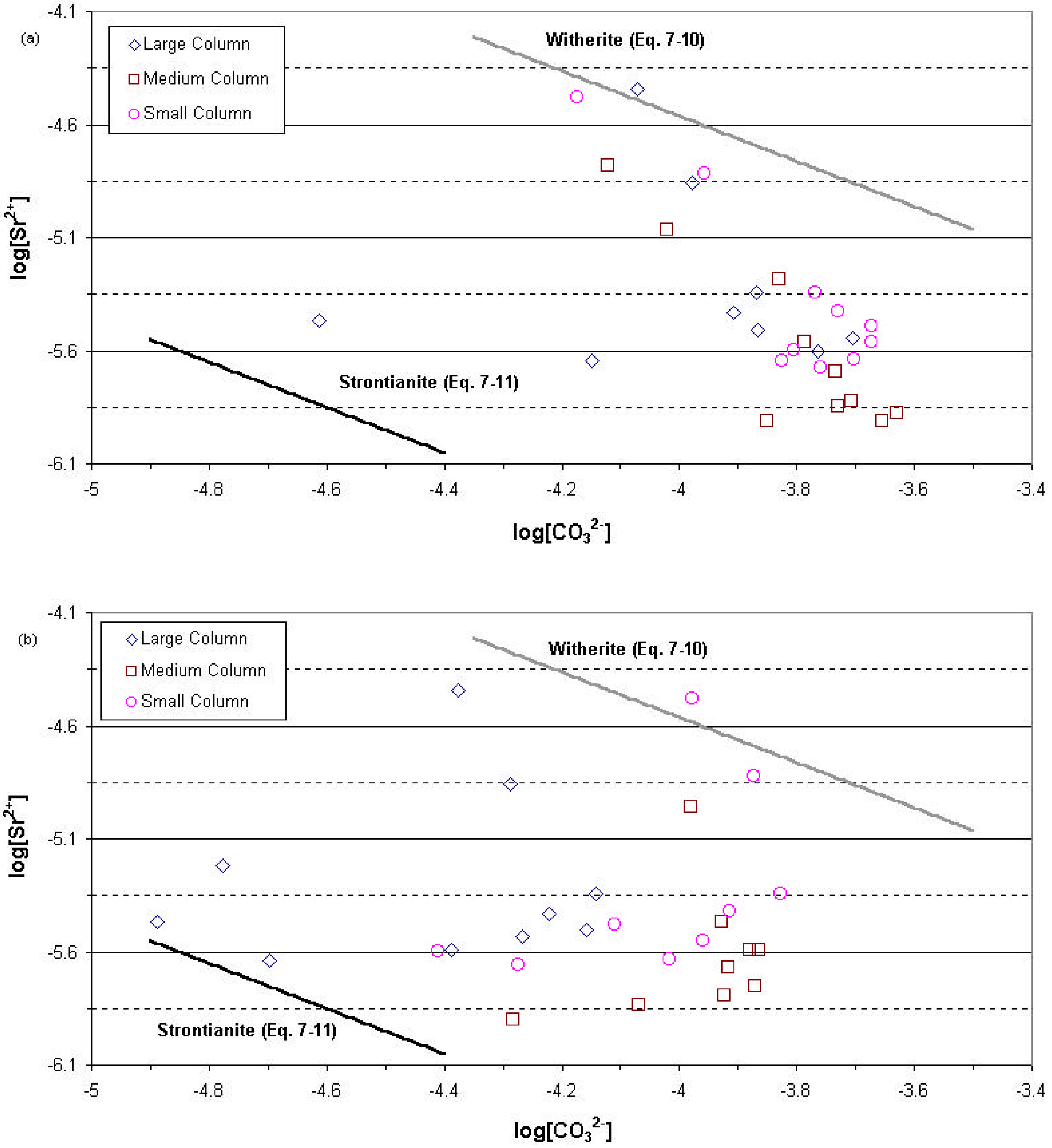


Figure 7.11 - Log Activity Plot of Sr vs CO_3 : (a) No CO_2 & (b) CO_2 Equilibrated (witherite included for comparison)

The possible behaviour of Ba and Sr as chemical analogues of Ca has not been investigated, although similar behaviour has been noted for Sr and SO_4 in particular. The geochemical controls on both Ba and Sr are therefore complex, with both sulfate and carbonate mineral phases appear to exert some influence, depending on the stage of leaching. Given the environmental significance of the possible concentrations in ash leachate, further research is recommended on Ba and Sr behaviour.

7.7 Risk Assessment of Trace Element Geochemistry

7.7.1 Arsenic

The trace element As is well known for its human health and environmental toxicity and has a complex geochemical behaviour (Ringwood, 1995). The global average soil concentration of As is about 7 mg/kg (Logan & Traina, 1993). The leached ash, which contains As at a similar concentration, is therefore not elevated with respect to As; however, its potential mobility is critical. Detailed reviews of As biogeochemistry and toxicity are given by Ringwood (1995) and ANZECC & ARMCANZ (1999).

Arsenic is generally of moderate solubility in most natural waters, since the oxidised form of As, As(V), undergoes strong adsorption onto ferric hydroxides (Bagchi, 1990; Fuller *et al.*, 1993; McBride, 1994; Smith *et al.*, 1996). Goldberg & Glaubig (1988a) have modelled As adsorption on calcareous, montmorillonic clay soils. In its reduced form of As(III), As is quite soluble (Fetter, 1993) and up to 25 to 100 times more toxic than its oxidised counterpart (Ferguson & Gavis, 1972; Morrison *et al.*, 1989; Ringwood, 1995; Smith *et al.*, 1996).

The solubility controls on As have not been studied, due to incomplete thermodynamic databases for As in the PHREEQC model (cf. Parkhurst, 1995) and no direct As speciation data in the various leachates. Geochemical modelling is considered of limited value due to the lack of thermodynamic equilibrium between As(III) and As(V) (ANZECC & ARMCANZ, 1999). On the basis of the redox stability diagrams for As in Fetter (1993) and Langmuir (1997), the As found in the ash leachate can be expected to be in the oxidised state, As (V) as arsenate (AsO_4^{3-}), and thus amenable to adsorption on the Fe and Al hydroxides in the ash (Stichbury *et al.*, 2000).

The concentration of As in the ash is low, generally less than 10 mg/kg and often below the analytical detection limit of 5 mg/kg. This compares to the proposed As guideline value for sediment quality of 20 mg/kg (ANZECC & ARMCANZ, 1999). It is worth noting that although the concentration of As in the ash is often below 5 mg/kg, it still appears at low concentrations in the leachate up to 0.01 mg/L (higher in the columns).

The drinking water standard for As in Australia was formerly 0.05 mg/L (ANZECC, 1992), although more stringent values of 0.0016 mg/L for As (III) and 0.0024 mg/L for As (V) have recently been proposed as a trigger level for more rigorous assessment of environmental and toxicological risk (ANZECC & ARMCANZ, 1999). The concentration of As in leachates from the field trials and the laboratory columns generally averages about 0.01 mg/L, although higher concentrations are found in the initial flush of leachates from the laboratory columns. These concentrations, although above the recent trigger levels of ANZECC & ARMCANZ (1999), do not appear to pose a significant environmental or toxicological risk and hence no further analysis is considered necessary.

7.7.2 Boron

The geochemistry of B warrants some brief attention. Compared to the global average in most surface soils of about 10 to 85 mg/kg (Logan & Traina, 1993; McBride, 1994), B is relatively enriched in the ash at around 170 mg/kg. It is generally considered to be a quite soluble element and therefore mobile in most environments (Bagchi, 1990; McBride, 1994). It typically forms boric acid - H_3BO_3 (or $B(OH)_3$), and at high pH's tends to convert to borate species - $B(OH)_4^-$ (McBride, 1994). Although easily leachable, B can accumulate to toxic concentrations in some alkaline soils with a lack of rainfall (McBride, 1994). A brief review of B biogeochemistry and toxicity is given by ANZECC & ARMCANZ (1999).

In the Wet Cell, the concentration of B gradually increased to about 6 mg/L until about March 1998 (about 0.81 pore volumes), from where it slowly began decreasing, finishing at a concentration higher than the initial leachate (final B of 4.8 mg/L compared to 2.6 mg/L initially). Similar behaviour was evident in the laboratory leaching columns, although the small column shows a significant decrease in B concentrations beginning to occur after about 4.5 pore volumes.

There is no available mineralogical speciation data for B in Latrobe Valley ashes, and other researchers have failed to demonstrate that soluble borate minerals control the concentrations in ash leachates (cf. EPRI, 1993; Fruchter *et al.*, 1990; Eary *et al.*, 1990).

Boron is known to undergo adsorption on iron and aluminium oxide surfaces (Bagchi, 1990; McBride, 1994), and this may help to explain the change in B concentrations over time (Sims & Bingham, 1968; Goldberg & Glaubig, 1985 & 1986; Huang *et al.*, 1998). Adsorption leads to retardation during moisture movement and solute transport, thereby controlling leachate concentrations of B.

The drinking water quality guideline for B in the USA is 1 mg/L (Manahan, 1991), and was formerly the same in Australia (ANZECC, 1992). A more stringent environmental and risk-based trigger level of 0.0048 mg/L has recently been proposed by ANZECC & ARMCANZ (1999). Although the concentration of B in leachate is above both these levels, its low toxicity precludes any significant ecotoxicological risk given the layout of the Loy Yang complex and ash disposal sites, especially given the mildly acidic nature of Latrobe Valley groundwaters.

7.7.3 Molybdenum

The concentration of Mo in the leachate is of concern, despite it being generally below analytical detection limits in ash samples, and therefore requires assessment in terms of geochemistry. The concentration of Mo in ash at about 8 mg/kg is enriched relative to the global average of about 1 to 3 mg/kg (Logan & Traina, 1993; McBride, 1994). This is still below the 40 mg/kg considered to be contaminated soil by EPAV (1993), although like As, the mobility of Mo is critical in assessing environmental risk. Molybdenum is an essential element for almost all organisms (Logan & Traina, 1993), as it is an enzyme cofactor in nitrogen fixation and nitrate reduction (McBride, 1994). A brief review of Mo biogeochemistry and toxicity is given by ANZECC & ARMCANZ (1999).

Molydenum is typically found in its oxidised form, Mo(VI), as the molybdate ion (MoO_4^{2-}), and has a higher solubility in neutral to alkaline soils (McBride, 1994). Both iron and calcium molybdate ($FeMoO_4$ and $CaMoO_4$) are quite insoluble, with solubility products of $10^{-10.45}$ and $10^{-8.7}$, representing possible solubility controls (Fetter, 1993).

The MoO_4^{2-} ion undergoes adsorption to iron and aluminium oxides, amorphous aluminosilicates and, to a lesser extent, layer silicate clays, with sorption on all minerals increasing at lower pH (Stollenwerk, 1991; McBride, 1994). The extent of MoO_4^{2-} adsorption is dependent on the prevailing pH and salinity (ie. ionic strength) of the solution (Stollenwerk, 1995; Kent *et al.*, 1995). Mildly acidic conditions and low salinity allow more adsorption than near neutral and higher salinity solutions, with competing anions such as phosphate and, to a lesser extent, SO_4, decreasing MoO_4^{2-} adsorption (Stollenwerk, 1995).

There was until recently no drinking water quality guideline for Mo in Australia, although a guideline value of 0.01 mg/L was used for irrigation water (ANZECC, 1992). A more stringent environmental and risk-based interim level of 0.0067 mg/L has recently been proposed by ANZECC & ARMCANZ (1999). An interim level is based on an insufficient exotoxicological dataset to derive a water quality guideline value.

The concentration of Mo in leachates is initially around 0.3 mg/L in both field trials, decreasing to about 0.01 mg/L by the end of the Wet Cell. The laboratory columns exhibited initially higher Mo values between 0.4 to 0.8 mg/L, decreasing to below analytical detection limits (<0.01 mg/L) by the end of the trials. This may indicate a strong control by MoO_4^{2-} adsorption onto oxide surfaces within the ash, although this is unclear and not validated from the experimental data available.

Without further mineral and leachate speciation data for Mo and adsorption, it is not possible to assess geochemical controls and sorption processes. It is recommended that monitoring and research into Mo behaviour in ash leachate be continued.

7.7.4 Selenium

The concentrations of the trace element Se in the leachate is of significance, and thus a brief review and assessment in terms of geochemistry is presented. The concentration of Se in the ash is most often below 5 mg/kg. Selenium is chemically similar to sulphur and can exist in a variety of oxidised or reduced states ranging from -2, -1, 0, +1, +4 and +6 (Bagchi, 1990; Davis *et al.*, 1993; Fetter, 1993; Carroll, 1996). It is an essential element for nutritional purposes in animals and plants, driving many enzyme and metabolic processes (Carroll, 1996; ANZECC & ARMCANZ, 1999). Detailed reviews of Se biogeochemistry and toxicity are given by White *et al.* (1991), Carroll (1996) and ANZECC & ARMCANZ (1999).

The most common forms of Se found are selenite - SeO_3^{2-} (Se IV), selenate - SeO_4^{2-} (Se VI) and its elemental form Se^0, depending on the prevailing geochemical conditions (Davis *et al.*, 1993; Fetter, 1993). Insoluble forms of Se minerals are often found in greater abundance in acidic, reducing environments (McBride, 1994), hence explaining the generally higher Se concentrations in coals and pyritic environments. Under alkaline and oxidising conditions, SeO_4^{2-} is the dominant species in solution, and is only weakly adsorbed by oxides or other minerals (Elrashidi *et al.*, 1987; McBride, 1994; Kent *et al.*, 1995). In acidic conditions, SeO_3^{2-} prevails and undergoes adsorption on oxides and aluminosilicates or precipitation as ferric selenite, $FeSeO_3$ (McBride, 1994). The hydrous oxides of Fe, Al and Mn can adsorb both Se(IV) and Se(VI), under favourable geochemical conditions (Davis *et al.*, 1993). Goldberg & Glaubig (1988b) modelled Se adsorption on calcareous, montmorillonic clay soils. In general, adsorption of Se is weak, relative to other species, making Se more sensitive to competition from available anions, with higher salinity acting to decrease Se adsorption (Kent *et al.*, 1995).

The toxicity of Se varies significantly with animal species, chemical speciation, biological pathway and length of exposure (Carroll, 1996). The selenite species bioaccumulates much more rapidly than does selenate, and it appears that selenite is generally more toxic than selenate (ANZECC & ARMCANZ, 1999). In the environment, Se can undergo bioaccumulation through the food chain, leading to chronic selenosis by ingestion of foodstuffs and water enriched in Se (Carroll, 1996). Some famous examples of selenosis occurring naturally is in Enshi province in China and the states of South Dakota and Nebraska in the USA (Combs & Combs, 1986).

The former drinking water quality guideline for Se in Australia was 0.01 mg/L (ANZECC, 1992). A more stringent environmental and risk-based level 1 of 0.0014 mg/L for Se(IV) and an interim level of 0.0023 mg/L for Se(VI) has recently been proposed by ANZECC & ARMCANZ (1999). An interim level is based on an insufficient exotoxicological dataset to derive a water quality guideline value, while a level 1 value is based on an adequate ecotoxicity dataset.

The concentration of Se in leachates initially ranged between 0.8 to 3.8 mg/L in both field trials, decreasing to about 0.08 mg/L by the end of the Wet Cell. The laboratory columns exhibited initially higher Se concentrations between 5 to 8 mg/L, decreasing to between 0.01 to 0.03 mg/L by the end of the trials.

Without further mineral and leachate speciation data for Se, it is not possible to assess geochemical controls and sorption behaviour. On the basis of the above review, Se concentrations are environmentally significant, although they do appear to be in the less toxic selenate form. It is recommended that monitoring and research into Se behaviour in ash leachate be continued.

7.7.5 Aluminium

Aluminium is a ubiquitous element in nature and is present in the ash at concentrations of about 3%. At near-neutral pH conditions, Al has a low solubility due to formation of aluminium hydroxides ($Al(OH)_3$) as well as a generally low toxicity. Under mildly acidic conditions (pH around 5), however, Al is more soluble and can reach concentrations which are toxic to aquatic flora and fauna (cf. ANZECC & ARMCANZ, 1999). Under alkaline conditions, there is conflicting evidence as to whether Al toxicity is again increased or remains the same as its near-neutral pH toxicity (ANZECC & ARMCANZ, 1999). The exact toxicity of Al depends on the pH, hardness and various complexing species that may be present.

The recent guideline for Al proposed by ANZECC & ARMCANZ (1999) is 0.0012 mg/L, which according to the method used for deriving this water quality limit, is independent of pH effects.

The normal range of Al in the various leachates is between 0.05 to 1.0 mg/L with the pH around 9. In this range, Al will only be moderately soluble, and may cause a greyish precipitate or floc in the leachate. However, if the leachate enters the more acidic groundwaters below (where pH is often <5), this would allow Al to speciate into a more toxic form. Although the concentrations of Al at present do not appear to present a significant environmental risk, it is recommended that it be continually monitored to ensure this minimal risk is avoided.

7.8 Summary of Geochemical Controls

The geochemical speciation modelling and analysis of ash leachate chemistry has been presented. This has enabled an assessment of the assumptions for solute transport modelling of dissolved species in the leachate, and hence provide the framework for a more rigorous approach to ash disposal management.

For the major soluble species, Na, SO_4 and Cl, a simple soluble mass approach appears reasonable to capture the simple mineral dissolution mechanisms, controlled by their respective mineral phases. Other less soluble species, such as Ca, Al, Fe and SiO_2, appear to be influenced by pH and/or the presence of atmospheric CO_2. Hence it would be necessary to account for this geochemical behaviour in solute transport modelling. Given their low concentrations in ash leachate and low toxicity, Ca, Al, Fe and SiO_2 will not be included in later modelling work. Together, Na, SO_4 and Cl comprise the majority of ash leachate salinity, and thus potential environmental impacts.

The geochemistry of the main trace elements detected in the leachate is complex, namely As, Ba, B, Mo, Se and Sr. It involves speciation differences (As, Se), mineral dissolution and co-precipitation (Ba/Sr) and possible adsorption controls on leachate concentrations (B, Ba, Mo, Se). The modelled effect of atmospheric CO_2 is significant but unclear for Sr, although it appears to have little effect on Ba. Given the complexity of the controls on the different solutes and the limited data available to accurately quantify the geochemical controls on these trace elements, no solute transport modelling will be undertaken.

Chapter 8

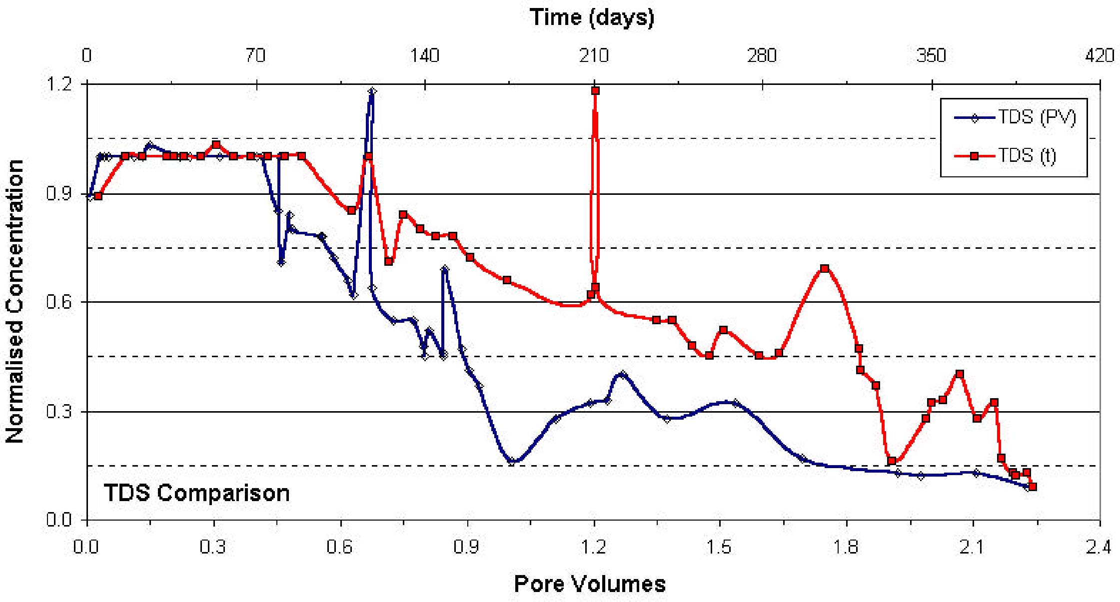
Solute Transport Modelling of Ash Leaching

A theoretical model of solute transport and ash leaching is developed and applied to column leaching data. The extension of this approach to account for unsaturated flow is discussed. A comparison and analysis of the various leaching curves derived from field and laboratory research is presented. A non-dimensional approach for modelling ash leaching is then developed and proposed.

8.1 Ash Leaching and Solute Transport in Saturated Porous Media

Previous chapters in this thesis have presented reviews of leaching phenomena in the literature and from earlier studies in the Latrobe Valley (Chapter 2), results from a 14 month field leaching trial (Chapter 5), additional laboratory leaching columns (Chapter 6) and an analysis of the apparent geochemical controls on the solutes typically found in ash leachate (Chapter 7).

As discussed in Chapters 2 and 3, there are numerous processes that occur and can compete during the migration of a solute within saturated porous media. These include bulk diffusion, advection, chemical reactions and surface transfer phenomena such as matrix dissolution and sorption processes (eg. Freeze & Cherry, 1979; Fetter, 1993; Zheng & Bennett, 1995). In Chapter 7, matrix dissolution and surface phenomena (adsorption) were shown to be important controlling processes for ash leaching. The initial washoff of solutes, driven by dissolution of the more soluble minerals within the ash, is considered to be the most significant mechanism in exchange of solutes between ash surfaces and aqueous solutions (Côté, 1986a). Adsorption has been shown to be important for some trace elements, such as As, B, Mo and Se, but the focus of this thesis has been on the migration of relatively conservative species such as Na, SO_4 and Cl. For the major soluble species in ash leachate, a solute transport model is required to describe the concentration over time, as shown in Figure 8.1 from field and laboratory data.



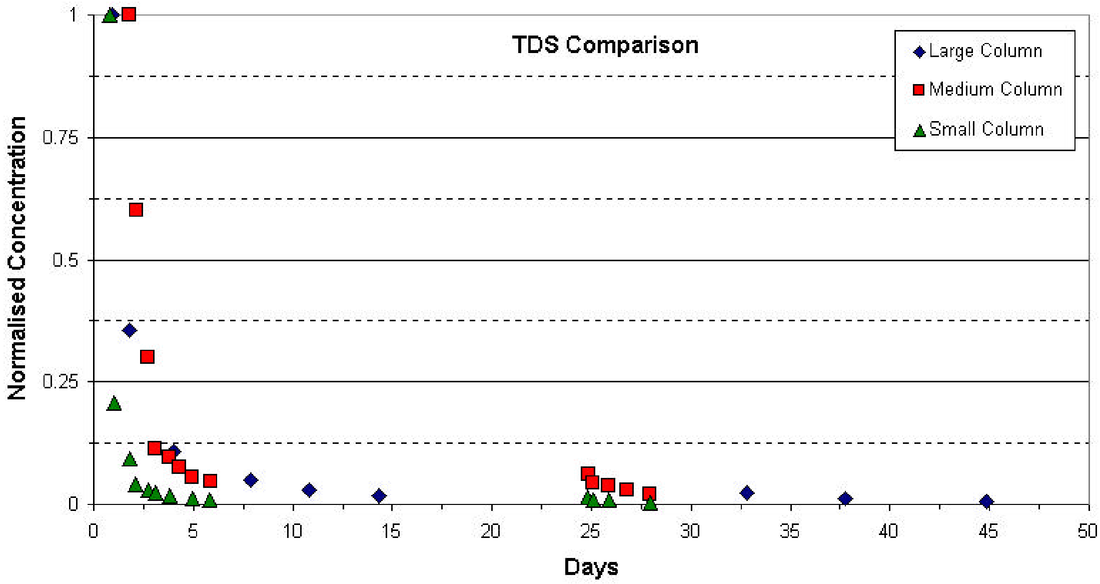


Figure 8.1 - TDS Leaching Curves Versus Time : (top) Wet Cell vs t / PV, (bottom) TDS vs t Laboratory Columns

The one-dimensional partial differential equation for describing the transport and chemical reactions of a solute within saturated porous media was presented in Section 3.11.2 (equation 3-10), and is known as the advection-dispersion equation (ADE) (eg. Freeze & Cherry, 1979; Fetter, 1993; Zheng & Bennett, 1995). A reaction term can be introduced into the ADE to incorporate leaching processes, using the same assumptions of steady state saturated flow, non-deforming, homogenous and isotropic conditions :

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} + L_R \qquad \text{8-1}$$

where C is solute concentration, t is time, D_z is hydrodynamic dispersion, z is distance, v_z is linear seepage velocity, and L_R is the chemical reaction or leaching term.

The boundary and initial conditions are assumed to be :

Initial Conditions :	$t = 0$	$C(z,0) = C_0$	8-2a
Boundary Conditions :	$z = 0$	$C(0,t) = g(t)$	8-2b
	$z = H$	$\frac{\partial C}{\partial z} = 0$	8-2c

where g (t) is the concentration of the influent water, H is the height of the ash, and C_0 is the initial concentration of a solute within the pore fluid of the ash.

By deriving an expression for L_R, it is possible to use equations 8-1 and 8-2 to model ash leaching behaviour under saturated, steady state conditions. This would be applicable to the ash pond at Loy Yang, where the high water level ensures the ash is saturated throughout the year. For ash disposal sites that are unsaturated (or effectively low moisture environments), such as the field cells and overburden disposal sites, this approach is not valid and requires the use of unsaturated flow theory and transient conditions. The saturated equations will be applied to the column leaching experiments of Black (1990a) and those presented in Chapter 6.

8.1.1 Reaction Term for Ash Leaching

The applicability of the ADE to modelling the observed behaviour of ash leaching is accomplished through the use of the reaction term, L_R. Straub & Lynch (1982) proposed that the leaching rate for a particular solute is proportional to the ratio of current soluble mass S (per unit volume) to the initial soluble mass S_0 (per unit volume) in the ash and a concentration deficit from a maximum value (C_{max}) to the current concentration (C) in aqueous solution. Mathematically this becomes :

$$L_R = \alpha \left(\frac{S}{S_0} \right)^{\beta} \left(C_{max} - C \right) \qquad 8\text{-}3$$

where α is a mass transfer coefficient and β is an exponent signifying the effect of decaying chemical mass, both are only applicable to a particular solute species. The mass transfer coefficient α has the units per time (eg. /day) and β is dimensionless.

The value of C_{max} represents the maximum concentration of a solute species in ash leachate or pore waters (the concentration at geochemical saturation for a particular mineral, for example). At a particular instant, the concentration deficit (C_{max} - C) provides the driving force for leaching by dissolution and surface phenomena. When this deficit is zero, it can be assumed that the system is in equilibrium. The model is considered to entail matrix dissolution of solutes from the surface to the aqueous phase under reducing chemical mass. The initial washoff is modelled by defining C_0 in the aqueous solution as equal to C_{max}. It is interesting to note that if β is assumed to be unity and $C_{max} - C \approx C_{max}$, the leaching rate given by 8-3 signifies a situation where the soluble mass decays exponentially with time.

The approach by Straub & Lynch (1982), primarily developed for modelling municipal landfills, has been used successfully by several workers to model leaching processes in hazardous waste landfills as well as ash disposal sites (eg. Demetracopoulos *et al.*, 1986; Lu & Bai, 1991; Lu, 1996; Gau & Chow, 1998; Huang *et al.*, 1998), and thus it is adopted for the theoretical modelling in this thesis.

8.1.2 Application to Column Leaching Experiments

Black (1990a) undertook several column leaching tests on various sources ash from the Hazelwood power station complex (see Section 2.2.4, Table 2.3 and Figure 2.5). The work included samples of both precipitator (unleached) ash and (leached) ash pond sediment, providing an opportunity to assess the effect of different ash quality on the α and β values needed for 8-3. The laboratory columns presented in Chapter 6 were also modelled, using a steady state velocity representative of the majority of time the respective column was in operation. In all columns, it was assumed that there is no permeability change over time due to pozzolanic activity (since Latrobe Valley ashes are not known to be strong pozzolans). This will be discussed further in the model results.

The columns by Black (1990a) were considered appropriate for modelling due to the constant flow nature for the duration of the tests and since they are also on ash from the Latrobe Valley. Hence the applicability of the parameters obtained are more relevant to Loy Yang than data on overseas ash or from elsewhere in Australia. The inflow and outflow versus time is not recorded by Black (1990a), only total outflow, and it is not stated whether the columns reached saturation or remained unsaturated. On the basis of total outflow volumes and the constant inflow rate, it will be assumed that the columns were near-saturated and that the velocity was at steady state for the duration of the experiment (164 days). The relevant column data is in Table 8.1. The model was also applied to K, due to a similar leaching curve and controls as Na, SO_4 and Cl.

Table 8.1 - Leaching Column Data for Black (1990a) (mm)

Ash Type	Ash Height	Pore Volume	Porosity	Flow Rate (mm/day)
HPA	161.3	110.7	0.69	16.0
HAPS	192.5	136.6	0.71	15.5

HPA - Hazelwood Precipitator Ash (unleached); HAPS - Hazelwood Ash Pond Sediment (leached).

The model was also applied to the leaching of the laboratory columns presented in Chapter 6. It was noted in Chapter 6 that after the flow was temporarily stopped during the testing, the subsequent leachate concentration increased when the flow was restarted (see Figures 6.9, 6.14 and 6.19). Since the model assumes a constant, steady state velocity, the effect of no flow for a period of time or the increase in leachate concentration at the restart of flow cannot be simulated with the current model. It is expected that if a more suitable transient flow model were to be adopted, the increase in concentration due to leaching and diffusion could be demonstrated and simulated.

8.1.3 Numerical Solution

A block-centred explicit, upward finite difference schemce (Zheng & Bennett, 1995) was used to solve simultaneously equations 8-1 to 8-3 (the same as that used in Section 3.11.3). The detail of this numerical technique is provided in Appendix A1. Given the similarity of the source code for this leaching model to that used for modelling solute transport in the groundwater (Section 3.11), it has not been included in an Appendix. The change in soluble mass incorporating the leaching rate can be expressed in difference form as :

$$S_{k+1} = S_k - (L_R)_k \Delta t \, n \qquad 8\text{-}4$$

where k is the time step number (iteration) and n is the porosity.

The problem of numerical dispersion will be controlled through maintaining a high spatial and temporal discretisation (see Appendix A1). The value adopted for hydrodynamic dispersion (D_z) was approximated from the general range of values given in Fetter (1993), and was calculated as :

$$D_z = \lambda \, v_z + D^* \qquad 8\text{-}5$$

where λ is longitudinal dispersivity, and D^* is the effective molecular diffusion coefficient for the porous medium and solute of concern.

8.1.4 Model Input Parameters

Based on Fetter (1993), λ is taken as H/10. However, since the flow system in the columns were dominated by advection, the value of λ was decreased to H/20. Assuming a coefficient of molecular diffusion of D^* of 4.32 x 10^{-5} m^2/day (Fetter, 1993), 8-5 gives D_z of 1.72 x 10^{-4} and 1.97 x 10^{-4} m^2/day for HPA and HAPS respectively. Numerical simulations have indicated that the value of λ chosen in this range does not significantly influence leachate concentration curves. It is not possible to use experimental data to examine the influence of this parameter in further detail since only a few data points during the initial washoff phase are available. The relevant input values are in Table 8.2.

Table 8.2 - Model Input Parameters (mg/L) : (a) Hazelwood Data (Black, 1990a)
(b) Column Leaching Tests (Chapter 6)

(a)	Hazelwood Precipitator Ash		Hazelwood Ash Pond Sediment	
Species	C_{max}	S_0	C_{max}	S_0
SO_4	94,315	125,063	31,690	86,679
Cl	28,636	3,790	740	1,032[1]
Na	76,570	49,273	27,440	17,464
K	7,494	4,737	2,709	2,382

(b)	Large Column		Medium Column		Small Column	
Species	C_{max}	S_0	C_{max}	S_0	C_{max}	S_0
SO_4	28,000	3,252	14,000	2,159	21,000	2,145
Cl	1,800	252	900	175	1,300	215
Na	9,500	5,303	6,400	4,794	8,900	4,598
K	320	451	250	441	380	374

Notes : [1] - The original value was below the detection limit (<0.1%), hence a minimum value of 0.13% was assumed to avoid a negative soluble mass in the computations.

The maximum concentration C_{max} was assumed to be the first available leachate concentration from the experiments. Since it is assumed that the pore waters of the ash became geochemically saturated with respect to the major soluble minerals prior to leaching, the initial concentration C_0 was approximated to be equal to C_{max}. The mass transfer coefficient α was determined by fitting the numerical results to the experimental data.

The value of α principally controls the residual concentration values after initial washoff and has a relatively low influence on the initial drop in concentration. The residual concentration is that when the leachate concentration is relatively steady and is the tail end of a leaching curve. The effect of β was also examined, and it was found that β does not have a significant impact primarily because the leaching is dominated by initial washoff and advective removal of solutes. Hence, the value of unity was adopted for β. In these numerical simulations, the goodness of fit was determined by visual inspection.

8.1.5 Model Results

The results of the leaching modelling are presented in Table 8.3 and Figures 8.2 through 8.6. In general, given the assumptions used, the model gives a reasonable estimate of the leaching behaviour of the various ash materials used and leaching conditions. Essentially, the major process being modelled is the advective leaching and removal of the majority of the soluble mass from the ash, or initial washoff.

Table 8.3 - Model Results for α and Residual Leachate Concentration (mg/L)

	Hazelwood Precipitator Ash			Hazelwood Ash Pond Sediment		
Species	α (day^{-1})	Model	Column	α (day^{-1})	Model	Column
SO_4	0.0018	1,100	1,034	0.0021	650	645
Cl	0.000005	<1	<1	0.00008	<1	<1
Na	0.001	330	358	0.0008	13.8	160
K	0.0014	44	40	0.001	17	31

	Large Leached Ash Column			Medium Leached Ash Column		
Species	α (day^{-1})	Model	Column$^{\#}$	α (day^{-1})	Model	Column$^{\#}$
SO_4	0.003	221	139	0.0125	343	345
Cl	0.0003	2.2	2.8	0.00055	1.0	1.0
Na	0.005	194	99	0.025	309	280
K	0.014	18	15	0.06	28	29

	Small Leached Ash Column		
Species	α (day^{-1})	Model	Column$^{\#}$
SO_4	0.005	95	73
Cl	0.002	2.5	2.5
Na	0.01	84	71
K	0.004	14	12

Note : $^{\#}$ - average of final leachate concentrations.

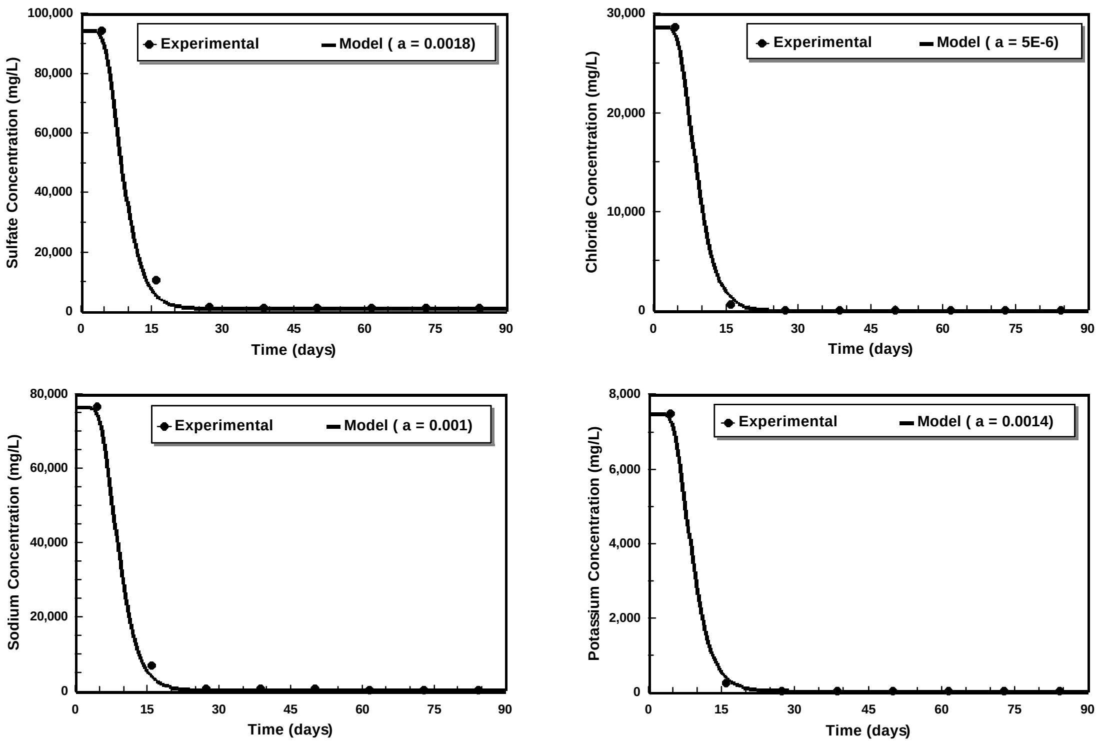


Figure 8.2 - Leaching Model Fit to Hazelwood Precipitator Ash Column (α day^{-1})

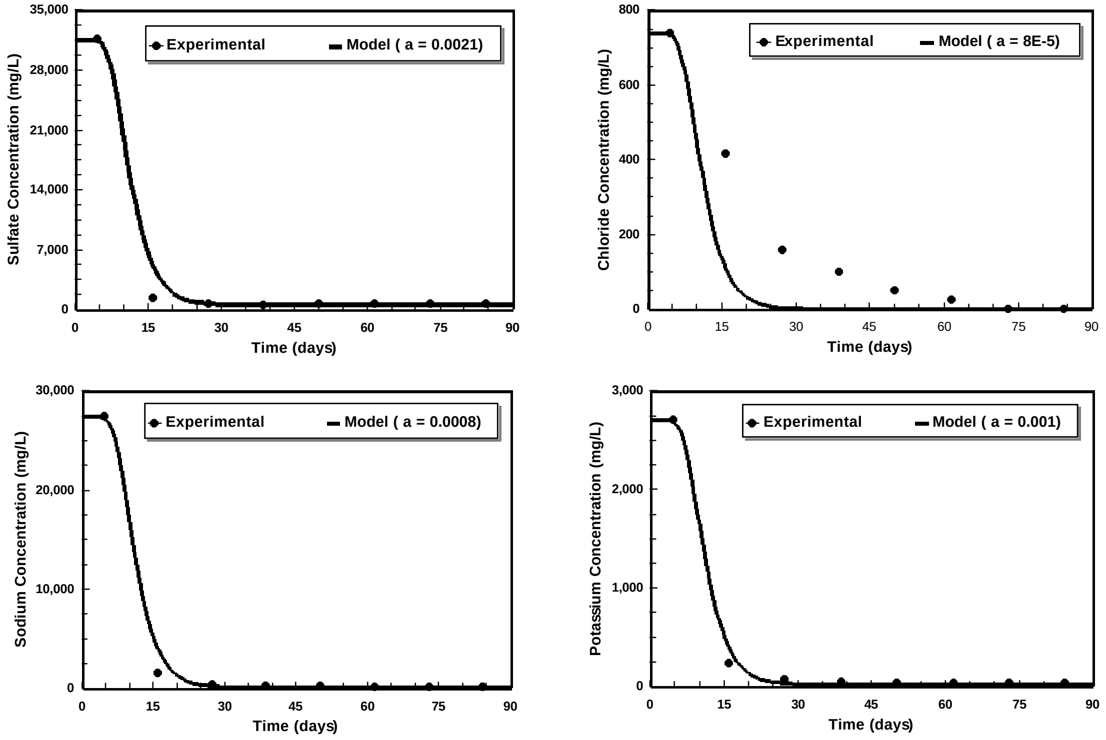


Figure 8.3 - Leaching Model Fit to Hazelwood Ash Pond Sediment Column (α day^{-1})

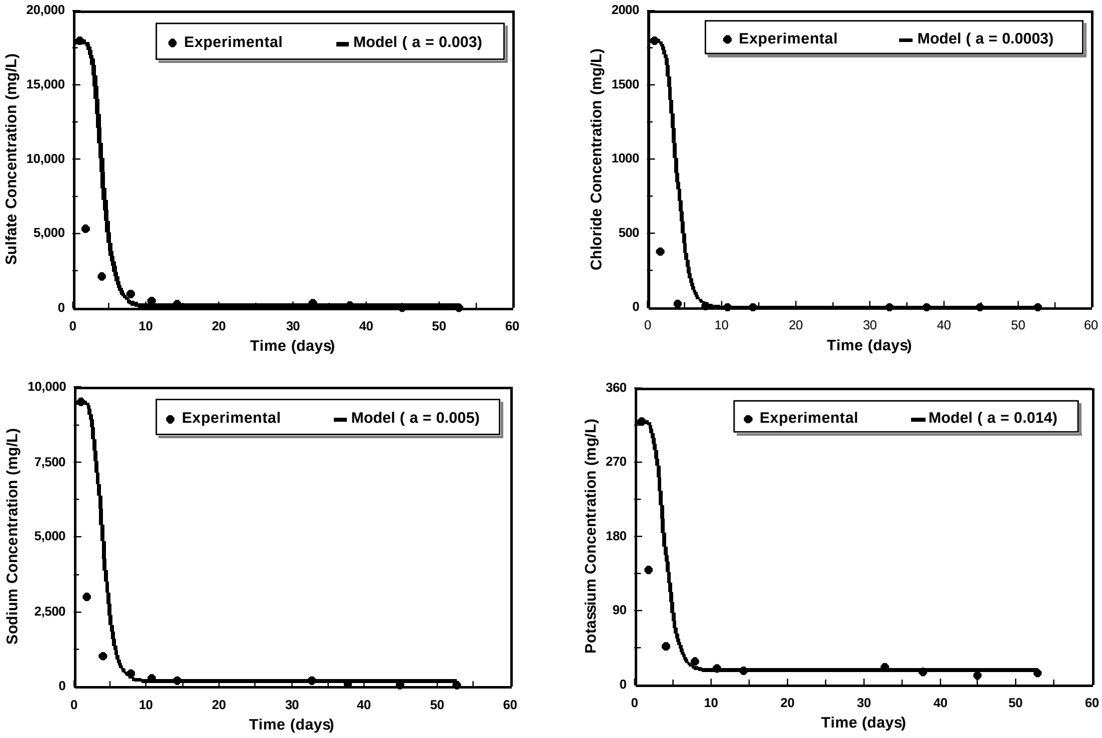


Figure 8.4 - Leaching Model Fit to Large Leached Ash Column (α day^{-1})

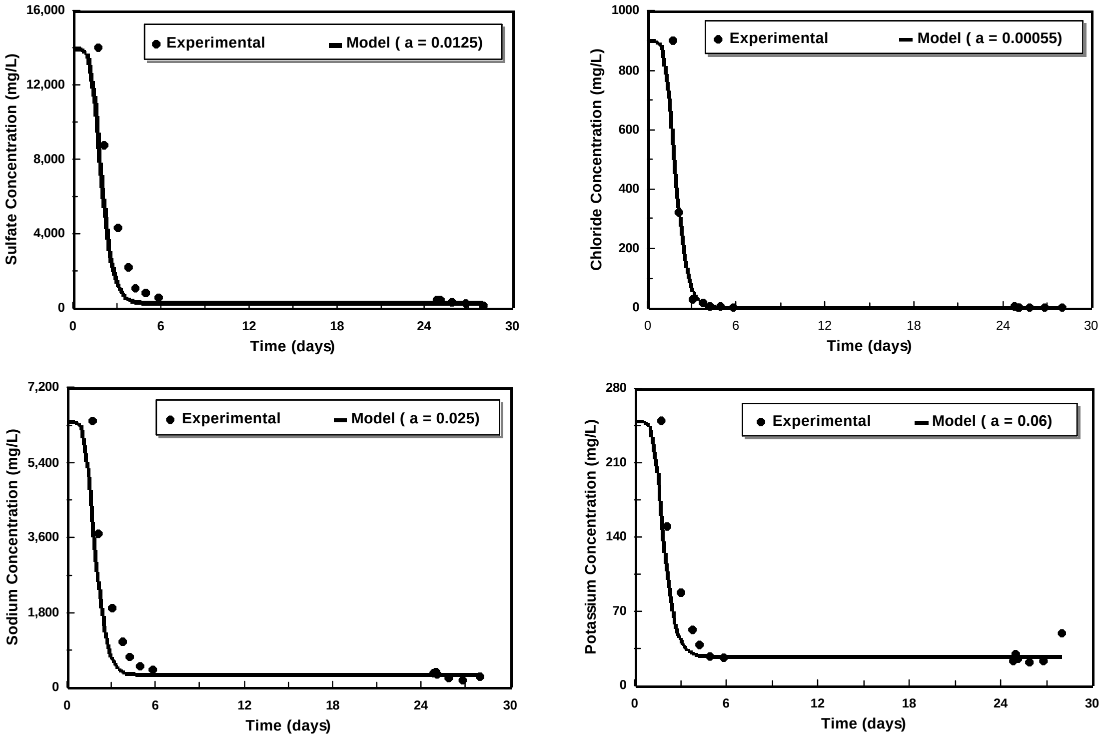


Figure 8.5 - Leaching Model Fit to Medium Leached Ash Column (α day^{-1})

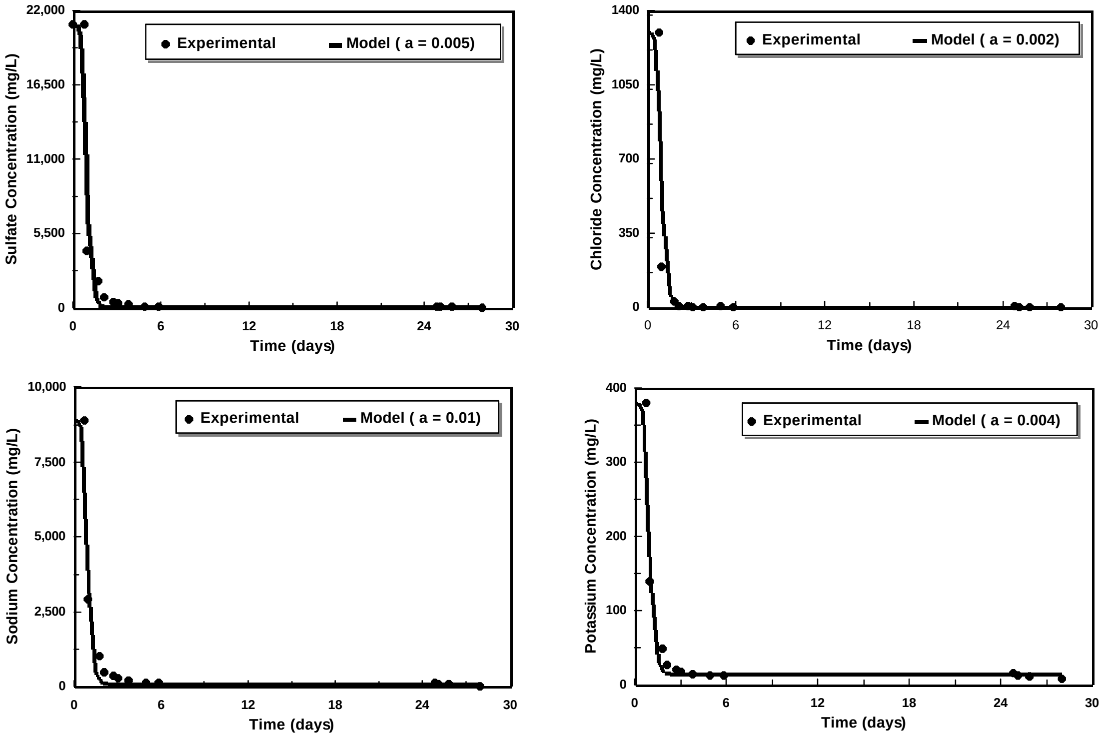


Figure 8.6 - Leaching Model Fit to Small Leached Ash Column (α day^{-1})

For the laboratory columns, however, the steady state model does not and cannot take into account the period of no flow within the columns, since it assumes constant flow throughout the period of operation. The initial leachate after a poeriod of now flow is marginally higher in concentration, expected to be due to diffusive processes within ash grains leading to gradual release of solutes into pore waters (see Figure 2.7). A transient solute transport and leaching model is expected to be able to account for this change in velocity and small increase in leachate concentration. For instance, if it is assumed in equations 8-1 and 8-3 that $v_z = 0$ and D_z is very small (ie. negligible), then $\delta C/\delta t = L_R$, which gives an increase in leachate concentration in the static ash pore water with time.

The values for α are generally different for each ash (Hazelwood or Loy Yang), with some differences due to column size or scale apparent, although not consistent. For example, the α value for Cl ranged from 0.000005 to 0.002 day^{-1}, compared with the α value for SO_4 ranging from 0.0018 to 0.0125 day^{-1}. Therefore, the α value appears to be specific to the leaching curve from a specific column test and experimental conditions.

The design and modelling of ash disposal sites in the field, however, is invariably different to the conditions used in a column experiment. In assessing and modelling the impact of ash disposal, it would be necessary to assign a value for α based on an understanding of the differences in scale and conditions. This would require either the operation of field trials at the intended site, taking into account the unsaturated behaviour of the disposal site, or an alternative approach based on theoretical scaling of column leaching test data to allow assessment of leaching phenomena irrespective of scale. The use of unsaturated flow is now reviewed, followed by an analysis of scale effects and leaching curves.

8.2 Ash Leaching and Solute Transport in Unsaturated Porous Media

The field cells highlighted the need to consider the flow of water within an ash disposal site as an unsaturated system, and therefore flow modelling and solute transport should, ideally, account for this behaviour. An attempt was made to develop and extend the saturated flow ash leaching model to unsaturated conditions, however, this proved beyond the scope of this thesis. A brief review of this work is presented here for completeness. It is recommended that this be a priority for further research.

8.2.1 Background Theory

For unsaturated porous media, the flow of moisture is still governed by Darcy's Law, however, the hydraulic conductivity will vary with the volumetric water content (θ). Due principally to capillary action within the pore structure of a soil, an unsaturated soil develops increasing matric suction (Ψ) as the water content decreases (Fredlund & Rahardjo, 1993). The relationship between θ and Ψ is called the Soil Water Characteristic Curve (SWCC) and was determined experimentally for Loy Yang leached ash in Chapter 6 (Section 6.9). The change in stress state in turn alters the hydraulic regime and further affects flow.

This behaviour is formally known as Richard's Equation and, for one-dimensional flow in which the z-axis is taken as positive in a downward direction (with depth), can be represented as (Fetter, 1993) :

$$\frac{\partial\theta}{\partial t}=\frac{\partial}{\partial z}\left(K(\psi)\frac{\partial\psi}{\partial z}\right)-\frac{\partial}{\partial z}\left(K(\psi)\right) \qquad \text{8-6}$$

where θ - volumetric water content (θ_s - saturated soil), Ψ - matric suction, and $K(\Psi)$ - hydraulic conductivity for a given Ψ (or θ, based on the SWCC). The last term on the right can be ignored if the matric suction gradient is much greater than gravity gradient (Fetter, 1993), leaving Darcy's Law.

There are varying formulations of the unsaturated flow equation, and some are based on water flow in response to a volumetric water content gradient (eg. Philip & de Vries, 1957). This is fundamentally incorrect, however, since water flows in response to hydraulic gradients, which is particularly important for heterogeneous systems (Wilson *et al.*, 1994). The Richard's Equation assumes no effect of evaporation and vapour flow within a soil on moisture behaviour, and also that flow is under steady state conditions and the soil is isotropic.

The advection-dispersion equation for solute transport, can be extended to unsaturated flow, and is generally written as (Fetter, 1993; Knox *et al.*, 1993) :

$$\frac{\partial(\theta C)}{\partial t}=\frac{\partial}{\partial z}\left(D_S\theta\frac{\partial C}{\partial z}-qC\right) \qquad \text{8-7a}$$

and $q = \upsilon\theta$ 8-7b

where D_S - hydrodynamic dispersion coefficient for unsaturated soil (which is in turn a function of both θ and υ), υ - unsaturated linear flow (seepage) velocity, and q - volumetric water flux.

The Richard's Equation and the unsaturated form of the ADE are coupled through the volumetric water flux, q, creating a system of equations to describe moisture and solute movement over time. There are several numerical models which solve the unsaturated flow equations, as well as a select few also coupling solute transport to the flow model (eg. SWIM; Ross, 1990). However, the field cells suggested that evaporative processes play a strong role in controlling the unsaturated behaviour of an ash disposal site, and therefore the model adopted needed to account for processes such as evaporation and vapour phase flow. After examing the various models that were available, it was decided that the SoilCover model, developed by Wilson and the Unsaturated Soils Group at the University of Saskatchewan in Canada, was the most appropriate for modelling coupled unsaturated-evaporative controlled behaviour. The SoilCover program does not include solute transport and it was planned to develop this capability as part of the final work for this thesis. A review of the approach to unsaturated soil behaviour taken in the SoilCover model will now be presented.

8.2.2 Overview of the SoilCover Unsaturated Flow and Soil Evaporation Model

The SoilCover model was originally developed by Wilson (1990) and has since been expanded and further refined by Joshi (1993), Tratch (1994), Wilson *et al.* (1994), Newman (1995 & 1996) and GeoAnalysis 2000 (1997). The fundamental basis for the approach used by SoilCover is to couple unsaturated flow with vapour and heat flow and atmospheric conditions to calculate the evaporative flux from a soil surface. The model was developed primarily to provide a rationale to assess the performance of covers for mine sites with acid mine drainage problems, hence the name 'SoilCover'. The model can also be used for assessing or predicting cover systems at landfill or other waste containment sites. The derivation of this approach will only be summarised here, but is available in the various references listed above (most notably Wilson, 1990).

The flow of moisture within an unsaturated soil can be described by 8-6 (ie. Darcy's Law). The flow of water vapour in an unsaturated soil is described using Fick's Law (Wilson *et al.*, 1994). Coupling these equations together results in a transient equation for the one-dimensional flow of liquid water and water vapour (Wilson *et al.*, 1994) :

$$\frac{\partial ?_w}{\partial t} = C_w \frac{\partial}{\partial y}\left(K_w \frac{\partial ?_w}{\partial y}\right) + C_v \frac{\partial}{\partial y}\left(D_v \frac{\partial P_v}{\partial y}\right) \qquad \text{8-8a}$$

and $C_w = \frac{1}{\rho_w \, g \, m_2^w}$ and $C_v = \frac{1}{(\rho_w)^2 \, g \, m_2^w}\left(\frac{P + P_v}{P}\right)$ 8-8b

where Ψ_w - matric suction at given water content,

C_w - modulus of volume change with respect to the liquid phase,

K_w - hydraulic conductivity at given water content,

C_v - modulus of volume change with respect to the vapour phase,

D_v - diffusion coefficient of water through the soil,

P_v - partial pressure in soil due to water vapour, g - gravity,

P - total atmospheric pressure, ρ_w - density of water,

$(P + P_v) / P$ - correction factor for vapour diffusion,

m_2^w - slope of the saturation line in the soil water characteristic curve.

The two principal variables in 8-8 are Ψ_w and P_v, and these are not independent and can be linked through (Wilson *et al.*, 1994) :

$$P_v = P_{vs} h_r \qquad \text{and } h_r = e^{(\psi_T g W_v / RT)} \qquad \text{8-9}$$

where Ψ_T - total potential in the water phase, W_v - molecular weight of water,

R - universal gas constant, T - temperature (in Kelvins).

The calculation of vapour pressure in 8-9 depends on the saturation vapour pressure and the temperature of the soil, and hence temperature needs to be incorporated through (Wilson *et al.*, 1994) :

$$C_h \frac{\partial T}{\partial t} = \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial t}\right) - L_v \left(\frac{P + P_v}{P}\right)\frac{\partial}{\partial y}\left(D_v \frac{\partial P_v}{\partial y}\right) \qquad \text{8-10}$$

where C_h - volumetric specific heat, λ - thermal conductivity,

L_v - latent heat of vapourisation for water.

By solving 8-8, 8-9 and 8-10 simultaneously, coupled unsaturated flow, heat flow and vapour flux can be modelled. The evaporative flux from a soil surface can then be calculated from a modification of the Penman method (Wilson, 1990) :

$$E = \frac{\Gamma Q_n + \eta E_a}{\Gamma + \eta A} \qquad \text{8-11}$$

where E - evaporative flux from soil surface, Q_n - net solar radiation,

Γ - slope of the saturation vapour pressure versus temperature curve at the mean air temperature, η - psyhcrometric constant,

A - inverse of the relative humidity at the soil surface,

E_a - function of wind speed, water vapour pressure above the soil surface and the inverse of the relative humidity in the air.

The SoilCover model uses a Galerkin finite element technique to simultaneously solve these equations (Joshi, 1993).

8.2.3 Coupling SoilCover and Solute Transport

The approach used to couple SoilCover with a solute transport and ash leaching model was through the Darcy velocity calculated by SoilCover. The approach of using seepage analysis to determine flow velocities and then using them in solute transport equations in an uncoupled way is common and has been used by several commercially available programs (eg. SEEP/W and CTRAN/W; Geo-Slope International, 1991). The solutes of concern in the ash will only be transported within the liquid phase, and since SoilCover already calculates the pore water velocity, this could then be used directly in the solute transport equation (8-7). A modified version of the SoilCover executable was obtained, courtesy of the Unsaturated Soils Group at the University of Saskatchewan, which created an additional output file of the calculated Darcy velocities and volumetric water contents. A new numerical model was then developed, based on the approach to ash leaching used for saturated porous media presented in Sections 8.2 to 8.4 and making use of the unsaturated form of the governing equations.

It is worth noting that the modelling presented by Straub & Lynch (1982), Demetracopoulos *et al.* (1986), Lu & Bai (1991), Lu (1996), Gau & Chow (1998) and Huang *et al.* (1998), all used unsaturated flow equations in their modelling of landfill, hazardous waste or ash disposal sites, uncoupled with solute transport using the approach described above. For the field cells, the strong unsaturated-evaporative behaviour requires this level of detailed flow modelling, however, the laboratory columns, which took approximately 1 to 2 days to reach apparent steady state flow conditions, can be assumed to be near-saturated and at steady velocity and hydraulic conductivities. The use of unsaturated flow equations for the columns is only considered necessary for this initial wetting phase of 1 to 2 days.

The new unsaturated solute transport model, however, proved numerically unstable and after a period of effort, it was decided that the problem appeared beyond the scope and time duration available for this thesis. It is recommended that development of a coupled flow-solute transport model be the subject of further active research.

8.3 Comparison of Leaching Curves and Scale Effects

The combination of field and laboratory studies in one thesis is perhaps rare, and provides the opportunity to examine scale effects on leaching curves and behaviour. The field studies were conducted at depths of 3 m while the laboratory columns included depths of 0.3, 0.75 and 1.5 m. In Chapter 2, it was highlighted that the most common method for reporting and comparing leaching curves from column experiments was through the use of pore volumes (PV). The use of normalised concentrations, or the concentration of a solute in the leachate relative to its initial concentration (C/C_0), is also common and has been used in this thesis.

The combined leaching curves for the normalised concentrations of Na, SO_4, Cl, K and B versus Pore Volumes are presented in Figure 8.7, including the available data from Hazelwood Ash Pond in Black (1990a). These curves show a large "initial washoff" of solutes, primarily due to dissolution of the more soluble mineral phases within the ash (eg. gypsum and halite). In contrast, B for example, shows some variability. Similar curves could also be established for TDS and some trace elements (eg. As, Mo, Se), although complex geochemical controls on trace elements precludes further analysis.

An important observation of the respective laboratory leaching curves for Na, SO_4 and Cl are that they appear to be identical. This behaviour is also observed for landfills (Brunner, 1979; Straub & Lynch, 1982). The field leaching curves (the Wet Cell) are within the same general trend, although they do appear to leach at a slightly slower rate than the laboratory columns. These curves suggest that the non-dimensionalised leaching curve, C/C_0 versus PV, is a unique property for a given ash and therefore may be utilised in theoretical solute transport modelling in order to properly take into account the scale effects of testing. The C versus t curves for each column are different (see Figure 8.1). The scale-up of laboratory results to a field situation is an important aspect in the mining industry for assessing and predicting acid mine drainage problems[1]. The shapes for each solute are also different, with Cl showing the sharpest gradient, SO_4 slightly more curved and Na being the slowest to leach of these solutes.

---

[1] - Workshop notes, *4^TH Australian Acid Mine Drainage Workshop*, Townsville, QLD, March 2000.

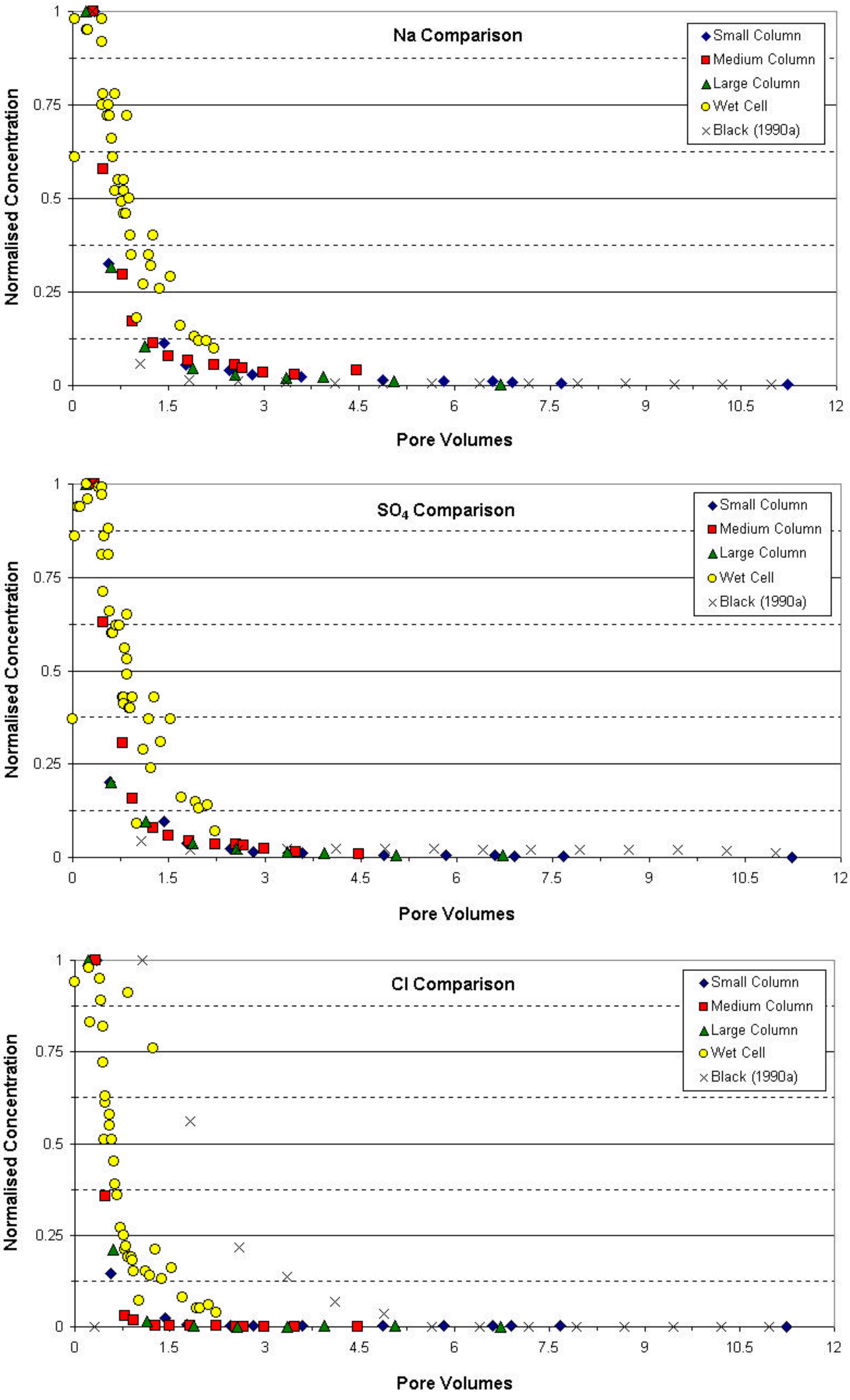


Figure 8.7 - Combined Leaching Curves : Na, SO_4 and Cl vs Pore Volumes

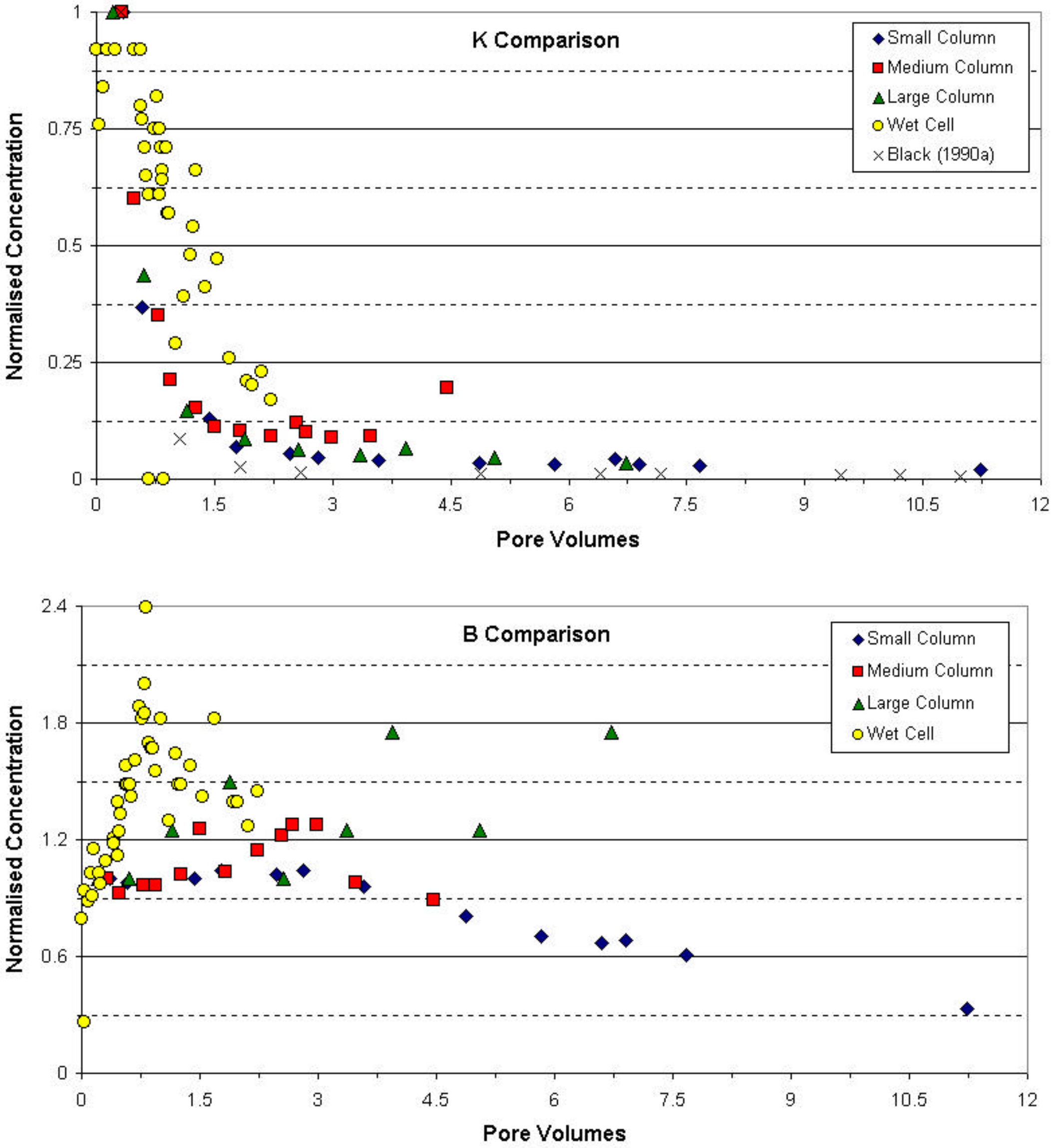


Figure 8.7 (cont'd) - Combined Leaching Curves : K and B vs Pore Volumes

Further to this, solute transport modelling is generally a deterministic process, using real variables (such as C, t) which are spatially and/or temporally continuous (eg. Sections 3.5.6 and 3.11). If C/C_0 versus t is plotted, the leaching curves for the respective columns are different, related to the increased time it takes for influent to flow through and leach a thicker ash profile. This is shown in Figure 8.1, with examples from the Wet Cell and laboratory columns (although the time scales for the field and laboratory work are not strictly comparable).

For the Wet Cell, it is clear that the curves of C/C_0 versus t and PV are somewhat different to each other (see Figure 8.1). The laboratory columns demonstrate that the leaching curves of TDS versus t are different for each column (see Figure 8.1), with varying gradients for the slope during initial washoff. The Small column leaches the most rapidly, with the Medium column appearing intermediate and the Large column the slowest to leach. The difference between the leaching rates of the Medium and Large columns does not seem significant, although the few data points makes this difficult to interpret accurately.

In order to capture and model these processes, a theoretical leaching and solute transport model will now be developed. This model will be applied to the laboratory leaching data of Black (1990a) and the results from this thesis demonstrated in Figure 8.1.

8.4 Non-Dimensional Modelling of Ash Leaching

8.4.1 Derivation of the Non-Dimensional Leaching Equations

The use of non-dimensionalised variables in solute transport has been presented by Fetter (1993), and is based on the use of redefining the main variables in an equation to become unitless or non-dimensionalised. This approach can be closely examined by non-dimensionalising the governing equations by defining the following variables :

$$C^* = \frac{C}{C_0} \qquad \& \qquad z^* = \frac{z}{H} \qquad \& \qquad t^* = \frac{t}{t_{PV}} = \frac{v_z t}{H} \tag{8-12}$$

where C^*, z^* and t^* - normalised concentration, distance and time, respectively,
t_{PV} - time per pore volume, since the time for one pore volume is H/v_z,
H - height of ash deposit, v_z - time-averaged linear seepage velocity.

This makes C^* versus t^* analogous to the normalised leaching curve and hence applicable to modelling the laboratory columns and field trials.

By substituting these new variables into the advection-dispersion-leaching equation, 8-1, it is possible to derive the non-dimensionalised form of this equation :

$$\left(\frac{C_0}{H/v_z}\right)\frac{\partial(C/C_0)}{\partial(t/t_{PV})} = D_z\left(\frac{C_0}{H^2}\right)\frac{\partial^2(C/C_0)}{\partial(z/H)^2} - v_z\left(\frac{C_0}{H}\right)\frac{\partial(C/C_0)}{\partial(z/H)} + L_R$$

to $$\left(\frac{C_0 v_z}{H}\right)\frac{\partial C^*}{\partial t^*} = \left(\frac{D_z C_0}{H^2}\right)\frac{\partial^2 C^*}{\partial(z^*)^2} - \left(\frac{C_0 v_z}{H}\right)\frac{\partial C^*}{\partial z^*} + L_R$$

giving $$\frac{\partial C^*}{\partial t^*} = \frac{1}{P_e}\frac{\partial^2 C^*}{\partial(z^*)^2} - \frac{\partial C^*}{\partial z^*} + L_R^* \qquad \text{with} \qquad P_e = \frac{v_z H}{D_z} \qquad \text{8-13a}$$

where $$L_R^* = \left(\frac{H}{C_0 v_z}\right)L_R = \alpha^*(S^*)^\beta(1 - C^*) \qquad \text{and} \qquad \alpha^* = \alpha\frac{H}{v_z} \qquad \text{8-13b}$$

S^* - normalised soluble mass, P_e - Peclet number (see App. A1)

This now gives an equation to calculate non-dimensional leaching parameters, that is, α^*. The calculated results for α^* from the five columns from earlier modelling in Section 8.1 are compiled in Table 8.4.

Table 8.4 - Estimated α^* Values for the Leaching Models of Laboratory Columns

	Large	Medium	Small	HAPS	HPA
SO_4	0.0130	0.0265	0.0046	0.0573	0.0491
Cl	0.0013	0.0012	0.0018	0.0022	0.0001
Na	0.0217	0.0530	0.0091	0.0218	0.0273
K	0.0609	0.1272	0.0036	0.0273	0.0382

Black (1990a) : HPA - Hazelwood Precipitator Ash; HAPS - Hazelwood Ash Pond Sediment.

In general, the estimated α* values are all of similar magnitude and show less variation than α values. For example, the α* values for SO_4 range from 0.0046 to 0.0573, with an average of about 0.030. The α* value of 0.0046 for the Small Column is somewhat lower than all other values. The α* values for Cl are also very similar, ranging from 0.00014 to 0.0022 with an average of about 0.0013. The HPA α* value is abot one order of magnitude lower at 0.00014. The α* values for Na also display similar values and range, while in comparison, α* values for K show large variation in all columns. The ranges and average values of both α and α* are compared in Table 8.5. Importantly, the α* values for both Hazelwood precipitator and leached ash remain within the ranges for Loy Yang leached ash.

Table 8.5 - Comparison of Averages and Ranges for α and α*

	α		α	α	α*		α	α*
	Min.		Max.	Average	Min.		Max.	Average
SO_4	0.0018	-	0.0125	0.0049	0.0046	-	0.0573	0.030
Cl	0.000005	-	0.002	0.00059	0.00014	-	0.0022	0.0013
Na	0.0008	-	0.025	0.0084	0.0091	-	0.0530	0.027
K	0.001	-	0.06	0.016	0.0036	-	0.1272	0.051

The variability in the α* values is significantly lower than that for the dimensionally based α values. The reasons for the variability in α* could include differences in ash, especially between leached ash pond sediments (Loy Yang versus Hazelwood) and precipitator ash (Hazelwood), experimental design and operating conditions, and the subjective choice of α in the solute transport modelling.

On the basis of the similarity in α* values, therefore, it appears reasonable that the non-dimensional approach to ash leaching and solute transport presents a rational basis for assessing ash disposal at various scales, smoothing out the variability due to experimental and site conditions and ash type. To verify these parameters for modelling, however, still requires the use of column tests. As noted in Chapter 2, these are time consuming and expensive, which is why batch test methodologies are generally preferred. A novel approach of extending the non-dimensional approach to batch tests and scale-up from batch tests to columns to the field scale to is now presented.

8.4.2 Use of the Non-Dimensional Leaching Curve for Scale-Up Predictions

An idealised representation of a leaching curve is presented in Figure 8.8, in the non-dimensionalised units of C/C_0 and PV. On the basis of this idealised curve, it is possible to derive some mathematical expressions for the volume leached and the cumulative mass leached by integrating the area under the curve.

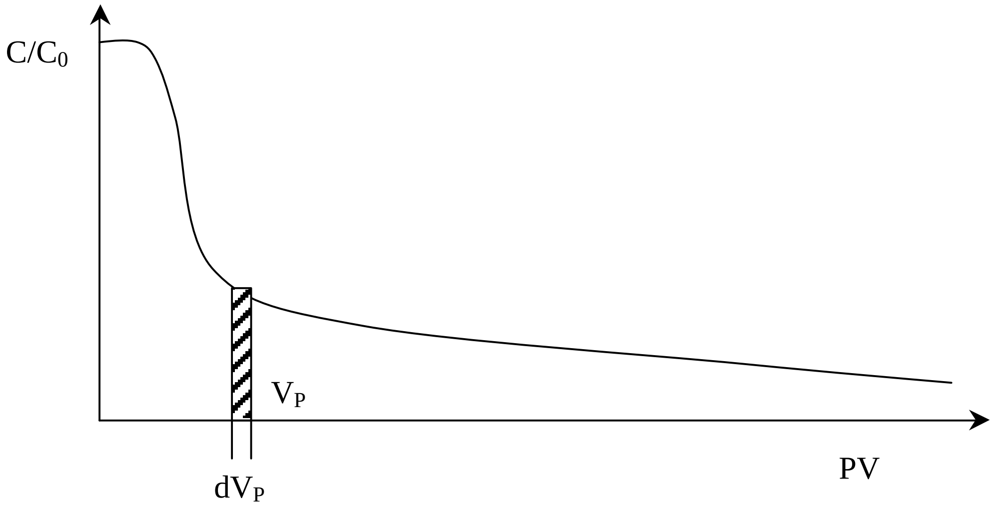


Figure 8.8 - Idealised Leaching Curve

where dV_P - difference in pore volumes, V_P - Point of Pore Volume.

$$\text{Volume Leached} = dV_P\ (nV) \tag{8-14}$$

$$\text{Mass Leached} = \delta M_L = C_0 \left(\frac{C}{C_0}\right) dV_P\ (nV) \tag{8-15}$$

where M_L - mass leached.

The Cumulative Mass Leached is the integral of the area under the leaching curve :

$$\text{Cumulative Mass Leached} \quad = \int \delta M_L = \int_0^{V_P} C_0 \left(\frac{C}{C_0} \right) (nV)\, dV_P \qquad \text{8-16a}$$

$$\text{giving} \qquad M_L = C_0 nV \int_0^{V_P} \left(\frac{C}{C_0} \right) dV_P \qquad \text{(mg)} \quad \text{8-16b}$$

Alternatively, the volume can be expressed in terms of dry density (ρ_D) and the contained mass of ash (M_S) :

$$\rho_D = M_S/V \qquad \text{or} \qquad V = M_S/\rho_D \qquad \text{8-17}$$

$$\text{and so} \qquad M_L = C_0 \left(n \frac{M_S}{\rho_D} \right) \int_0^{V_P} \left(\frac{C}{C_0} \right) dV_P \qquad \text{8-18}$$

$$\text{re-arranging gives} \qquad \frac{M_L}{M_S} = C_0 \left(\frac{n}{\rho_D} \right) \int_0^{V_P} \left(\frac{C}{C_0} \right) dV_P \qquad \text{(mg/kg)} \quad \text{8-19}$$

$$\text{further re-arranging gives} \qquad \frac{M_L}{M_S} = \int_0^{V_P^*} (C*)\, dV_P^* \qquad \text{(mg/kg)} \qquad \text{8-20a}$$

$$\text{where} \quad dV_P^* = \frac{C_0 n}{\rho_D} dV_P \qquad \text{8-20b}$$

These equations mathematically formalise the methodology to calculate mass leached, which has been used empirically in Chapters 5 and 6. The equation for Cumulative Mass Leached (M_L), derived from the non-dimensional leaching curve, has units of concentration (eg. mg/kg). Straub & Lynch (1982), assuming steady state behaviour, used an exponential function to describe the rapid decline in concentration (initial washoff). Given the results from a column test, however, the calculations can be undertaken more accurately since the curve for C* vs PV is known, thereby providing a way to calculate C_0 from batch test results.

It is possible to adapt 8-19 (or 8-20) for use with sequential batch tests. In essence, a sequential batch test allows the contact of large quantities of water (or leaching solution) to contact a waste, allowing similar points to be established on the leaching curve since these high liquid-to-solid ratios can be equated to pore volumes used for column tests through an assumed density. For example, the batch tests presented in Chapter 4 used 100 g in 2 litres, which is about 16 PV per test (using a ρ_D of 600 kg/m^3 and a porosity of 75%) and much higher than all column tests. For solutes which are predominantly leached through mineral dissolution independent of time, 8-19 can be further adapted :

$$\text{Mass Leached (Batch Tests}^{\,B}) = \frac{M_L^B}{M_S^B} = \sum_{i=1}^{k} \frac{C_i^B\ V_i^B}{M_{S,i}^B} \qquad 8\text{-}21$$

where k - total number of sequential batch tests, i - batch test number.

The sum in 8-21 can be equated to the area under the idealised leaching curve established experimentally by a column test. The sequential batch tests using deionised water, presented in Chapter 4, will be used to establish the leaching curve since this test best represents the leaching solutions in the various column tests and the field trials. Only the first extraction is considered, since this contributes to the initial leaching and therefore C_0. The calculated areas under the leaching curves and the estimated values for C_0 are compiled in Table 8.6.

Table 8.6 - Estimates of C_0 Based on Batch Test Leachability Results

	Batch Leachability	Area Under Leaching Curve - C* vs PV			
	$(M_L/M_S)^B$ (mg/kg)	Small	Medium	Large	Wet Cell
SO_4	4,000	0.704	0.764	0.706	1.071
Cl	841	0.576	0.505	0.518	0.821
Na	4,600	0.853	0.823	0.722	1.040
K	307	1.073	1.068	0.993	1.207

C_0 (mg/L)	Small		Medium		Large		Wet Cell	
	Calc.	Actual	Calc.	Actual	Calc.	Actual	Calc.	Actual
SO_4	4,719	21,000	4,563	14,000	4,428	18,000	2,610	6,780
Cl	1,214	1,300	1,450	900	1,269	1,800	715	671
Na	4,478	8,900	4,867	6,400	4,976	9,500	3,091	3,467
K	238	380	250	250	242	320	178	119

The various estimated C_0 values are generally comparable and of similar magnitude for the columns and Wet Cell, except for SO_4. Importantly, the C_0 values for the three different size columns are very similar and appear to adequately account for the scale-up of each column. The above approach could help to improve the applicability of batch tests through designing tests with lower liquid-to-solid ratios, that is, low water contact or pore volumes, which are more akin to column tests and field conditions. The process of using batch and column tests to scale-up predictions of field therefore appears promising.

8.5 Discussion and Application to Field Disposal Sites

This chapter has developed a methodology for modelling the solute transport arising from the leaching and disposal of ash. By incorporating a leaching term into the advection-dispersion term for solute transport in groundwater (or saturated porous media), it has been shown that the results of column tests can be modelled on a specific basis. That is, the parameters obtained were specific for each experimental design, solute and material source. In order to eliminate these scale effects, a new approach was developed using non-dimensionalised parameters. This approach, based on the identical leaching curves for a particular solute from all tests, was able to show that the non-dimensionalised parameters for leaching are similar. This thereby avoids the use of specific scale effects from a column and allows prediction of field scale behaviour based on limited laboratory data. A further advantage of this approach is the ability to use the total mass leached from batch tests to predict the initial concentration, C_0, for a particular ash (or waste material).

For the field situation, it must be highlighted that the laboratory columns and the Wet Cell were operated under artificially high moisture conditions to accelerate the leaching to a high number of pore volumes. The Dry Cell, which is the most realistic representation of current and future ash disposal sites at Loy Yang, did not reach a significant degree of pore volumes and, according to the curves and methodology presented, would remain at C_0 for some time until after about 0.5 pore volumes. It is interesting to note that the area under the Wet Cell leaching curves (see Table 8.6) is generally slightly higher than for the columns. Given the longer time over which the field trials were operated (about 400 days), the higher area could be expected to be due to a more significant proportion of diffusive leaching fluxes within the ash due to the low flow regime in the field (except at irrigation times).

In summary, the methodology presented in this chapter provides a rational basis for assessing the potential impacts from ash disposal by quantifying the leaching fluxes over time. This allows appropriate engineering design to be implemented for the ash disposal sites and efficient groundwater and environmental monitoring regimes to be established. The methodology is, however, an approximate and conceptual approach and needs to be validated with more rigourous analysis and monitoring. To continue to improve this approach, it is recommended that the development and extension of the solute transport model and leaching parameters to incorporate unsaturated flow be undertaken.

Chapter 9

Summary and Recommendations for Further Research

The work presented in this thesis and the key research findings are summarised. Areas considered important for further research are then recommended.

9.1 Summary of Solute Transport from Ash Disposal

The central aim of this thesis has been to investigate the controls on the transport of solutes from ash disposal. This thesis has presented the results from extensive field, laboratory and modelling studies of solute transport and leaching arising from the disposal of coal ash at the Loy Yang power station complex in the Latrobe Valley. Overall, the thesis represents a substantive case study and analysis of ash management and disposal. The main findings of this research can be summarised as follows :

- The major minerals contained in ash contains a significant proportion of soluble minerals, such as gypsum, halite and thenardite. Their dissolution is rapid and leads to a sodium-sulfate-chloride type leachate chemistry. The impurities in the coal, as supplied to the power stations, tends to control the amount of calcium, silica, iron and aluminium found in the ash, which generally has minor effects on leachate chemistry (although high calcium can significantly increase pH).

- The solubility of most trace elements in ash leachate appears limited by the alkaline conditions maintained in the ash pond (or disposal) environment. The elements which have been detected in leachate include arsenic, boron, barium, molybdenum, selenium and strontium. These elements are not being detected in groundwater monitoring to date, and hence the environmental risk appears low, although strontium, selenium and molybdenum can be of concern. The geochemical controls on trace elements in leachate appear complex and include adsorption and co-precipitation.

- The leaching of the ash begins from the mixing of precipitator (and bottom) ash with water inside the power station and during slurrying and disposal in the ash pond. After some months, the ash in the pond is effectively leached and can be considered as a more benign and less hazardous solid waste than unleached precipitator ash.

- There is seepage emanating from Loy Yang Ash Pond which is affecting the Shallow Aquifer Systems within the Haunted Hill Formation. The major seepage pathways appear confined to downgradient zones to the west and north. The groundwater in these regions is monitored regularly. The chemistry of the seepage is of a sodium-sulfate-chloride type, and has a salinity marginally higher than the typical range for HHF groundwaters, which is of a sodium-chloride type chemistry.

- Analytical and geochemical studies of the western seepage pathway have highlighted attenuation mechanisms acting to decrease the impact of the seepage on the shallow groundwater at Loy Yang. This is through the action of specialised sulfate-reducing bacteria (SRB), which convert the sulfate to insoluble sulfides coupled with the oxidation of organic matter contained within the aquifer sediments, thereby removing the majority of the salinity (ie. sulfate). Preliminary indications of the presence and activity of SRB were found from groundwater samples, as well as suitable geochemical conditions to facilitate the attenuation.

- The geochemical process of sulfate reduction is kinetic or rate-dependent and was modelled using a kinetic reaction term in a one-dimensional solute transport model for the western seepage pathway. The groundwater flow and solute transport parameters were first calibrated against chloride transport, which is conservative, using both a constant and variable concentration source from the ash pond seepage. The variable source (ie. increasing over time) gave reasonable results when fitted to sulfate monitoring data.

- Long term (14 month) and large scale, controlled field studies were undertaken on leached ash excavated from the ash pond. Two identical cells lined with HDPE were operated, one with active irrigation and the second open only to rainfall. Together, they highlighted that disposal of ash outside the pond needs to be considered as an unsaturated flow system. The high porosity and fine grained nature of the ash gives it a strong ability to retain moisture without downward flow (gravity drainage). The evaporative (climatic) conditions in the Latrobe Valley can exhibit a strong influence on the unsaturated behaviour of ash disposal sites. The use of clay covers and a prepared clay base for ash disposal sites, combined with the properties of the ash to retain and evaporate moisture, should lead to minimal leachate generation and possible seepage impacts.

- The field trials also highlighted the low overall leachability of excavated or leached ash. The leachate was moderately saline initially, but declined rapidly with further irrigation (or rainfall). The long term impacts on groundwater, should seepage from ash disposal sites in the Loy Yang Overburden Dump impact on shallow groundwaters, is therefore expected to be minimal and well within the attenuation capacity of the aquifers.

- A series of different scale laboratory columns were operated, and further demonstrated the unsaturated behaviour of the ash. The use of Time Domain Reflectometry for electronically monitoring the volumetric moisture content of the ash inside the columns was less than ideal in terms of accuracy, although they were able to document the relative changes over time. The Soil Water Characteristic Curve was also measured for the ash up to 290 kPa, and demonstrated the moisture retention capacity. The Air Entry Value was estimated to be about 40 kPa.

- A one-dimensional solute transport model was developed for application to the column tests, as these were considered as steady state systems that could be more readily modelled with conservative assumptions. The model, which takes into account the advective-dominated nature of leaching, gave good agreement to the column results. The model could not be used to assess the situation in the columns when the velocity was zero, although the leachate results showed a small increase in salinity, most likely due to diffusive processes within the ash grains.

- An analysis of the different scales at which ash leaching tests were undertaken showed that, on a normalised basis, the leaching curves for respective solutes was nearly identical for each test, including the laboratory and field tests. On this basis, it is expected that a mathematical model can be developed to account for the scale effects in relating laboratory results to large field disposal sites.

In large part, this thesis has concentrated on determining the qualitative processes which control solute transport arising from ash disposal at the Loy Yang complex in the Latrobe Valley. The heterogeneity of such large systems required an overall and simplified approach to be developed to allow the assessment of the current ash pond and future ash disposal sites. The one-dimensional model of solute transport and ash leaching, on the basis of the conservative assumptions used and the qualitative processes identified, appears to be a reasonable methodology for assessing the potential impacts of large scale ash disposal. Thus this thesis should be a significant contribution to the continued success of power generation from low rank brown coal in the Latrobe Valley via an improved understanding and engineering of ash disposal sites.

9.2 Recommendations for Further Research

To further validate and quantify ash disposal, the following key areas are considered suitable for further research :

- Detailed study of the bacterial and geochemical controls on the process of sulfate reduction, with a view to quantifying the assumptions used for the reactivity of organic matter and long term reaction rates. With the slow increases in sulfate and salinity occurring at the ash pond, better quantification of the controlling geochemical rates and parameters will allow a longer term model to be developed, which can more realistically be extrapolated beyond the existing monitoring data to 50 years into the future for site closure.

- Study of the geochemical speciation and behaviour of barium, molybdenum, selenium and strontium in ash leachate. This would allow controls to be established for these species and solute transport modelling to be applied, thereby improving the assessment of environmental risk from disposal sites, especially with regards to potential for groundwater impacts.

- Study of the unsaturated behaviour of leached ash. The effect of self-weight consolidation and potential overburden stresses should be assessed.

- Given the moisture retention properties of leached ash and its alkaline nature, leached ash may be suitable as cover materials for potential acid generating materials, such as some parts of Overburden Dump at Loy Yang. This project is considered a priority.

- The effect of acidic solutions entering ash disposal sites is considered an important aspect to be investigated. If, as a potential scenario, acidic solutions were to percolate from the Overburden Dump through the clay cover into an ash disposal site, over time this may lead to mobilisation of more heavy metals than presented in this thesis due to removal of alkalinity in the ash. This project is also considered a priority.

- Development of a solute transport and leaching model coupled to an unsaturated flow model, such as SoilCover, is strongly recommended. This would provide a more realistic engineering design or assessment tool for disposal sites, providing more confidence in the cover systems or potential rates of leachate generation.

- Extension of the mathematics controlling scale effects for solute transport and leaching is warranted. This would involve non-dimensionalising the governing equations for unsaturated flow to allow scale independent values for leaching parameters to be determined for more realistic field disposal site conditions.

Chapter 10

References

Ahmed, I. & Lovell, C. W., 1992, *Use of Waste Products in Highway Construction*. Proc. "Environmental Geotechnology", Ed's Usmen & Acar, Pub. Balkema, Rotterdam, pp 409-418.

Ainsworth, C. C. & Rai, D., 1987, *Chemical Characterization of Fossil Fuel Wastes*. Electric Power Research Institute, EPRI EA-5321, Palo Alto, CA.

Aitken, R. L., Campbell, D. J. & Bell, L. C., 1984, *Properties of Australian Fly Ashes Relevant to Their Agronomic Utilisation*. Australian Journal of Soil Research, 22, pp 443-453.

Aitken, R. L. & Bell, L. C., 1985, *Plant Uptake and Phytotoxicity of Boron in Australian Fly Ashes*. Plant and Soil, 84, pp 245-257.

Allison, J. D., Brown, D. S. & Novo-Gradac, K. J., 1991, *MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems : Version 3.0 Users Manual*, U.S. Environmental Protection Agency, Environmental Research Laboratory, Athens, GA, March 1991, 106 p.

Andrews, C. B. & Anderson, M. P., 1978, *Impact of a Power Plant on the Ground-Water System of a Wetland*. Ground Water, 16 (2), pp 105-111.

ANZECC, 1992, *Australian Water Quality Guidelines For Fresh and Marine Waters*. National Water Quality Management Strategy, ANZECC (Australian and New Zealand Environment and Conservation Council), November 1992.

ANZECC & ARMCANZ, 1999, *Draft Australian and New Zealand Guidelines For Fresh and Marine Water Quality*. National Water Quality Management Strategy, Australian and New Zealand Environment and Conservation Council (ANZECC) & Agriculture and Resource Management Council of Australia and New Zealand (ARMCANZ), July 1999.

APHA, 1992, *Standard Methods for the Examination of Water and Wastewater*. 18^{TH} Edition. American Public Health Association (APHA), American Water Works Association & Water Pollution Control Federation, Washington DC, USA.

Appelo, C. A. J. & Postma, D., 1994, *Geochemistry, Groundwater and Pollution*. A A Balkema, Rotterdam, 552 p.

ASTM, 1994, *1994 Annual Book of ASTM Standards*, Section 11 - Water and Environmental Technology, Volume 11.04 Pesticides, Resource Recovery, Hazardous Substances and Oil Spill Responses, Waste Management, Biological Effects, American Society for the Testing of Materials.

Bagchi, A., 1990, *Design, Construction, and Monitoring of Sanitary Landfill*. John Wiley & Sons, Wisconsin, USA, 284 p.

Bahour, M. P., McLaren, R. J., Niece, J. E. & Pederson, H. C., 1981, *Coal Ash Disposal Manual - 2^ND^ Edition*. Electric Power Research Institute (EPRI), CS-2049, Palo Alto, California, USA.

Bajjali, W., Clark, I. D. & Fritz, P., 1997, *The Artesian Thermal Groundwaters of Northern Jordan : Insights Into Their Recharge History and Age*. Journal of Hydrology, 192, pp 355-382.

Barone, F. S., 1990, *Determination of Diffusion and Adsorption Coefficients for Some Contaminants in Clayey Soil and Rock; Laboratory Determination and Field Evaluation*. PhD Thesis, University of Western Ontario, Canada, 325 p.

Barton, C. M, Bolger, P. F., Holdgate, G. R., Thompson, B. R. & Reid, M. A., 1992, *Monograph Paper : The Brown Coal Geology of the Gippsland Basin*. Proc. "Energy, Economics and Environment - Gipplsand Basin Symposium", Australasian Institute of Mining and Metallurgy, Publication 3/92, Ed. C. M. Barton (Chair) and others, Melbourne, Victoria, June 1992, pp. i-xviii.

Balsamo, N., 1998, *Beneficial Use Coal Combustion Products*. World Coal, March 1998, pp 50-55.

Barton, C. M. (Chair) and others (Ed.'s), 1992, *Energy, Economics and Environment - Gipplsand Basin Symposium*. Proc., Australasian Institute of Mining and Metallurgy, Publication 3/92, Melbourne, Victoria, June 1992, 324 p.

Bear, J., 1972, *Dynamics of Fluids in Porous Media*. American Elsevier, USA.

Bedient, P. B., Rifai, H. S. & Newell, C. J., 1994, *Ground water Contamination - Transport and Remediation*. PTR Prentice Hall, USA, 556 p.

Beretka, J. & Brown, T., 1976, *Properties and Pozzolanic Behaviour of Australian Fly Ash*. Journal of the Australian Ceramics Society, 12 (1), pp 13-19.

Beretka, J. & Brown, T., 1977, *The Utilisation of Fly Ash in Building*. Journal of the Australian Ceramics Society, 13 (2).

Berner, R. A., 1964, *An Idealized Model of Dissolved Sulfate Distribution in Recent Sediments*. Geochimica et Cosmochimica Acta, 28, pp 1497-1503.

Berner, R. A., 1971, *Principles of Chemical Sedimentology*. McGraw Hill, USA.

Berner, R. A., 1980, *Early Diagenesis - A Theoretical Approach*. Princeton University Press, USA.

Berner, R. A., 1981, *Authigenic Mineral Formation Resulting From Organic Matter Decomposition in Modern Sediments*. Fortschritte der Mineralogie, 59 (1), pp 117-135.

Berner, R. A., 1982, *Burial of Organic Carbon and Pyrite Sulfur in the Modern Ocean : Its Geochemical and Environmental Significance*. American Journal of Science, 282, pp 451-473.

Berner, R. A. & Westrich, J. T., 1985, *Bioturbation and The Early Diagenesis of Carbon and Sulfur*. American Journal of Science, 285, pp 193-206.

Black, C. J., 1988, *Determination of the Soluble Fractions of LV Precipitator Ashes by Sequential Batch Leaching*. SECV, Dept. of Chemical Technology, Report CT/88/104, Dec. 20, 1988.

Black, C. J., 1989, *Table 11 - Summary of Phases Identified by X-Ray Diffraction*. SECV, Research and Development Dept., Report LC/89/245.

Black, C. J., 1990a, *Leachability of Morwell Brown Coal Ash*, M App Sci (Env Eng) Thesis, Dept. of Chemical Engineering, University of Melbourne, 131 p.

Black, C. J., 1990b, *Yallourn W Ash Leaching*. SECV, Report SC/90/174, 59 p.

Black, C. J., Brockway, D., Hodges, S. & Milner, A., 1992, *Utilisation of Latrobe Valley Brown Coal Fly-Ash*. Proc. "Energy, Economics and Environment - Gipplsand Basin Symposium", AusIMM, Pub. 3/92, Ed. C. M. Barton (Chair) and others, Melbourne, VIC, June 1992, pp 149-155.

Black, C. J. & Wright, B., 1992, *Comparison of Latrobe Valley Ash Pond Sediments*. HRL Technology Pty Ltd, Report CO/91/473.

Blight, G. E., 2000, *Solar Energy and Evapotranspiration : A Control of the Unsaturation State*. Proc. "Unsaturated Soils for Asia", Ed's H. Rahardjo, D. G. Toll & E. C. Leong, Singapore, May. 18-19, 2000, A A Balkema, pp 33-40.

Bolger, P. F., 1984, *Lithofacies Assemblages and Boundary Relationships of the Tertiary Latrobe Valley Group and Overlying Strata in the Latrobe Valley, Victoria*. M Sc Thesis, Dept. of Earth Sciences, Monash University, Melbourne, Australia, December 1984, 216 p.

Bone, K. M. & Schaap, H. A., 1980, *Solubility of Minor and Trace Elements in Brown Coal Ash : A Preliminary Study*. SECV, Report SO/80/4. Feb. 1980, 27 p.

Bone, K. M. & Schaap, H. A., 1981, *Trace Elements in Latrobe Valley Brown Coal : Environmental and Geochemical Implications*. SECV, Report SO/80/15, April 1981, 43 p.

Boudreau, B. P. & Ruddick, B. R., 1991, *On A Reactive Continuum Representation of Organic Matter Diagenesis*. American Journal of Science, 291, pp 507-538.

Boudreau, B. P. & Westrich, J. T., 1984, *The Dependence of Bacterial Sulfate Reduction on Sulfate Concentration in Marine Sediments*. Geochimica et Cosmochimica Acta, 48, pp 2503-2516.

Bouwer, H., 1996, *New Developments in Groundwater Recharge and Soil Aquifer Treatment of Wastewater for Reuse*. Proc. "Water Reuse '96", San Diego, CA, USA, Feb. 25-28, 1996.

Bradley, J., 1998, *Personal Communication*. Hydrogeologist, Geo-Eng Australia Pty Ltd, Morwell, VIC.

Brannon, J. M. & Myers, T. E., 1994, *Leachate Testing and Evaluation for Freshwater Sediments*. Proc. "Dredging '94 - 2ND International Conference on Dredging and Dredged Material Placement", Ed. E. C. McNair (Jr), USA, pp 737-746.

Brown, J., Ray, N. J. & Ball,, 1976, *The Disposal of Pulverised Fuel Ash in Water Supply Catchment Areas*. Water Research, 10, pp 1115-1121.

Brown, J. & Ray, N. J., 1983, *The Handling and Disposal of Coal Ash in the CEGB in Relation to the Aqueous Environment*. Water Science & Technology, 15, pp 11-24.

Brumley, J. C., Barton, C. M., Holdgate, G. R. & Reid, M. A., 1981, *Regional Groundwater Investigation of the Latrobe Valley 1976 - 1981*. State Electricity Commission of Victoria (SECV) and Victorian Department of Minerals & Energy (DME), Dec. 1981, 84 p.

Brunner, D. R., 1979, *Forecasting Production of Landfill Leachate*. Proc. "5TH Annual Research Symposium on Municipal Solid Waste : Land Disposal", EPA-600/9-79-023a, USA.

Brusseau, M. A., 1992, *Factors Influencing the Transport and Fate of Contaminants in the Subsurface*. Journal of Hazardous Materials, 32, pp 137-143.

Canfield, D. E. & Des Marais, D., 1991, *Aerobic Sulfate Reduction in Microbial Mats*. Science, 251, pp 1471-1473.

Carroll, B., 1996, *A Review of Selenium and Heavy Metal Contamination of Lake Macquarie, New South Wales, Due to Power Generation and Lead-Zinc Smelting*. Literature Review, Occasional Paper No. 7, Australian Minerals and Energy Environment Foundation, Melbourne, VIC, 39 p. (www.ameef.com.au)

Cashion, J. D. & Brown, L. J., 1996, *Ash Phases in Australian Brown Coals*. Proc. "7TH Australian Coal Science Conference", Australian Institute of Energy - Gippsland Group, Ed. P. T. Waring, Churchill, VIC, December 2-4, 1996, pp 373-379.

Chander, D. V. Ravi, Venkobachar, C. & Raymahashay, B. C., 1994, *Retention of Fly Ash-Derived Copper in Sediments of the Pandu River Near Kanpur, India*. Environmental Geology, 24, pp 133-139.

Chao, T. T., Harward, M. E. & Fang, S. C., 1962, *Soil Constituents and Properties in the Adsorption of Sulfate Ions*. Soil Science, 94, pp 276-283.

Chapelle, F. H., 1993, *Ground-water Microbiology and Geochemistry*. John Wiley & Sons, New York, USA.

Chapelle, F. H. & Lovley, D. R., 1992, *Competitive Exclusion of Sulfate Reduction by Fe(III)-Reducing Bacteria : A Mechanism for Producing Discrete Zones of High-Iron Ground Water*. Ground Water, 30 (1), pp 29-36.

Charbeneau, R. J. & Weaver, J. W., 1992, *Modeling Contaminant Transport Through Subsurface Systems*. Journal of Hazardous Materials, 32, pp 293-311.

Cherkauer, D. S., 1980, *The Effect of Flyash Disposal on a Shallow Ground-Water System*. Ground Water, 18 (6), pp 544-550.

Chichester, D. L. & Landsberger, S., 1996, *Determination of the Leaching Dynamics of Metals From Municipal Solid Waste Incinerator Fly Ash Using a Column Test*. Journal of the Air & Waste Management Association, 46, pp 643-649.

Combs, G. F. (Jr) & Combs, S. B., 1986, *The Role of Selenium in Nutrition*. Academic Press, Orlando, USA.

Côté, P., Bridle, T. R. & Benedek, A., 1986, *An Approach for Evaluating Long-Term Leachability From Measuremen of Intrinsic Waste Properties*. In "Hazardous and Industrial Solid Waste Testing and Disposal", Vol. 6, Ed's D. Lorenzen and others, American Society for the Testing of Materials, USA, pp 63-78.

Côté, P., 1986, *Contaminant Leaching From Cement-Based Waste Forms Under Acidic Conditions*. PhD Thesis, McMaster University, USA.

Creagh, C., 1992, *Catching Coal Ash*. Ecos, Winter 1992, 72, pp 20-22.

Cypionka, H., Widdel, F. & Pfennig, N., 1985, *Survival of Sulphate Reducing Bacteria After Oxygen Stress and Growth in Sulphate Free Sulphide Gradients*. FEMS Microbiol Ecol., 31, pp 39-45.

Daniels, C. W., Reinsch, G. & McKinley, T., 1993, *Loy Yang B Power Station and Ash Pond Area - Hydrogeological and Geotechnical Study*. Geo-Eng Pty Ltd, Report 1159/4, March 1993, 41 p.

Daniels, C. W., 1994a, *Loy Yang B Power Station and Ash Pond Area - Hydrogeological and Geotechnical Study Update*. Geo-Eng Pty Ltd, Report 1243/6, June 1994, 27 p.

Daniels, C. W., 1994b, *Loy Yang Mine - Aquifer Depressurisation Report 1994*. Geo-Eng Pty Ltd, Report 1204/4.

Davis, J. A., Kent, D. B., Rea, B. A., Maest, A. S. & Garabedian, S. P., 1993, *Influence of Redox Environment and Aqueous Speciation on Metal Transport in Groundwater : Preliminary Results of Trace Injection Studies*. In "Metals in Groundwater", Chapter 8, Ed's H. E. Allen, E. M. Perdue & D. S. Brown, Lewis Publishers, USA, pp 223-273.

Davison, R. D., Natusch, D., Wallace, J. & Evans, C., 1974, *Trace Elements in Flay Ash - Dependence of Concentration on Particle Size*. Environmental Science & Technology, 18 (13), pp 1107-1113.

Deed, R., 1969, *Characteristics of Ash Solutions From Morwell Coal*. SECV, Report MR 195.

Deed, R., 1973, *Brown Coal Ash - It's Formation and Solubility*. SECV, Report 258.

Deed, R., 1981 *Behaviour of Some Latrobe Valley Ashes on Their Internment in Overburden Dumps*. SECV, Research & Development Dept., Report LO/81/139.

Delta-T, 1998, *ThetaProbe Soil Moisture Sensor Type ML2 - User Manual*. Delta-T Devices Ltd, Cambridge, UK, March 1998, 23 p.

Demetracopoulos, A. C., Sehayek, L. & Erdogan, H., 1986, *Modeling Leachate Production From Municipal Landfills*. Journal of Environmental Engineering, ASCE, 112 (5), pp 849-866.

Devol, A. H. & Ahmed, S. I., 1981, *Are High Rates of Sulphate Reduction Associated With Anaerobic Oxidation of Methane ?* Nature, June 1981, 291, pp 407-408.

Dockins, W. A., Olson, G. J., McFeters, G. A. & Turbak, S. C., 1980, *Dissimlatory Bacterial Sulfate Reduction in Montana Groundwaters*. Geomicrobiology Journal, 2 (1), pp 83-98.

Douglas, J. G. & Ferguson, J. A. (Ed's), 1988, *Geology of Victoria*. Geological Society of Australia Inc., Victorian Division, August 1988, pp 453-601.

Drever, J. I., 1997, *The Geochemistry of Natural Waters - Surface and Groundwater Environments*. Prentice Hall, New Jersey, USA.

Drummond, A. R., 1988, *Phase Identification in Small Samples Using X-Ray Diffractometry*. Proc. "Australian X-Ray Analytical Association's 7TH National Schools Conference - New Horizons in Analytical Science", Perth, WA, August 14-19, 1988, 7 p.

Drummond, A. R., 1991, [DETAILS UNKNOWN]. Ref. in McKinley (1995).

Dudas, M. J., 1981, *Long-Term Leachability of Selected Elements From Fly Ash*. Environmental Science & Technology, 15 (7), pp 840-843.

Dusing, D. C., Bishop, P. L. & Keener, T. C., 1992, *Effect of Redox Potential on Leaching From Stablized / Solidified Waste Materials*. Journal of the Air & Waste Management Association, 42 (1), pp 56-61.

Dvorak, D. H., Hedin, R. S., Edenborn, H. M. & McIntyre, P. E., 1992, *Treatment of Metal-Contaminated Water Using Bacterial Sulfate Reduction : Results from Pilot-Scale Reactors*. Biotechnology & Bioengineering, 40, pp 609-616.

Eary, L. E., Rai, D., Mattigod, S. V. & Ainsworth, C. C., 1990, *Geochemical Factors Controlling the Mobilization of Inorganic Constituents From Fossil Fuel Combustion Residues : II. Review of the Minor Elements*. Journal of Environmental Quality, 19, pp 188-201.

Eighmy, T. T., Eusden (Jr.), J. D., Krzanowksi, J. E., Domingo, D. S., Stampeli, D., Martin, J. R. & Erickson, P. M., 1995, *Comprehensive Approach Toward Understanding Element Speciation and Leaching Behaviour in Municipal Solid Waste Incineration Electrostatic Precipitator Ash*. Environmental Science & Technology, 29 (3)**,** pp 629-646.

Elrashidi, M. A., Adriano, D. C., Workman, S. M. & Lindsay, W. L., 1987, *Chemical Equilibrium of Selenium in Soils : A Theoretical Development*. Soil Science, 144 (2), pp 141-152.

Elseewi, J. M., Page, A. L. & Grimm, S. R., 1980, *Chemical Characteristics of Fly Ash Aqueous Systems*. Journal of Environmental Quality, 9, pp 424-428.

EML, 1997a, *Water Analysis for Desulfovibrio*. Report to Gavin Mudd, Dept. of Civil & Building Eng., Victoria University of Technology, by EML Consulting Services Pty Ltd, Report 9707167, Sept. 13, 1997, 3 p.

EML, 1997b, *Water Analysis for Desulfovibrio*. Report to Gavin Mudd, Dept. of Civil & Building Eng., Victoria University of Technology, by EML Consulting Services Pty Ltd, Report 9707216, Sept. 13, 1997, 8 p.

EPAV, 1986, *Elutriation Test Method*. Environment Protection Authority of Victoria (EPAV), Melbourne, VIC.

EPAV, 1993, *Guidelines for the Sampling and Analysis of Contaminated Soils*. Environment Protection Authority of Victoria (EPAV), Melbourne, VIC, 45 p.

EPAV, 1997, *State Environment Protection Policy (Groundwaters of Victoria)*. Environment Protection Authority (Victoria) (EPAV), December, 1997.

EPRI, 1986, *MYGRT : An IBM Personal Computer Code for Simulating Solute Migration in Groundwater - User's Manual*. Electric Power Research Institute (EPRI), EA 4543-CCM, Project 2485-1, Computer Code Manual, Palo Alto, California, USA, May 1986.

EPRI, 1993, *The Fossil Fuel Combustion Waste Leaching Code - Including the GMIN Geochemical Equilbrium Model and the HELP Water Balance Model*. Electric Power Research Institute (EPRI), TR-103343, Project 2485-08, Vol. 1 - User's Guide for the FOWL-GH Code, Vol. 2 - Technical Manual for the FOWL-GH Code, Palo Alto, California, USA, December 1993.

Evett, S. R., 2000, *Some Aspects of Time Domain Reflectometry, Neutron Scattering, and Capacitance Methods for Soil Water Content Measurement*. In "Comparison of Soil Water Measurement Using the Neutron Scattering, Time Domain Reflectometry and Capacitance Methods", TECDOC-1137, IAEA, Vienna, Austria, February 2000, pp 5-49.

Fahey, M., 1997, *Geotechnical Behaviour of Mining Wastes*. Proc. "Geoenvironment '97", Workshop Notes, Editors A Bouazza, J Kodikara & R Parker, Melbourne, VIC, Nov. 26-28, 1997, 125 p.

Fahey, M. & Newson, T. A., 1997, *Aspects of the Geotechnics of Mining Wastes and Tailings Dams*. Proc. "Geoenvironment '97", Editors A Bouazza, J Kodikara & R Parker, Melbourne, VIC, Nov. 26-28, 1997, pp 115-134.

Fang, H-Y., 1997, *Introduction to Environmental Geotechnology*. CRC Press, Boca Raton, USA, 652 p.

Farquhar, G. J., 1989, *Leachate : Production and Characterization*. Canadian Journal of Civil Engineering, 16, pp 317-315.

Felmy, A. R., Rai, D. & Moore, D. A., 1993, *The Solubility of* $(Ba,Sr)SO_4$ *Precipitates : Thermodynamic Equilibrium and Reaction Path Analysis*. Geochimica et Cosmochimica Acta, 57, pp 4345-4363.

Ferguson, J. F. & Gavis, J., 1972, *A Review of the Arsenic Cycle in Natural Waters*. Water Research, 6, pp 1259-1274.

Fetter, C. W., 1993, *Contaminant Hydrogeology*. Macmillan Publishing Company, USA, 458 p.

Fredlund, D. G. & Rahardjo, H., 1993, *Soil Mechanics for Unsaturated Soils*. John Wiley & Sons Inc., New York, USA, 517 p.

Fredlund, D. G. & Xing, A., 1994, *Equations for the Soil-Water Characteristic Curve*. Canadian Geotechnical Journal, 31, pp 521-532.

Fredlund, D. G., Xing, A. & Huang, S., 1994, *Predicting the Permeability Function for Unsaturated Soils Using the Soil-Water Characteristic Curve*. Canadian Geotechnical Journal, 31, pp 533-546.

Freeze, R. A. & Cherry, J. A., 1979, *Groundwater*. Prentice Hall, USA, 620 p.

Fruchter, J. S., Rai, D., Zachara, J. M. & Schmidt, R. L., 1988, *Leachate Chemistry at the Montour Fly Ash Test Cell*. Electric Power Research Institute, EPRI EA-5922, Palo Alto, CA.

Fruchter, J. S., Rai, D., & Zachara, J. M., 1990, *Identification of Solubility-Controlling Solid Phases in a Large Fly Ash Field Lysimeter*. Environmental Science & Technology, 24, pp 1173-1179.

Fuller, C. C., Davis, J. A. & Waychunas, G. A., 1993, *Surface Chemistry of Ferrihydrite - 2, Kinetics of Arsenate Adsorption and Coprecipitation*. Geochimica et Cosmochimca Acta, 57 (10), pp 2271-2282.

Gau, S-H. & Chow, J-D., 1998, *Landfill Leachate Characteristics and Modeling of Municipal Solid Wastes Combined With Incinerated Residuals*. Journal of Hazardous Materials, 58, pp 249-259.

Gelhar, L. W., Mantoglou, A., Welty, C. & Rehfeldt, K. R., 1985, *A Review of Field Scale Physical Solute Transport Processess in Saturated and Unsaturated Media*. Prepared by Tennessee Valley Authority for the Electric Power Research Institute (EPRI), EA-4190 Research Project 2485-5, August 1985, 112p.

Gelhar, L. W., 1986, *Stochastic Subsurface Hydrology From Theory to Applications*. Water Resources Research, 22 (9), pp 135S-145S.

Gelhar, L. W., Welty, C. & Rehfeldt; K. W., 1992, *A Critical Reviwe of Data on Field-Scale Dispersion*. Water Resources Research, 28 (7), pp 1955-1974.

GeoAnalysis 2000 Ltd, 1997, *Users Manual - SoilCover Version 4*. Unsaturated Soils Group, Dept. of Civil Eng., Uni. of Saskatchewan, Canada.

Geo-Eng, 1995, *The Hydrogeology of the Hazelwood Brown Coal Mine*. Unpublished manuscript, 6 p.

Geo-Eng, 1999, *Loy Yang Ash Pond Groundwater Monitoring Annual Report*. Report Prepared for Infrastructure Services Group, Loy Yang Power Ltd, Report No. 1191/7000, April 1999.

Geo-Slope International Ltd, 1991a, *SEEP/W and CTRAN/W User's Manuals*. Calgary, Alberta, Canada.

Gleeson, L. T., 1972, *Economic Review of Australia's Energy Resources*. Proc. "Symposium on The Role of Nuclear Energy in Australia's Development", Sponsored by Australian Academy of Science, Society for Social Responsibility in Science (ACT) & Australian Atomic Energy Commission, Paper 2, Canberra, ACT, June 1-2, 1972, 12 p.

Gloe, C. S. & Holdgate, G. R., 1991, *Geology and Resources*. In "The Science of Victorian Brown Coal - Structure, Properties and Consequences for Utilisation", R A Durie (Ed.), Butterworth-Heineman.

Goetz, L., 1983, *Radiochemical Techniques Applied to Laboratory Studies of Water Leaching of Heavy Metals From Coal Fly Ash*. Water Science & Technology, 15, pp 25-47.

Goldberg, S. & Glaubig, R. A., 1985, *Boron Adsorption on Aluminium and Iron Oxide Minerals*. Soil Science Society of America Journal, 49, pp 1374-1379.

Goldberg, S. & Glaubig, R. A., 1986, *Boron Adsorption on California Soils*. Soil Science Society of America Journal, 50, pp 1173-1176.

Goldberg, S. & Glaubig, R. A., 1988a, *Anion Sorption on a Calcareous, Montmorillonic Soil - Arsenic*. Soil Science Society of America Journal, 52, pp 1297-1300.

Goldberg, S. & Glaubig, R. A., 1988b, *Anion Sorption on a Calcareous, Montmorillonic Soil - Selenium*. Soil Science Society of America Journal, 52, pp 954-958.

Golden, D. M., 1983, *Water Pollution Arising From Solid Waste (Coal, Fly Ash, Slag) Disposal, and Measures to Prevent Water Pollution*. Water Science & Technology, 15, pp 1-10.

Goldhaber, M. B. & Kaplan, I. R., 1974, *The Sulphur Cycle*. In "The Sea", Vol. 5, Marine Chemistry, Ed. E. D. Goldberg, John Wiley & Sons, pp 569-655.

Goldhaber, M. B. & Kaplan, I. R., 1975, *Controls and Consequences of Sulfate Reduction Rates in Recent Marine Sediments*. Soil Science, 119 (1), pp 42-55.

Gray, D. H. & Lin, Y-K., 1972, *Engineering Properties of Compacted Fly Ash*. Journal of Soil Mechanics and Foundations Division, American Society of Civil Engineers, pp 361-382.

de Groote, G. J., Wijkstra, J., Hoede, D. & van der Sloot, H. A., 1989, *Leaching Characteristics of Selected Elements From Coal Fly Ash as a Function of the Acidity of the Contact Solution and the Liquid/Solid Ratio*. In "Environmental Aspects of Stabilization and Solidification of Hazardous and Radioactive Wastes", Ed's P. L. Côté & T. M. Gilliam, ASTM STP 1033, American Society for Testing and Materials, Philadelphia, USA, pp 170-183.

Hammack, R. W. & Edenborn, H. M., 1992, *The Removal of Nickel from Mine Waters Using Bacterial Sulfate Reduction*. Appl. Microbiol. Biotechnol., 37, pp 674-678.

Hansen, L. & Fischer, G., 1980, *Elemental Distribution in Coal Ash Particles*. Environmental Science & Technology, 14 (9), pp 1111-1117.

Hard, B. C. & Babel, W., 1995, *Characterization of a Methanol-Utilizing Sulfate-Reducing Bacterium Isolated from a Wastewater Pond*. J. Basic. Microbiol., 35 (6), pp 385-392.

Hard, B. C., Friedrich, S. & Babel, W., 1997, *Bioremediation of Acid Mine Water Using Facultatively Methylotrophic Metal-Tolerant Sulfate-Reducing Bacteria*. Microbiol Res., 152, pp 65-73.

Hardy, J. A. & Hamilton, W. A., 1981, *The Oxygen Tolerance of Sulphate Reducing Bacteria From North Sea Waters*. Curr. Microbiol., 6, pp 265-292.

Harvey, C., 1993, *Yallourn Power Station - A History 1919 to 1989*. State Electricity Commission of Victoria (SECV), Melbourne, VIC, 460 p.

Hasselriis, F., 1994, *Analysis of Data Obtained from an Historic Ash Residue Leaching Investigation*. Proc. "16TH Biennial National Waste Processing Conference", ASME, USA, pp 107-118.

Havukainen, J. & Viitasalo, I., 1992, *A Case History of Coal Ash Amended Soil*. Proc. "Environmental Geotechnology", Ed's Usmen & Acar, Pub. Balkema, Rotterdam, pp 453-456.

Hem, J. D., 1985, *Study and Interpretation of the Chemical Characteristics of Natural Waters*. 3RD Edition, U.S. Geological Survey, Water Supply Paper 2254.

Hocking, J. B., Gloe, C. S., Threlfall, W. F., Holdgate G. R. & Bolger, P. F., 1988, *Gippsland Basin*. In "Geology of Victoria", Douglas, J G & Ferguson, J A (Ed's). Victorian Division - Geological Society of Australia Inc., August 1988, pp 322-347.

Houston, S. L., 2000, *Geotechnical Aspects of Groundwater Recharge in Arid Regions*. Proc. "Unsaturated Soils for Asia", Ed's H. Rahardjo, D. G. Toll & E. C. Leong, Singapore, May. 18-19, 2000, A A Balkema, pp 69-82.

Huang, C., Lu, C. & Tzeng, J., 1998, *Model of Leaching Behaviour From Fly Ash Landfills With Different Age Refuses*. Journal of Environmental Engineering, ASCE, 124 (8), pp 767-775.

Hudson, M. R., 1990, *Depositional and Deformational Histories of the Loy Yang Open Cut Area*. Honours Thesis, Dept. of Geology, University of Melbourne, Australia, October 1990.

Igarashi, T. & Shimogaki, H., 1996, *Lysimeter Experiment for Sea-Area Land Reclamation Utilizing Coal Ash*. Proc. "Environmental Geotechnics", Ed. Kamon, Pub. Balkema, Rotterdam, pp 67-72.

Jackson, K., Garrell, B. & Bishop, T., 1984, *Comparison of Batch and Column Methods for Assessing Leachability of Hazardous Waste*. Environmental Science & Technology, 18 (9), pp 668-673.

Johnson, C. A., Richner, G. A., Vitvar, T., Schittli, N. & Eberhard, M., 1998, *Hydrological and Geochemical Factors Affecting Leachate Composition in Municipal Solid Waste Incinerator Ash Part I : The Hydrology of the Landfill Lostorf, Switzerland*. Journal of Contaminant Hydrology, 33, pp 361-376.

Jones, D R, Inman, M, Ragusa, S, Shinners, S, McAllister, R & Unger, C, 1996, *The Construction and Performance of Large-Scale Wetlands at the Ranger Uranium Mine*. Proc. "21^{ST} and 3^{RD} International Environmental Workshop", Minerals Council of Australia, Newcastle, NSW, October 14-18, 1996, Vol. 2, pp 116-128.

Jørgensen, B. B., 1977, *The Sulfur Cycle of a Coastal Marine Sediment (Limfjorden, Denmark)*. Limnology and Oceanography, 22 (5), pp 814-832.

Jørgensen, B. B., 1978a, *A Comparison of Methods for the Quantification of Bacterial Sulfate Reduction in Coastal Marine Sediments - III. Estimation From Chemical and Bacteriological Field Data*. Geomicrobiology Journal, 1 (1), pp 49-64.

Jørgensen, B. B., 1978b, *A Comparison of Methods for the Quantification of Bacterial Sulfate Reduction in Coastal Marine Sediments - I. Measurement With Radiotracer Techniques*. Geomicrobiology Journal, 1 (1), pp 11-27.

Jørgensen, B. B., 1978c, *A Comparison of Methods for the Quantification of Bacterial Sulfate Reduction in Coastal Marine Sediments - II. Calculation From Mathematical Models*. Geomicrobiology Journal, 1 (1), pp 29-47.

Jørgensen, B. B., 1983, *The Microbial Sulfur Cycle*. In "Microbial Geochemistry", W. E. Krumbein (Ed), Blackwell Scientific Publications, pp 91-124.

Jørgensen, B. B., Isaksen, M. F. & Jannasch, H. W., 1992, *Bacterial Sulfate Reduction Above 100 ^{0}C in Deep-Sea Hydrothermal Vent Sediments*. Science, 258, pp 1756-1757.

Joshi, B., 1993, *A Finite Element Model for the Coupled Flow of Moisture and Heat in Soils Under Atmospheric Forcing*. M Sc Thesis, Dept. of Civil Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Kacavenda, S., 1994, *Loy Yang Ash Pond - Geotechnical Properties of Ash : Preliminary Investigation*. Geo-Eng Pty Ltd, Report 1231/2, January 25, 1994.

Kacavenda, S. & McKinley, T., 1994, *Loy Yang Ash Pond - Geotechnical and Environmental Aspects of Ash Disposal into the Overburden Dump*. Geo-Eng Pty Ltd, Report 1248/4, June 1994.

Kenley, P. R., 1990, *The Discovery, Exploration and Development of Coal Mining in Victoria*. In "Geological Aspects of the Discovery of Some Important Mineral Deposits in Australia", Ed.'s K. R. Glasson & J. H. Rattigan, Australasian Institute of Mining and Metallurgy (AusIMM), Monograph 17, pp 347-351.

Kent, D. B., Davis, J. A., Anderson, L. C. D. & Rea, B. A., 1995, *Transport of Chromium and Selenium in a Pristine Sand and Gravel Aquifer : Role of Adsorption Processes*. Water Resources Research, 31 (4), pp 1041-1050.

Knox, R. C., Sabatini, D. A. & Canter, L. W., 1993, *Subsurface Transport and Fate Processes*. Lewis Publishers, Boca Raton, USA, 445 p.

Koerner, R. M., 1998, *Designing With Geosynthetics*. 4^{TH} Ed., Prentice Hall, New Jersey, USA, 761 p.

Koerner, R. M. & Daniel, D. E., 1997, *Final Covers for Solid Waste Landfills and Abandoned Dumps*. ASCE Press & Thomas Telford, USA, 267 p.

Konikow, L. F. & Bredehoeft, J. D., 1978, *Computer Model of Two Dimensional Solute Transport and Dispersion in Groundwater*. In "Techniques of Water Resources Investigations", Chapter 2 - Data Processing and Computation, U.S. Geological Survey (USGS), Report TWI 7-C2.

Korfiatis, G. P., Demetracopoulos, A. C., Bourodimos, E. L. & Nawy, G., 1984, *Moisture Transport in a Solid Waste Column*. Journal of Environmental Engineering, ASCE, 110 (4), pp 780-796.

Kosson, D. S., van der Sloot, H. A. & Eighmy, T. T., 1996, *An Approach for Estimation of Contaminant Release During Utilization and Disposal of Municipal Waste Combustion Residues*. Journal of Hazardous Materials, 47, pp 43-75.

Langmuir, D., 1997, *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey, USA, 600 p.

Lahey, 1994, *FORTRAN 77 Version 4 - Users Manual*. Lahey Systems Corporation, USA.

Le Seur Spencer, L. & Drake, D., 1987, *Hydrogeology of Alkaline Fly Ash Landfill in Eastern Iowa*. Ground Water, 25 (5), pp 519-526.

Libicki, J., 1978, *Effects of the Disposal of Coal Waste and Ashes in Open Pits*. U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Office of Research & Development, EPA-600/7-78-067, Cincinatti, Ohio, USA, April 1978, 295 p.

Libicki, J., 1983, *Impact of Coal Refuse Disposal on Groundwater*. U.S. Environmental Protection Agency, Municpal Environmental Research Laboratory, Office of Research & Development, EPA-600/2-83-028, Cincinatti, Ohio, USA, April 1983, 169 p.

Logan, T. J. & Traina, S. J., 1993, *Trace Metals in Agricultural Soils*. In "Metals in Groundwater", Chapter 10, Ed's H. E. Allen, E. M. Perdue & D. S. Brown, Lewis Publishers, USA, pp 309-347.

Lu, C., 1996, *A Model of Leaching Behaviour From MSW Incinerator Residue Landfills*. Waste Management & Research 14, pp 51-70.

Lu, C. & Bai, H., 1991, *Leaching From Solid Waste Landfills Part I : Modeling*. Environmental Technology, 12, pp 545-558.

Machel, H. G., 1989, *Relationships Between Sulphate Reduction and Oxidation of Organic Compounds to Carbonate Diagenesis, Hydrocarbon Accumulations, Salt Domes, and Metal Sulphide Deposits*. Carbonates and Evaporites, 4 (2), pp 137-151.

Macphee, D. E., Black, C. J. & Taylor, A. H., 1994, *Cements Incorporating Brown Coal Fly Ash From the Latrobe Valley Region of Victoria, Australia*. Conference paper, Unknown Date (presumed to be 1994), 10 p.

Maher, M. H., Butziger, J. M. & Chae, Y. S., 1992, *Utilization of Municipal Solid Waste Ash as a Construction Material*. Proc. "Environmental Geotechnology", Ed's Usmen & Acar, Pub. Balkema, Rotterdam, pp 457-465.

Mamane, Y. & Gottlieb, J., 1992, *Utilization of Coal Ash as a Cover Material in a Municipal Refuse Disposal Site*. Proc. "Environmental Geotechnology", Ed's Usmen & Acar, Pub. Balkema, Rotterdam, pp 429-435.

Manahan, S. E., 1991, *Enviroinmental Chemistry*. 5TH Edition, Lewis Publishers, Michigan, USA, 583 p.

Manassero, M., Pasqualina, E. & Sani, D., 1998, *Potassium Sorption Isotherms of a Natural Clayey-Silt for Pollutant Containment*. Proc. "Environmental Geotechnics", Ed. S. E. Pinto, Balkema, Rotterdam.

Mantyvirta, T. J. & Clancy, S., 1989, *Report on Additional Ash Storage Options for Loy Yang Power Station*. State Electricity Commission of Victoria, Geotechnical and Design Division; Report No. GDD 30.

Marcus, D. & Sangrey, D. A., 1981, *Stabilization of Fine Uranium Mill Tailings*. Proc. "Symposium on Uranium Mill Tailings Management", Colorado State University, Fort Collins, Colorado, USA, October 26-27, 1981, pp 489-505.

Matthess, G., 1982, *The Properties of Groundwater*. John Wiley & Sons, USA.

Mattigod, S. V., Rai, D., Eary, L. E. & Ainsworth, C. C., 1990, *Geochemical Factors Controlling the Mobilization of Inorganic Constituents From Fossil Fuel Combustion Residues : I. Review of the Major Elements*. Journal of Environmental Quality, 19, pp 188-201.

McBride, M. B., 1994, *Environmental Chemistry of Soils*. Oxford University Press, New York, USA, 406 p.

McKinley, T., 1992, *Loy Yang Ash Pond Groundwater Quality Monitoring - July 1992*. Geo-Eng Pty Ltd, Report 1050/1, July 1992.

McKinley, T., 1993, *Loy Yang Ash Pond Groundwater Quality Monitoring - July 1993*. Geo-Eng Pty Ltd, Report 1050/3, July 1993.

McKinley, T., 1994a, *Loy Yang Ash Pond Groundwater Quality Monitoring - April 1994*. Geo-Eng Pty Ltd, Report 1050/21, April 1994.

McKinley, T., 1994b, *Loy Ash Pond Groundwater Quality Bore LY2104L*. Geo-Eng Pty Ltd, Report 1050/23, June 1994.

McKinley, T., 1995, *Loy Yang Ash Pond - Leached Ash Quality*. Geo-Eng Pty Ltd. Report 1324/10, August 1995.

McKinley, T., 1997, *Monitoring the Impact of Ash Tailings on Groundwater*. Proc. "Tailings Management Symposium", Sydney, NSW, November 1997, 10 p.

McKinley, T., 1998, *Personal Communication*. Manager - Environment, Geo-Eng Australia Pty Ltd.

McLaughlin, R. & Knight, M. J., 1989, *Corrosion and Incrustation in Bores : A Critical Review*. Centre for Groundwater Management and Hydrogeology, University of New South Wales, Research Publication 1/89, Sydney, NSW, 49 p.

McNab, J. F. & Dunlap, W. J., 1975. *Subsurface Biological Activity in Relation to Ground-Water Pollution*. Ground Water, 13 (1), pp 33-44.

Middelburg, J. J., 1989, *A Simple Rate Model for Organic Matter Decomposition in Marine Sediments*. Geochimica et Cosmochimica Acta, 53, pp 1577-1581.

Miller, C. T. & Weber, W. J. (Jr), 1984. *Modeling Organic Contamination Partitioning in Ground-Water Systems*. Ground Water, 22 (5), pp 584-592.

Milligan, J. D. & Ruane, R. J., 1980, *Effects of Coal Ash Leachate on Groundwater Quality*. Tennessee Valley Authority and U.S. Environmental Protection Agency, EPA-600/7-80-066.

Misra, M., Yang, K. & Mehta, R. K., 1996, *Application of Fly Ash in the Agglomeration of Reactive Mine Tailings*. Journal of Hazardous Materials, 51, pp 181-192.

Morrison, G. M. P., Batley, G. E. & Florence, T. M., 1989, *Metal Speciation and Toxicity*. Chemistry in Britain., 25, pp 791-796.

Morse, J. W., Millero, F. J., Cornwell, J. C. & Rickard, D., 1987, *The Chemistry of the Hydrogen Sulfide and Iron Sulfide Systems in Natural Waters*. Earth-Science Reviews, 24, pp 1-42.

Mulder, H. & Pedler, I. V., 1990, *Report on Loy Yang Ash Pond Modifcations Solute Transport Study*. State Electricity Commission of Victoria; Report GDD 63, October 1990, 118 p.

Murray, J. W., Grundmanis, V. & Smethie, W. M. (Jr), 1978, *Interstitial Water Chemistry in the Sediments of Saanich Inlet*. Geochimica et Cosmochimica Acta, 42, pp 1011-1026.

Nataatmadja, A. & Morgan, P., 1999, *Characterisation of Queensland's Fly Ash*. Proc. "8TH Australia New Zealand Conference on Geomechanics", Hobart, TAS, Vol. 2, pp 769-774.

Newman, G. P., 1995, *Heat and Mass Transfer in Unsaturated Soils During Freezing*. M Sc Thesis, Dept. of Civil Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Newman, G. P., 1996, *SoilCover Versions 2.0 and 3.0*. Unsaturated Soils Group, Dept. of Civil Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Newson, T. A. & Fahey, M., 1998, *Saline Tailings Disposal and Decommissioning*. MERIWA Project No. M241, Joint Report by MERIWA, UWA and ACG, Perth, WA, April 1998.

Noorishad, J., Tsang, C. F., Perrochet, P. & Musy, A., 1992, *A Perspective on the Numerical Solution of Convection-Dominated Transport Problems : A Price to Pay for the Easy Way Out*. Water Resources Research, 28, pp 551-561.

O'Connor, K. M. Poulter, D. A. & Znidarcic, D., 2000, *Tailings Management Using TDR Technology*. Proc. "Tailings & Mine Waste '00", 7TH International Conference, Fort Collins, CO, USA, January 23-26, 2000, pp 451-460.

Ogata, A. & Banks, R. B., 1961, *A Solution of the Differential Equation of Longitudinal Dispersion in Porous Media*. U.S. Geological Survey Professional Paper 411-I.

Parkhurst, D. L., 1995, *User’s Guide to PHREEQC - A Computer Program for Speciation, Reaction-Path, Advective-Transport and Inverse Geochemical Calculations*, U.S. Geological Survey, Water Resources Investigations Report 95-4227, Lakewood, Colorado.

Peaceman, 1977, *Fundamentals of Numerical Reservoir Simulation*. Developments in Petroleum Science, 6, Elsevier Scientific Publishing Company, Amsterdam.

Pedler, I. V. & Raisbeck, D., 1988, *Report on Geotechnical Performance and Safety of Major Dams at Loy Yang*. State Electricity Commission of Victoria (SECV), Geotechnical and Design Division, Design Engineering and Environment Department, Report No. GDD 22.

Pentland, R., 1995, *Personal Communication*. Senior Engineer, Infrastructure Services Group, Loy Yang Power Ltd, Traralgon, VIC.

Pentland, R., 1998, *Personal Communication*. Senior Civil Engineer, Infrastructure Services Group, Loy Yang Power Ltd, Traralgon, VIC.

Peterson, R. C., Schneider, P. & Raisbeck, D., 1982, *Latrobe Valley Ash Properties Investigation*. SECV, Geotechnical Engineering Section, Investigation Division, Report No. ID30, October 1982, 230 p.

Philip, J. R. & de Vries, D. A., 1957, *Moisture Movement in Porous Materials Under Under Temperature Gradients*. Transactions, American Geophysical Union, 38 (2), pp 222-232.

Postgate, J. R., 1984, *The Sulphate-Reducing Bacteria*. 2ND Edition, Cambridge University Press, Great Britain, 208 p.

Raisbeck, D., 1990, *Engineering Properties of Sedimented Ash From Brown Coal*. Proc. "International Symposium on Safety and Rehabilitation of Tailings Dams", ICOLD & ANCOLD, Sydney, NSW, May 23, 1990, pp 125-136.

Rassam, D. W. & Williams, D. J., 1997, *Application of Time Domain Reflectometry to Mine Waste Rehabilitation*. Proc. "GeoEnvironment '97 - Environmental Geotechnics", Eds J Kodikara, M Bouazza & R Parker, Melbourne, VIC, December 1997, pp 433-438.

Reardon, E. J., 1981, *K_d's Can They be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration ?* Ground Water, 19 (3), pp 279-286.

Reinsch, G., Wood, P. & Regan, W., 1982, *Loy Yang Project - Ash Pond Seepage Investigation*. State Electricity Commission of Victoria (SECV), General Engineering and Construction Department, Report No. ID 21.

Richards, F. A., 1965, *Anoxic Basins and Fjords*. In "Chemical Oceanography", Ed's J. P. Riley & G. Skirrow, Academic Press, Vol. 1, pp 611-645.

Ringwood, K., 1995, *Arsenic in the Gold and Base-Metal Mining Industry*. Literature Review, Occasional Paper No. 4, Australian Minerals and Energy Environment Foundation, Melbourne, VIC, 48 p. (www.ameef.com.au)

Ritcey, G. M., 1989, *Tailings Management - Problems and Solutions in the Mining Industry*. Elsevier Science, Netherlands, 970 p.

Rogers, R. B. & Kean, W. F., 1980, *Monitoring Ground-Water Contamination at a Fly Ash Disposal Site Using Surface Electrical Resistivity Methods*. Ground Water, 18 (5), pp 472-478.

Ross, P. J., 1990, *SWIM - Soil Water Infiltration and Movement, Versions 1 & 2*. Division of Soils, Commonwealth Scientific & Industrial Research Organisation (CSIRO), Townsville, QLD. (www.csiro.au)

Rowe, R. K., Quigley, R. M. & Booker, J. R., 1995, *Clayey Barrier Systems for Waste Disposal Facilities*. E & FN Spon, UK.

Roy, W. R., Griffin, R. A., Dickerson, D. R. & Schuller, R. M., 1984, *Illinois Basin Coal Fly Ashes : 1 Chemical Characterization and Solubility*. Environmental Science & Technology, 18, pp 734-739.

Roy, W. R. & Griffin, R. A., 1984, *Illinois Basin Coal Fly Ashes : 2 Equilibria Relationships and Qualitative Modeling of Ash-Water Reactions*. Environmental Science & Technology, 18, pp 739-742.

Schaap, H. A., 1983, *Selenium in Coal Combustion Products and Derived Effluents*. SECV, Research and Development Department, Report No. SO/83/56.

Schaeffer, J., 1996, *Hazelwood Mine - Aquifer Depressurisation Overview*. Geo-Eng Pty. Ltd., Report 1575/6, June 1996, 49 p.

Selig, E. T. & Mansukhani, S., 1975, *Relationship of Soil Moisture to the Dielectric Property*. ASCE J Geotech Div, 101 (GT8), pp 757-770.

Shannon, D. G. & Fine, L. O., 1974, *Cation Solubilities of Lignite Fly Ashes*. Environmental Science & Technology, 8, pp 1026-1028.

Sims, J. R. & Bingham, F. T., 1968, *Retention of Boron by Layer Silicates, Sesguioxides, and Soil Materials : III Iron and Aluminium Coated Layer Silicates and and Soil Materials*. Soil Science Society of America Journal, 32, pp 369-373.

Simsiman, G. V., Chetter, G. & Andren, A. W., 1987, *Effect of Ash Disposal Ponds on Groundwater Quality at a Coal-Fired Power Plant*. Water Research, 21 (4), pp 417-426.

van der Sloot, H. A., Piepers, N. & Kok, A., 1984, *A Standard Leaching Test for Combustion Residues*. Energy Research Foundation, Petten, The Netherlands, Report No. BEOP-31.

Smith, E., Naidu, R., Alston, A. & Laurence, G., 1996, *Sorption Behaviour of Pentavalent Arsenic Species by Oxidic Soils*. Proc. "Australian and New Zealand National Soils Conference 1996", Uni. of Melbourne, Melbourne, VIC, July 1-4, 1996, Vol. 2, pp 259-260.

Sorokin, Y. I., 1962, *Experimental Investigation of Bacterial Sulfate Reduction in the Black Sea Using* S^{35}. Mikrobiologiya, 31, pp 402-410.

Stichbury, M-L K, Bain, J G, Blowes, D W & Gould, W D, 2000, *Microbially-Mediated Reductive Dissolution of Arsenic-Bearing Minerals in a Gold Tailings Impoundment*. In "5TH International Conference on Acid Rock Drainage (ICARD)", Organised by Society for Mining, Metallurgy & Exploration Inc., Denver, Colorado, USA, May 2000, Vol. 1, pp 759-764.

Stollenwerk, K. G., 1991, *Simulation of Molybdate Sorption With the Diffuse Layer Surface-Complexation Model*. In "U.S. Geological Survey Toxic Substances Hydrology Program", Proc. of Technical Meeting, Ed's G. E. Mallard & D. A. Aronson, U.S. Geological Survey Water Resources Investigation Report 91-4034, pp 47-52.

Stollenwerk, K. G., 1995, *Modeling the Effects of Variable Groundwater Chemistry on Adsorption of Molybdate*. Water Resources Research, 31 (2), pp 347-357.

Straub, W. A. & Lynch, D. R., 1982, *Models of Landfill Leaching : Moisture Flow and Inorganic Strength*. Journal of the Environmental Engineering Division, ASCE, 108, pp 231-250.

Stumm, W. & Morgan, J. J., 1996, *Aquatic Chemistry*. 3RD Edition, John Wiley & Sons, USA, 1,022 p.

Summers, K. V., Rupp, G. L. & Gherini, S. A., 1983, *Physical-Chemical Characteristcs of Utility Solid Wastes*. Electric Power Research Institute (EPRI), EA-3236, Palo Alto, California, USA.

Thatcher, R. C., 1976, *Loy Yang Project - Aquifer Characteristics From Pump Tests Conducted During 1975*. State Electricity Commission of Victoria, Report DD 111.

Theis, T. L., Westrick, J. D., Hsu, C. L. & Marley, J. J., 1978, *Field Investigation of Trace Metals in Groundwater From Fly Ash Disposal*. Journal of the Water Pollution Control Federation, 50 (11), pp 2457-2469.

Theis, T. L. & Wirth, J. L., 1977, *Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems*. Environmental Science & Technology, 15 (7), pp 840-843.

Thomas, D. E. & Baragwanath, W., 1949, *Geology of the Brown Coals of Victoria, Part 2*. Min. Geol. J. Vict., 3 (6), pp 26-55.

Thorstenson, D. C., Fisher, D. W. & Croft, M. G., 1979, *The Geochemistry of the Fox Hills-Basal Hell Creek Aquifer in Southwestern North Dakota and Northwestern South Dakota*. Water Resources Research, 15 (6), pp 1479-1498.

Topp, G. C. & Ferré, P. A., 2000, *Measuring Water Content in Soil Using TDR : A State-of-theArt in 1998*. In "Comparison of Soil Water Measurement Using the Neutron Scattering, Time Domain Reflectometry and Capacitance Methods", TECDOC-1137, IAEA, Vienna, Austria, February 2000, pp 111-124.

Tratch, D., 1994, *Moisture Uptake Within the Root Zone*. M Sc Thesis, Dept. of Civil Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Usmen, M. A., Baradan, B. & Yazici, S., 1992, *Geotechnical and Geoenvironmental Properties of Stabilized Lignite Fly Ash*. Proc. "Environmental Geotechnology", Ed's Usmen & Acar, Pub. Balkema, Rotterdam, pp 419-427.

US-EPA, 1979, *Effects of Flue Gas Cleaning Waste on Groundwater Quality and Soil Characteristics*. U.S. Environmental Protection Agency (US-EPA), Municpal Environmental Research Laboratory, Office of Research & Development, EPA-600/2-79-164, Cincinatti, Ohio, USA, August 1979, 129 p.

US-EPA, 1990, *Method 1311 - Toxicity Characteristic Leaching Procedure (TCLP)*. Federal Register, Part II, Vol. 55, No. 61, March 29, 1990.

Waghorne, E., 1993, *Brown Coal Mining in the Latrobe Valley*. In "The Sir Maurice Mawby Memorial Volume - Second Edition", Ed.'s J. T. Woodcock & J. K. Hamilton, Australasian Institute of Mining and Metallurgy (AusIMM), Monograph 19, Vol. 2, pp 1533-1542.

Wakao, N., Takahashi, T., Sakurai, Y. & Shiota, H., 1979, *A Treatment of Acid Mine Water Using Sulfate-Reducting Bacteria*. J. Ferment. Technol., 57 (5), pp 445-452.

Walsh, J. J. & Kinman, R. N., 1979, *Leachate and Gas Production Under Controlled Moisture Conditions*. Proc. "5TH Annual Research Symposium on Municipal Solid Waste : Land Disposal", EPA-600/9-79-023a, USA.

Walsh, J. J., Vogt, G., Kinman, R., Rickabaugh, J., 1981, *Leachate and Gas From Municipal Solid Waste Landfill Simulators*. Proc. "4TH Annual Madison Conference of Applied Research and Practice on Municipal and Industrial Waste", Wisconsin, USA.

Waples, D. W., 1985, *Geochemistry in Petroleum Exploration*. International Human Resources Development Corporation, USA.

Waring, P. T., Draper, I. D. & Fitzclarence, N., 1996, *The Control of Fouling in Large Boilers Fired With Loy Yang Brown Coal*. Proc. "7TH Australian Coal Science Conference", Australian Institute of Energy - Gippsland Group, Ed. P. T. Waring, Churchill, VIC, December 2-4, 1996, pp 91-100.

Warren, C. J. & Dudas, M. J., 1986, *Mobilization and Attenuation of Trace Elements in an Artificially Weathered Fly Ash*. Electric Power Research Institute (EPRI), EA 4747, Palo Alto, California, USA.

Westrich, J. T., 1983, *The Consequences and Controls of Bacterial Sulfate Reduction in Marine Sediments*. PhD Thesis, Yale University, USA, 530 p.

Westrich, J. T. & Berner, R. A., 1984, *The Role of Sedimentary Organic Matter in Bacterial Sulfate Reduction : The G Model Tested*. Limnology & Oceanography, 29 (2), pp 236-249.

Whalley, W. R., 1993, *Considerations on the Use of Time-Domain Reflectometry (TDR) for Measuring Soil Water Content*. Jnl Soil Science, 44, pp 1-9.

White, A. F., Benson, S. M., Yee, A. W., Wollenberg, H. A. & Flexer, S., 1991, *Groundwater Contamination at Kestersen National Wildlife Range, CA, Part II, Geochemical Parameters Influencing Selenium Mobility*. Water Resources Research, 27, pp 1085-1098.

White, J. H., Knight, S. J., Zegelin, G. C. & Topp, G. C., 1994, *Comment on 'Considerations on the Use of Time-Domain Reflectometry (TDR) for Measuring Soil Water Content'*. Euro J Soil Sci, 45, pp 503-508.

Widdel, F., 1988, *Microbiology and Ecology of Sulfate- and Sulphur-Reducing Bacteria*. In : "Biology of Anaerobic Microorganisms", Zehnder, A J B (Ed.), John Wiley & Sons, New York, USA, pp 469-586.

Wilson, G. W., 1990, *Soil Evaporative Fluxes for Geotechnical Engineering Problems*, PhD Thesis, Dept. of Civil Engineering, University of Saskatchewan, Saskatoon, Saskatchewan, Canada, 464 p.

Wilson, G. W., Fredlund, D. G. & Barbour, S. L., 1994, *Coupled Soil-Atmosphere Modelnig for the Soil Evaporation*. Canadian Geotechnical Journal, 31, pp 151-161.

Wilson, G. W., Fredlund, D. G. & Barbour, S. L., 1994, *Coupled Soil-Atmosphere Modelling for Soil Evaporation*. Canadian Geotechnical Journal, 31**,** pp 151-161.

Wood, P., 1993, *Loy Yang Mine - Aquifer Depressurisation Report 1993*. Geo-Eng Pty. Ltd., Report 1204/1.

Wood, P., Reinsch, G. & Regan, W., 1982, *Loy Yang Project Ash Pond Seepage Investigation - Interim Report*. State Electricity Commission of Victoria (SECV), General Engineering and Construction Department, Report No. ID 31.

Zehnder, A. J. B. (Ed.), 1988, *Biology of Anaerobic Microorganisms*. John Wiley & Sons, New York, USA.

Zheng, C. & Bennett; G. D., 1995; *Applied Contaminant Transport Modeling : Theory and Practice*; Van Nostrand Reinhold, New York, 440 p.

APPENDICES

Appendix A1 - Finite Difference Solution to the Advection-Dispersion Equation

Appendix A1 - Finite Difference Solution to the Advection-Dispersion Equation

A1.1 Overview

The advection-dispersion equation (ADE), presented and used in Sections 3.5.6, 3.11.3 and 8.2 to 8.4, is mathematically represented as (3-1, pp 73) (Freeze & Cherry, 1979) :

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - v_z \frac{\partial C}{\partial z} \qquad \text{A1-1}$$

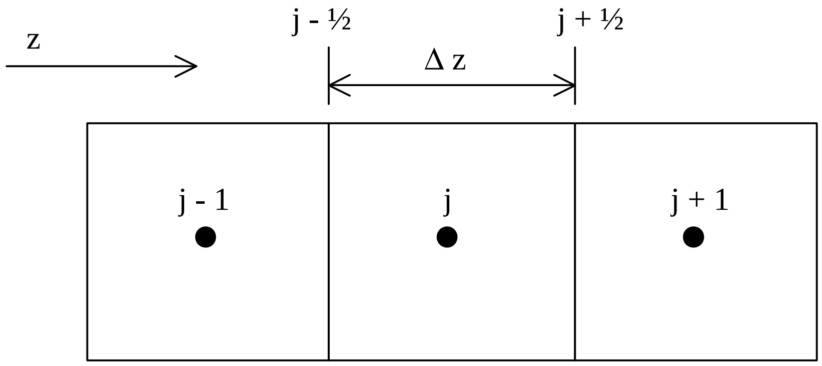
This equation describes the conservative or non-reactive transport of a solute in groundwater due to advection, transport with flowing groundwater, and dispersion, mixing due to diffusion and tortuous flow paths around pore spaces. The assumptions for this model have been described in the relevant chapters, principally Section 3.5.6. All symbols retain the same definition. The ADE forms the basis for the modelling of solute transport in groundwater, and hence a technique to solve this numerically is required. The Finite Difference technique is a robust and relatively simple mathematical technique that has been successfully applied to groundwater flow and solute transport modelling for the past three decades. A particular form of Finite Difference was employed within this research to model various aspects of ash seepage migration and leaching behaviour. The boundary and initial conditions used for the model are :

Boundary	$z = 0$	$C(0, t) = g(t)$	A1-2a
	$z = z_{max}$	$\frac{\partial C}{\partial t} = 0$	A1-2b
Initial	$t = 0$	$C(t, 0) = C_0$	A1-2c

where C_0 - background concentration in the groundwater (or ash, eg. C_{max}).

A1.2 Finite Difference Solution to the ADE

The Finite Difference solution technique used to solve the ADE and model solute transport in groundwater (or ash leaching), is adapted from Zheng & Bennett (1995). They present a block-centred explicit, upward finite difference scheme, shown diagrammatically in Figure A1.1.



where j - cell number; Δ z - cell size.

Figure A1.1 - Block-Centred, Upward Finite Difference Scheme (Zheng & Bennett, 1995)

The first order derivative, is approximated by :

$$\frac{\partial C}{\partial z} = (C_{j+½} - C_{j-½}) / \Delta z \qquad \text{A1-3a}$$

where $C_{j+½} = (1 - \alpha)\, C_j + \alpha\, C_{j-1}$ A1-3b

and $\alpha = 0$ if $v_z > 0$ or $\alpha = 1$ if $v_z < 0$ A1-3c

For both the solute transport and ash leaching models, the seepage (or flow) velocity is greater than zero, and so A!-3b becomes :

$$\frac{\partial C}{\partial z} = (C_j - C_{j-1}) / \Delta z \qquad \text{A1-4}$$

The second order derivative, is approximated by :

$$\frac{\partial^2 C}{\partial z^2} = \left[\left(\frac{\partial C}{\partial z}\right)_{j+½} - \left(\frac{\partial C}{\partial z}\right)_{j-½}\right] / \Delta z \qquad \text{A1-5a}$$

where $$\left(\frac{\partial C}{\partial z}\right)_{j+½} = (C_{j+1} - C_j) / \Delta z \qquad \text{A1-5b}$$

$$\left(\frac{\partial C}{\partial z}\right)_{j-½} = (C_j - C_{j-1}) / \Delta z \qquad \text{A1-5c}$$

giving $$\frac{\partial^2 C}{\partial z^2} = (C_{j+1} - 2C_j + C_{j-1}) / (\Delta z)^2 \qquad \text{A1-5d}$$

For the boundary $z = z_{max}$, a fictitious point is added at (n+1) so that the boundary condition can be approximated as :

$$\frac{\partial C}{\partial z} = (C_{n+1} - C_n) / \Delta z = 0 \qquad \text{A1-6a}$$

where n - maximum number of nodes (or cells).

giving $$C_{n+1} = C_n \qquad \text{A1-6b}$$

For the boundary z = 0, equation A1-4 becomes :

$$\frac{\partial C}{\partial z} = (C_1 - g(t)) / \Delta z \qquad \text{A1-7a}$$

$$\frac{\partial^2 C}{\partial z^2} = (C_2 - 2C_1 + g(t)) / (\Delta z)^2 \qquad \text{A1-7b}$$

The time derivative, is approximated by :

$$\frac{\partial C}{\partial t} = (C^{k+1} - C^k) / \Delta t \qquad \text{A1-8}$$

where Δt - time step.

By substituting A1-4, A1-5d and A1-8 into A1-1, we can derive the finite difference form of the ADE as :

For j = 1

$$C_1^{k+1} = C_1^k + D_z \frac{\Delta t}{(\Delta z)^2} (C_2^k - 2C_1^k + g^k(t)) - v_z \frac{\Delta t}{\Delta z} (C_1^k - g^k(t)) \qquad \text{A1-9a}$$

For j = 2, 3, … , n-1

$$C_j^{k+1} = C_j^k + D_z \frac{\Delta t}{(\Delta z)^2} (C_{j+1}^k - 2C_j^k + C_{j-1}^k) - v_z \frac{\Delta t}{\Delta z} (C_j^k - g^k(t)) \qquad \text{A1-9b}$$

For j = n

$$C_n^{k+1} = C_n^k - D_z \frac{\Delta t}{(\Delta z)^2} (C_n^k - C_{n-1}^k) - v_z \frac{\Delta t}{\Delta z} (C_n^k - C_{n-1}^k) \qquad \text{A1-9c}$$

The stability criteria for this scheme are based on constraining the numerical dispersion, or computational error. This stability is achieved through limiting the time step (Δt) and cell size (Δz), to ensure that the distance travelled by a solute over one time step is lower than the size of a single cell. Mathematically, this is expressed as :

$$\frac{D_z \Delta t}{(\Delta z)^2} \leq \frac{1}{2} \qquad \text{A1-10a} \qquad \& \qquad \frac{v_z \Delta t}{\Delta z} \leq 1 \qquad \text{A1-10b}$$

giving $\Delta t \leq \dfrac{(\Delta z)^2}{2D_z + v_z \Delta z}$ A1-11

The above series of equations, A1-9a-c and A1-11, provide the basis for a numerical model of conservative solute transport. Through defining the chemical reaction terms appropriately, it is possible to include kinetic or leaching reactions into the solute transport model, as developed in Sections 3.11 and 8.2 to 8.4.

A common problem encountered while solving the ADE is a phenemenon known as 'numerical dispersion'. This results in artificial smearing of the advective solute front. Detailed accounts of the source and control of numerical dispersion are given in Peaceman (1977), Noorishad *et al.* (1992) and Zheng & Bennett (1995).

There are two dimensionless parameters which can be used to help minimise the effects of numerical dispersion. They are the Courant number, C_r, (controlling advective flow) and the Peclet number, P_e, (controlling hydrodynamic dispersion), shown below (Zheng & Bennett, 1995). By maintaining low C_r and P_e numbers, that is, a high spatial and temporal discretization, it is possible to reduce the effects of numerical dispersion.

$$C_r = \frac{v_z \Delta t}{\Delta x} \qquad P_e = \frac{v_z \Delta x}{D_z} = \frac{\Delta x}{\alpha_z} \qquad \text{A1-12}$$

For the one-dimensional case of explicit upwind scheme, the numerical dispersion can be calculated by the following relation (Peaceman, 1977; Zheng & Bennett, 1995) :

$$D_{num} = \tfrac{1}{2}\, v_z\, D_z\, (1 - C_r) \qquad \text{A1-13}$$

For advective flow only, where hydrodynamic dispersion (D_z) can be taken as zero, the ADE equation represents a plug flow with a sharp (or rectangular) concentration front, except for the smearing due to numerical dispersion. Nevertheless, if the values of Δz and Δt are chosen so that $C_r = 1$ and $D_{num} = 0$, a step concentration can be modelled exactly without numerical dispersion. All modelling undertaken in this thesis uses a high spatial and temporal discretisation to minimise the possible adverse effects of numerical dispersion.

Appendix A2 - Source Code for the Kinetic Solute Transport Model

Appendix A2 - Source Code for the Kinetic Solute Transport Model

A2.1 Overview

Chapter 3 developed a solute transport model which incorporated a kinetic reaction to allow for sulphate reduction coupled with the oxidation of organic matter. The model used a finite difference technique for numerical solution, presented in Appendix A1. The program was developed in FORTRAN 77 (Lahey, 1994) on an IBM-Microsoft DOS based personal computer, for programming simplicity. The code for the model was modified manually for each variation of the relevant input parameters.

A2.2 Source Code Used for Sulphate Transport

```
      PROGRAM KINTRAN1
C Developed by    :  Gavin Mudd
C Started on      :  March 19, 1997
C-------------------------------------------------->
C Define Variables and Arrays for the main Kinetic Transport routine
C
      REAL CBAK,B1DIS,B2DIS,YEAR,DTSTAB,B1O,B2o,B3O,B1F,B2F,DTCOUR,
     +     DTPEC,TOUTIN,B3F
      DOUBLE PRECISION CNEW,COLD,SOURCE,DX,DT,COUR,DTZZ,HYDDIS,VEL,
     +     EFFPOR,B3DIS,LINVEL,PECLET,TDAYS,TYEARS,GORG,GBAK,KDEG,
     +     KDEGB,KRATE,CIN
      INTEGER NDIV,MONIN,B1INT,B2INT,TINT,STEP,DAYSTEP,MDAYS
      DIMENSION CNEW(1000),COLD(1000),MDAYS(100),YEAR(100),B1F(100),
     +          B2F(100),B3F(100),TOUT(1000),TINT(1000),DAYSTEP(100),
     +          GORG(1000),CIN(1000)
      CHARACTER RUNTITLE*80,INFILE*12,BORE1*8,BORE2*8,BORE3*8,
     +          TOUTFILE*12,OUTFILE*12
C-------------------------------------------------->
C Array Variables
C COLD/CNEW - Sulphate Concentration (mg/l)
C-------------------------------------------------->
C Definition of Constants
C
C VEL - Darcy velocity (m/day) ---> B?LV - Seepage Vel. (m/day)
C POR - Porosity               ---> TEND - Simulation length (days)
C NDIV - Number of Divisions or Nodes
C SOURCE - Source Concentration (mg/l)
C DX - Delta X (m)             --->  DT - Delta T (days)
C-------------------------------------------------->
C Read Input File of Values
C
C     WRITE(*,*)'Please type the input file name  : '
C     READ(*,3)INFILE
      INFILE='hhf-so4.txt'
3     FORMAT(A12)
      OPEN(9,INFILE,STATUS='OLD')
```

```
      READ(9,6)RUNTITLE
6     FORMAT(A80)
      READ(9,*)
      READ(9,*)VEL
      READ(9,*)HYDDIS
      READ(9,*)EFFPOR
      READ(9,*)SOURCE
      READ(9,*)CBAK
      READ(9,10)BORE1
10    FORMAT(A8)
      READ(9,*)B1DIS
      READ(9,10)BORE2
      READ(9,*)B2DIS
      READ(9,10)BORE3
      READ(9,*)B3DIS
      READ(9,*)NDIV
      READ(9,*)MONIN
      READ(9,*)GBAK
      READ(9,*)KRATE
      READ(9,*)
      READ(9,*)
      DO J=1,MONIN
         READ(9,*)MDAYS(J),YEAR(J),B1F(J),B2F(J),B3F(J),CIN(J)
      END DO
      OUTFILE='hhf-so4.out'
C
C Set and calculate various constants
C
      LINVEL=VEL/EFFPOR
      DX=B3DIS/NDIV
      B1INT=INT(B1DIS/DX)
      B2INT=INT(B2DIS/DX)
      DTSTAB=(DX*DX)/(2*HYDDIS+LINVEL*DX)
      DTCOUR=DX/LINVEL
      DTPEC=(DX**2)/HYDDIS
      WRITE(*,*)'Courant based DT is   < ',DTCOUR
      WRITE(*,*)'Peclet based DT is    < ',DTPEC
      WRITE(*,*)'Stable DT range is    < ',DTSTAB
      WRITE(*,*)
      DT=0.999999*DTSTAB
C     DT=0.9999*((B3DIS/NDIV)**2)/(2*HYDDIS+(VEL/EFFPOR)*(B3DIS/NDIV))
C    + (VEL/EFFPOR)*(B3DIS/NDIV)))
      PECLET=LINVEL*DX/HYDDIS
      COUR=LINVEL*DT/DX
      DTZZ=HYDDIS*DT/(DX**2)
      WRITE(*,*)'Courant Number    : ',COUR
      WRITE(*,*)'Peclet Number     : ',PECLET
      WRITE(*,*)
      WRITE(*,*)'Time Step (days)  : ',DT
      WRITE(*,*)
      DO J=1,MONIN
         DAYSTEP(J)=INT(MDAYS(J)/DT)
      END DO
      B1FNUL=0.0
      B2FNUL=0.0
      B3FNUL=0.0
C------------------------------------------------->
C Read in "tout.txt" file of output times
      TOUTFILE='tout.txt'
      OPEN(5,TOUTFILE,STATUS='OLD')
      READ(5,*)TOUTIN
      DO J=1,TOUTIN
         READ(5,*)TOUT(J)
         TINT(J)=INT(TOUT(J)/DT)
      END DO
C------------------------------------------------->
C Open output file and write basic input parameters
C
      OPEN(2,OUTFILE,STATUS='UNKNOWN')
```

```
      WRITE(2,6)RUNTITLE
      WRITE(2,12)
12    FORMAT(77('-'))
      WRITE(2,*)
      WRITE(2,15)LINVEL
15    FORMAT('Average Linear Velocity            = ',F9.4,
     +       '  (m/day)')
      WRITE(2,18)SOURCE
18    FORMAT('Ash Pond Concentration             = ',F6.1,
     +       '     (mg/l)')
      WRITE(2,20)HYDDIS
20    FORMAT('Hydrodynamic Dispersion Coeff.     = ',F7.2,
     +       '    (m^2/day)')
      WRITE(2,*)
      WRITE(2,23)KRATE
23    FORMAT('Kinetic Sulphate Degradation Rate  = ',F9.4,'  (/day)')
      WRITE(2,*)
      WRITE(2,27)NDIV,DX
27    FORMAT('Spatial Resolution (n = ',I3,') (DX)  = ',F7.2,'    (m)')
      WRITE(2,28)DT
28    FORMAT('Time Step Used (DT)                = ',1x,F8.4,'  (days)')
      WRITE(2,*)
      WRITE(2,30)PECLET,COUR
30    FORMAT('Peclet No. = ',F7.4,' & Courant No. = ',F7.4)
      WRITE(2,*)
      WRITE(2,*)'All Concentration Values in mg/l'
      WRITE(2,*)
      WRITE(2,33)BORE1,BORE2,BORE3
33    FORMAT('                     Bore ',A8,2x,'      Bore ',A8,2x,
     +       '      Bore ',A8)
      WRITE(2,34)
34    FORMAT(' Days    Year    Field  Model  Org. ',
     +       '  Field  Model  Org.   Field  Model  Org. ')
      WRITE(2,*)
C---------------------------------------------------->
C Initialize the Concentration, Time and Bore Arrays
C
      TDAYS=0.0
      TYEARS=YEAR(1)
      STEP=0
      B1C=CBAK
      B2C=CBAK
      B3C=CBAK
      B1O=GBAK
      B2O=GBAK
      B3O=GBAK
      KDEGB=0.5*KRATE*GBAK
      DO J=1,NDIV
         COLD(J)=CBAK
         GORG(J)=GBAK
      END DO
      WRITE(2,42)TDAYS,TYEARS,B1F(1),B1C,B1O,B2F(1),B2C,B2O,
     +           B3F(1),B3C,B3O
42    FORMAT(I5,2x,F8.3,9(F7.1))
C---------------------------------------------------->
C Begin Kinetic Transport - Main Finite Difference Routine
C
C     CNEW(1)=SOURCE
      CNEW(1)=CIN(1)
50    TDAYS=TDAYS+DT
      TYEARS=TYEARS+(DT/365)
      STEP=STEP+1
      DO J=2,NDIV-1
         GORG(J)=(GORG(J))*(1-KRATE*DT)
         KDEG=KRATE*GORG(J)
         IF(KDEG.LE.KDEGB)THEN
           KDEG=KDEGB
           ELSE
           KDEG=0.5*KRATE*GORG(J)
```

```
         END IF
         CNEW(J)=COLD(J)-COUR*(COLD(J)-COLD(J-1))
     +   +DTZZ*(COLD(J+1)-2*COLD(J)+COLD(J-1))-KDEG*DT
         IF(CNEW(J).LT.0.0)CNEW(J)=0.5
      END DO
      GORG(NDIV)=(GORG(NDIV))*(1-KRATE*DT)
      CNEW(NDIV)=COLD(NDIV)-COUR*(COLD(NDIV)-COLD(NDIV-1))
     +    -DTZZ*(COLD(NDIV)-COLD(NDIV-1))-0.5*KRATE*GORG(NDIV)*DT
      IF(CNEW(NDIV).LT.0.0)CNEW(NDIV)=0.5
      DO J=1,NDIV
         COLD(J)=CNEW(J)
      END DO
C
      DO J=1,TOUTIN
         IF(STEP.EQ.TINT(J))THEN
           B1C=CNEW(B1INT)
           B2C=CNEW(B2INT)
           B3C=CNEW(NDIV)
           B1O=GORG(B1INT)
           B2O=GORG(B2INT)
           B3O=GORG(NDIV)
           WRITE(2,42)TDAYS,TYEARS,B1FNUL,B1C,B1O,
     +                B2FNUL,B2C,B2O,B3FNUL,B3C,B3O
         END IF
      END DO
      DO J=2,MONIN
         IF(STEP.EQ.DAYSTEP(J))THEN
           CNEW(1)=CIN(J)
           B1O=GORG(B1INT)
           B2O=GORG(B2INT)
           B3O=GORG(NDIV)
           WRITE(2,42)TDAYS,TYEARS,B1F(J),B1C,B1O,B2F(J),B2C,B2O,
     +          B3F(J),B3C,B3O
         END IF
      END DO
      IF(TDAYS.LT.MDAYS(MONIN)) GOTO 50
      WRITE(2,42)TDAYS,TYEARS,B1F(MONIN),B1C,B1O,B2F(MONIN),B2C,B2O,
     +           B3F(1),B3C,B3O
      CLOSE(2)
      CLOSE(5)
      CLOSE(9)
      STOP
      END
```

Appendix A3 - Field Leaching Cells

Photos of the Construction Sequence

Figures

Figure A3.1 - Top - Excavation for installation of the Dry Cell (facing east);
Bottom - Leachate collection pipe (facing east).

Figure A3.2 - Coarse drainage layer; bitton cloth, steel framework.

Figure A3.3 - One third backfilled; half backfilled; completed.

Appendix A4 - Loy Yang Climate Data

July 1997 to August 1998

Tables

Table A1 - Loy Yang Maximum & Minimum Temperature (^{0}C)

1997	September		October		November		December		January '98	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
1			16.5	6.0	18.4	10.4	19.9	8.8	30.9	14.5
2			20.9	10.3	15.0	8.1	26.7	14.9	37.0	18.8
3			22.2	6.4	16.3	6.1	20.6	8.1	26.6	13.4
4			11.1	2.9	14.8	6.0	19.7	6.2	24.1	11.9
5			15.0	4.9	18.6	8.9	21.4	11.2	24.9	13.5
6			13.4	2.7	22.3	11.3	20.2	14.3	24.8	11.5
7			18.2	7.7	29.1	13.1	19.1	14.4	26.6	15.4
8			18.8	10.6	21.7	9.3	21.0	13.0	27.7	15.7
9			16.6	8.8	22.3	9.2	19.2	15.4	23.6	17.3
10			20.9	10.4	27.0	11.5	23.4	13.5	29.4	18.2
11			28.5	17.9	25.9	14.2	23.2	11.6	29.9	16.5
12			21.9	12.2	17.0	9.6	32.5	14.9	31.5	17.6
13			15.1	5.4	15.2	8.9	34.7	14.3	34.3	21.2
14			40.9	6.4	22.6	11.9	31.0	13.7	32.9	19.1
15			20.9	5.3	12.9	5.8	21.8	11.5	35.5	16.1
16			14.1	10.1	14.2	5.7	21.4	11.6	23.1	13.8
17			18.6	6.6	16.4	6.5	21.9	10.3	27.6	16.5
18			13.7	3.7	14.5	10.1	24.1	13.1	39.6	15.6
19	12.0	7.3	13.5	4.3	16.3	11.1	21.7	12.3	21.7	13.4
20	13.6	8.9	12.9	6.9	21.6	10.6	18.6	10.2	27.8	15.3
21	16.5	7.2	13.7	6.1	19.2	10.5	30.2	16.4	24.4	14.9
22	15.4	7.1	17.5	8.1	26.0	10.6	33.9	11.2	24.0	16.6
23	13.5	6.0	17.7	9.8	31.7	18.4	20.3	12.0	35.3	15.2
24	13.2	5.8	21.6	10.0	34.5	9.0	20.6	13.2	25.5	12.2
25	14.9	6.3	27.8	10.6	26.2	10.7	21.3	7.0	28.5	14.8
26	17.1	6.4	28.5	14.1	32.9	18.5	29.3	13.9	15.9	12.3
27	17.7	11.2	33.1	13.8	37.8	16.4	20.0	8.2	17.7	13.8
28	17.6	5.1	19.4	8.9	26.2	10.8	19.1	8.8	28.0	14.2
29	13.5	2.0	20.4	11.1	20.1	9.6	24.4	10.8	19.3	11.2
30	15.0	2.3	19.9	11.1	21.9	11.6	31.0	9.9	21.2	10.5
31			26.1	13.0			27.5	14.3	23.3	14.0

Table A1 (cont'd) - Loy Yang Maximum & Minimum Temperature (^{0}C)

'98	February		March		April		May		June		July		August	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
1	29.5	13.4	21.4	11.6					13.8	9.2	10.5	2.1	10.1	7.0
2	30.7	17.0	23.8	14.2					15.5	7.7	9.1	5.5	12.6	5.2
3	34.5	15.3	27.3	14.2					11.6	8.7	10.5	3.2	13.4	7.9
4	25.4	11.5	32.1	14.7					15.8	7.0	11.1	4.8	16.5	6.6
5	29.5	13.3	25.5	11.5			16.1	9.7	19.0	7.4	13.8	5.1	13.6	6.5
6	33.3	17.6	17.8	12.4			16.5	9.5	19.1	10.3	15.7	9.6	13.7	5.8
7	24.1	16.7	17.8	10.4			17.1	8.0	15.1	8.5	12.6	4.4	13.7	8.8
8	35.9	13.2	17.3	9.4			10.6	5.8	10.9	7.4	13.8	5.8	12.9	10.0
9	18.8	9.9	22.5	9.0			12.0	6.6	11.8	6.4	12.9	2.8	13.6	3.9
10	23.1	14.0	25.9	11.9			11.9	3.5	13.2	5.2	7.5	2.6	12.9	4.2
11	28.7	14.0	32.2	11.1			13.7	7.6	13.6	6.1	9.5	3.0	15.2	6.9
12	31.6	16.8	34.7	16.5			14.9	9.7	15.1	8.5	10.2	6.1	12.3	6.2
13	29.9	11.5	39.0	21.1			14.1	10.5	13.8	9.7	11.0	2.9	9.1	6.8
14	24.1	11.3	27.3	13.8			17.6	9.1	12.6	7.1	10.3	4.7	11.3	8.3
15	27.6	14.6	17.0	9.7			20.8	12.1	15.6	7.8	10.6	0.8	12.8	2.8
16	20.6	9.9	16.5	11.4			17.4	10.3	13.3	6.0	10.7	3.0	12.0	5.8
17	13.5	6.9	17.2	9.3			17.2	13.1	10.6	2.7	10.4	0.2	11.5	7.1
18	19.3	10.0	21.6	11.4			16.9	11.7	10.0	0.9	10.3	1.8	13.2	8.1
19	28.2	11.8	21.7	8.0			18.6	10.1	10.9	0.2	13.0	0.8	13.8	8.7
20	30.0	13.6	26.6	9.5			18.1	10.6	12.3	5.2	13.4	1.8	15.0	7.8
21	19.7	11.1	31.3	15.8			13.3	10.8	14.9	8.7	9.4	4.3	14.2	8.8
22	21.5	13.0	27.8	13.7			12.9	6.0	16.0	5.6	10.3	5.7	19.5	9.5
23	20.1	10.0	37.4	13.5			15.4	7.5	9.6	7.1	12.1	4.8	17.0	6.7
24	21.3	10.3	28.3	10.0			14.5	8.6	9.2	6.9	10.5	1.7	12.7	4.2
25	30.3	15.0	18.4	6.5			13.3	8.9	10.0	7.0	12.7	4.1	14.2	4.3
26	36.4	16.8	20.6	9.9			13.8	5.2	10.5	4.5	11.8	6.4	16.1	6.1
27	40.4	14.2	21.4	13.6			13.6	5.3	10.7	1.0	12.4	6.6	16.6	4.9
28	19.3	8.3	24.4	10.7			16.2	8.5	10.1	0.1	13.9	8.1	14.9	5.1
29			19.7	7.4			18.8	9.6	12.1	2.8	11	4.8	18.7	5.6
30			16.5	11.8			19.5	10.7	12.0	1.6	9.1	5.2	17.6	8.8
31			18.2	11.1			16.3	7.5			9.1	5.5	14.2	6.0

Table A2 - Loy Yang Rainfall June 1997 to August 1998 (mm)

	July	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	April	May	June	July	Aug
1			1.2	0.6	2.6								0.2	2.0
2			6.8	5.2	0.4	0.2							1.4	
3	1.0		1.2			0.2		0.4						0.2
4	0.8	0.2	7.2							0.6				
5	0.2					3.4						0.2		1.2
6	0.2				0.4			2.8	1.6	0.6		1.4	4.4	0.2
7		5.2	11.4								0.4	16.8	0.2	1.4
8	18.0	4.0	3.6	8.6				27.2			5.4	1.6		0.8
9	8.8	2.0	0.2					0.2			2.6		14.2	0.2
10	0.8				12.6		1.4				0.2		3.6	
11		6.0			14.4		8.4				0.4	0.2	0.6	0.8
12		0.8		3.8				3.8		9.7	1.0		0.2	2.2
13				4.4					0.4	3.8	0.2	0.6		7.0
14			10.6	9.2	23.8	4.0	2.2		1.6				4.8	0.4
15	3.6		4.6				5.4					1.4		0.4
16	3.2			2.6	8.4			10.0			0.6	10.4	0.2	2.4
17	0.2	8.2		3.4	1.0			16.8				0.2	0.2	1.0
18	0.4	3.4		0.8										1.0
19		0.8	0.2	0.8		9.5								0.2
20	0.2					1.4	1.8			8.2	4.0			
21	0.2							0.4			2.2		1.0	
22	0.2		2.2			0.2					0.4	1.8	1.6	2.2
23		8	2.8				0.8		2.2			3.0	0.6	2.6
24		14.8				1.8					9.8	6.8	0.2	0.8
25		1.6					6.8				5.0	6.0		
26	0.2	2.2			0.2		21.2			3.8		0.2		
27	0.2		3.0		2.0		0.2	0.6		0.4	0.2	0.2	1.0	0.4
28	3.0		0.2				0.6		0.8				2.4	
29	0.6				3.8		1.4			1.8		0.4	1.8	
30	0.4			9.8			0.2		0.2	1.0			1.0	
31	1.0			5.2					0.4				1.2	

Table A3 - Loy Yang Average Daily Wind Speed (km/hr)

1997	July	Aug	Sep	Oct	Nov	Dec
1				4.13	16.38	11.75
2				13.13	9.88	24.75
3				18.44	4.50	10.88
4				5.43	5.38	6.88
5				8.63	8.00	8.88
6				8.00	5.13	8.38
7				11.50	16.75	8.88
8				8.57	11.50	10.00
9				6.75	7.00	6.88
10				3.89	5.22	13.78
11				21.63	13.25	7.13
12				22.13	15.63	5.75
13				10.38	7.75	8.00
14				16.63	4.38	14.88
15				16.75	7.63	20.50
16				17.86	13.43	13.00
17				22.63	14.25	14.13
18			10.00	10.38	17.75	7.25
19			5.75	10.25	15.88	5.29
20			13.14	9.13	13.13	7.88
21			10.25	11.38	6.13	12.25
22			5.00	11.25	6.00	26.88
23			11.00	8.38	10.25	17.88
24			9.00	6.25	4.71	13.88
25			8.00	5.25	5.88	6.88
26			4.88	4.75	10.38	14.75
27			9.25	11.25	9.38	14.75
28			6.57	5.25	8.25	7.63
29			6.63	9.43	10.25	9.88
30			6.57	8.00	11.63	8.25
31				6.63		8.29

Table A3 (cont'd) - Loy Yang Average Daily Wind Speed (km/hr)

1998	Jan	Feb	March	April	May	June	July	August
1	8.00	7.38	6.29	9.67		4.63	8.88	11.00
2	9.25	12.13	6.50			5.50	14.75	3.25
3	9.25	11.63	8.29			7.13	3.63	3.88
4	6.43	7.14	10.43		9.00	2.75	3.63	2.88
5	6.29	6.00	14.13		6.50	3.88	4.75	7.25
6	7.13	4.88	23.63		9.38	4.25	11.63	10.00
7	7.63	6.13	9.75		11.25	6.88	6.14	6.50
8	12.13	15.50	6.25		12.75	4.71	12.71	5.38
9	9.57	4.63	5.00		15.88	6.00	18.00	3.00
10	5.43	7.88	6.63		7.38	5.75	7.50	6.57
11	7.67	4.88	3.88		12.14	6.13	7.50	9.00
12	17.25	16.13	3.75		7.38	13.50	5.71	5.13
13	4.50	8.75	13.38		4.29	13.29	3.33	9.25
14	8.00	6.00	15.63		4.63	6.17	6.71	4.00
15	18.88	8.75	3.75		2.57	16.50	7.13	6.75
16	10.00	13.88	7.63		1.33	10.88	4.00	12.63
17	7.88	11.38	10.50		9.50	5.00	3.83	9.00
18	20.88	6.29	9.00		8.25	4.71	3.38	7.50
19	8.75	7.71	6.14		4.13	4.00	2.88	6.38
20	11.75	22.13	12.67		17.75	2.57	3.33	6.13
21	16.25	11.63	8.88		18.50	4.00	9.75	4.38
22	12.00	21.63	10.14		8.88	8.00	8.88	14.38
23	10.88	8.13	9.25		21.00	13.88	5.50	19.00
24	7.50	5.25	10.13		23.50	19.25	3.50	6.75
25	9.63	8.00	4.00		9.50	15.63	4.38	5.00
26	18.25	8.29	6.25		5.00	7.25	4.88	7.00
27	11.88	15.63	5.63		4.75	2.75	4.00	6.50
28	19.00	4.63	11.50		8.00	2.29	13.50	6.63
29	12.63		13.75		6.57	9.57	25.25	9.75
30	13.00		15.38		8.71	2.75	12.63	6.88
31	7.50		20.88		3.43		18.75	5.63

Table A4 - Loy Yang Measured Pan Evaporation July 1997 to August 1998 (mm)

	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	April	May	June	Jul	Aug
1				16.4						2.4	11.6		1.0	
2				5.8		40.0								
3					9.8			35.4		8.8			0.0	
4		13.4							27.2		4.6			4.6
5									6.4			8.8		
6		3.3			12.0			3.8	7.8	6.2	2.2		0.0	
7	5.4	1.3			10.5					3.9			0.0	
8		2.3	19.0								3.6			
9						39.4		8.8		11.0		3.3	4.4	
10	3.0					5.8			19.2			1.0	0.4	5.0
11		6.0				6.6			7.4					
12		0.6			25.8			19.4			5.4	4.2		
13		4.2						7.8	20.4					
14	3.0			26.0	8.1					10.6	2.6		2.6	4.0
15		4.7		2.0		34.8				0.6				
16										2.0	1.2	6.4	0.4	
17			16.3										1.2	
18			4.0		16.6				16.2			1.0		
19						23.6		11.8						4.6
20		11.2		19.0				10.8	8.0		6.2			1.2
21							50.2				0.0		2.8	
22	2.4					25.7				9.0	2.2			
23	1.5		10.4				16.8	18.4	24.6					
24	1.6		2.0	14.2	39.8			5.8	5.2	3.2		4.4	2.6	
25		8.6	3.8					7.0	4.6		7.2	0.0		12.6
26			3.4				12.8	11.6	3.2					
27							3.2	8.6	3.4					
28		8.6											4.0	
29				32.4		47.2						3.6	3.6	
30						14.0	18.6							
31				5.6					11.0				4.0	

Table A5 - Loy Yang Relative Humidity (%)

1997	September		October		November		December		January '98	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
1			100	39	100	62	98	42	100	25
2			93	47	95	56	86	51	82	50
3			97	68	95	65	88	48	99	42
4			97	54	90	56	90	50	85	45
5			91	66	97	62	100	72	80	42
6			97	47	87	41	100	88	97	36
7			99	42	97	60	100	72	91	45
8			100	80	91	52	97	61	90	75
9			100	50	100	34	100	58	98	41
10			97	34	100	51	91	47	95	54
11			60	37	100	80	100	28	93	43
12			81	56	97	68	69	29	100	43
13			100	52	100	49	89	34	100	44
14			100	46	100	82	100	54	100	31
15			87	63	100	60	88	43	91	58
16			100	48	100	48	94	48	90	45
17			94	57	100	60	98	37	90	23
18	85	66	98	57	92	69	100	48	80	57
19	97	73	98	70	99	68	100	68	99	46
20	95	63	100	61	94	63	100	34	100	60
21	97	67	95	63	100	42	69	30	94	59
22	96	75	100	70	97	30	81	38	100	22
23	94	75	97	59	86	36	100	55	96	44
24	100	65	98	37	95	40	100	52	84	46
25	98	54	100	41	79	33	86	22	100	83
26	98	49	82	24	62	24	93	53	100	93
27	100	60	94	65	98	67	87	45	100	47
28	100	46	95	62	92	49	82	42	100	59
29	92	49	100	62	89	61	99	31	97	49
30	93	55	100	45	94	54	97	46	98	50
31			100	64			97	41	92	29

Table A5 (cont'd) - Loy Yang Relative Humidity (%)

'98	February		March		April		May		June		July		August	
	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max	Min
1	100	42	88	52	93	84			100	72	100	100	100	83
2	100	26	96	59					98	72	100	94	100	66
3	91	37	100	27					100	75	100	80	88	53
4	97	34	100	45			98	78	100	63	100	60	99	79
5	100	32	91	53			100	87	100	61	96	77	100	65
6	100	74	90	67			100	78	100	84	100	81	100	72
7	100	28	83	50			100	85	100	96	100	64	100	87
8	100	48	93	49			100	70	100	76	89	64	100	84
9	97	57	100	40			100	84	100	76	100	86	100	74
10	94	49	95	24			97	64	100	72	98	74	100	75
11	95	37	87	20			85	68	100	71	100	77	98	60
12	100	43	52	21			100	77	93	50	99	73	100	85
13	93	43	93	55			97	74	93	75	100	90	100	88
14	100	44	100	71			95	59	96	60	100	84	100	85
15	100	76	93	61			100	89	100	65	100	82	100	84
16	100	85	82	60			100	91	100	66	100	72	100	78
17	100	54	95	55			100	85	100	73	100	72	100	89
18	99	30	97	56			100	60	100	72	100	60	100	86
19	84	40	100	48			100	75	100	67	100	60	100	75
20	88	50	100	25			100	93	89	58	100	86	100	86
21	100	53	91	47			100	87	100	77	100	86	100	57
22	93	54	100	20			99	54	100	87	100	78	100	52
23	86	46	100	39			72	52	97	84	100	92	88	52
24	100	25	100	51			100	90	100	72	100	67	100	57
25	64	20	99	54			100	85	100	80	100	88	100	42
26	62	21	97	59			100	83	100	71	100	84	100	59
27	97	53	97	50			100	61	100	81	100	76	100	61
28	94	49	100	70			75	57	100	59	89	62	100	43
29			97	68			84	45	99	67	100	63	98	55
30			100	65			97	62	100	81	100	87	100	63
31			100	68			100	78			100	80	100	57

Appendix A5 - Dry Cell

Flow Monitoring Data

Tables

Table A5.1 - Dry Cell Flow Data

Day	Flow Rate (mm/hr)	Outflow (mm)	Inflow (mm)
0.451	31.997[#]	8.00	0
0.550	0.510	8.00	0
0.588	0.429	8.44	0
2.465	0.300	24.84	1.8
3.446	0.226	31.04	2.0
7.454	0.112	47.24	29.0
8.606	0.075	49.84	29.8
8.632	0.076	49.88	29.8
9.588	0.058	51.44	29.8
14.597	0.102	61.08	36.6
14.611	0.148	61.12	36.6
15.640	0.081	63.92	36.8
16.423	0.027	64.92	37.2
18.532	0.079	67.64	37.4
18.560	0.075	67.68	37.4
21.993	0.050	72.84	37.8
22.451	0.026	73.24	37.8
25.607	0.022	75.04	38.2
25.633	0.017	75.08	38.2
38.000	0.000	77.72	54.6
42.665	0.010	78.28	61.4
49.000	0.000	79.00	73.8
56.655	0.128	90.84	100.4
57.659	0.071	93.24	100.4
58.926	0.056	95.16	100.4
59.471	0.056	95.92	100.4
59.648	0.065	96.16	100.4
60.693	0.036	97.44	100.4
71.000	0.029	105.52	132.0
73.642	0.017	106.96	132.0
74.472	0.019	107.32	142.6
74.671	0.045	107.48	142.6
80.453	0.040	113.36	147.4
80.677	0.027	113.56	147.4
81.392	0.010	113.88	147.4
84.458	0.000	114.28	152.4
87.375	0.000	114.28	155.4
92.354	0.000	114.28	161.4
99.535	0.000	114.28	170.0
107.045	0.000	114.28	193.4
108.446	0.000	114.28	194.2
109.619	0.000	114.28	195.0
113.625	0.000	114.28	195.0
126.699	0.000	114.28	213.0
127.500	0.058	114.80	213.0
129.604	0.000	116.28	213.4
135.500	0.000	116.28	213.4
140.410	0.108	122.64	273.6
142.759	0.000	125.68	273.6
155.588	0.000	125.68	279.8
171.472	0.000	125.68	287.4
172.604	0.000	125.68	296.92
173.563	0.000	125.68	298.32
205.488	0.000	125.68	319.52
206.731	0.000	125.68	319.52
207.474	0.000	125.68	320.32
212.514	0.000	125.68	349.12
213.606	0.000	125.68	350.52
214.698	0.000	125.68	350.72
221.451	0.000	125.68	353.92
230.471	0.000	125.68	385.12
231.476	0.000	125.68	395.12
232.017	0.000	125.68	411.92
238.667	0.000	125.68	412.32
242.667	0.000	125.68	412.92
251.667	0.000	125.68	414.52
252.667	0.000	125.68	414.52
253.667	0.000	125.68	414.52
254.667	0.000	125.68	414.52
255.667	0.000	125.68	414.52
256.667	0.000	125.68	414.92
273.667	0.000	125.68	419.72
274.667	0.000	125.68	420.12
275.667	0.000	125.68	420.12
276.667	0.000	125.68	420.12
302.667	0.000	125.68	447.2
308.667	0.000	125.68	450.0
328.969	0.000	125.68	477.2
351.640	0.000	125.68	515.0
373.693	0.000	125.68	539.8
408.472	0.000	125.68	583.4
408.573	0.000	125.68	743.4
408.758	0.000	125.68	743.4
408.933	0.000	125.68	743.4
409.073	0.000	125.68	750.4
409.414	0.000	125.68	750.4
409.417	0.580	125.68	750.4
409.420	0.878	125.76	750.4
409.423	0.881	125.80	750.4
409.478	1.385	127.32	750.4

- The collection pipe had become curved upwards, preventing natural discharge. This flow rate is the initial and rapid discharge of residual water within the drainage layer.

Table A5.1 (cont'd) - Dry Cell Flow Data

Day	Flow (mm/hr)	Outflow (mm)	Inflow (mm)
409.514	1.675	128.64	750.4
409.532	1.823	129.36	750.4
409.596	7.579	136.64	750.4
409.597	7.579	136.76	750.4
409.665	5.142	147.16	750.4
409.665	5.142	147.24	750.4
409.727	3.600	153.72	750.4
409.728	3.600	153.80	750.4
409.954	1.800	168.44	750.4
410.416	1.014	184.04	750.8
410.579	0.878	187.72	750.8
413.417	0.240	225.80	754.6
414.539	0.181	231.48	755.6
415.469	0.157	235.24	755.8
418.667	0.000	241.24	755.8

Appendix A6 - Wet Cell

Flow Graphs and Minor Trace Elements

Figures

Tables

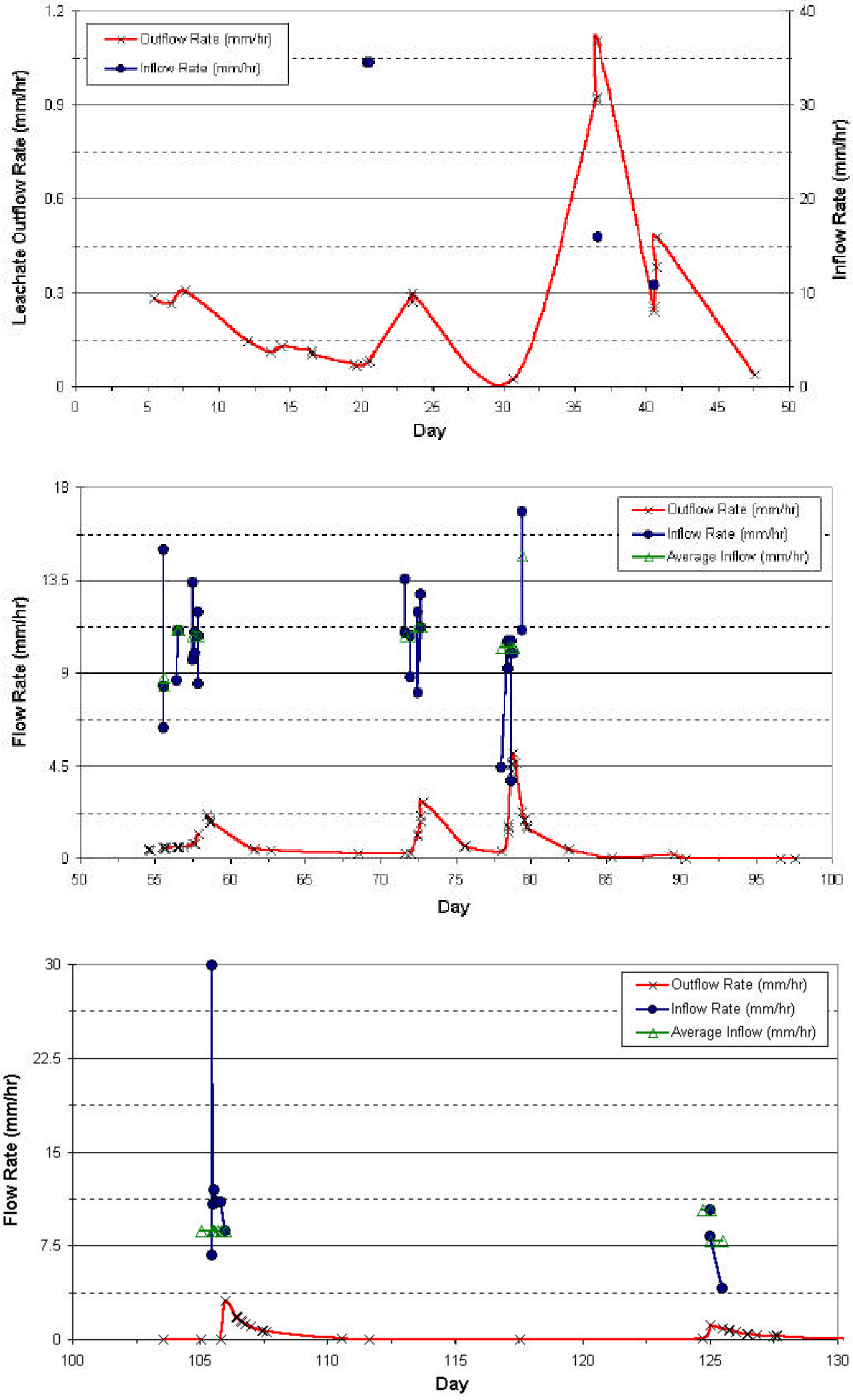


Figure A6.1 - Wet Cell Flow Data : Days 0 to 50; 50 to 100; and 100 to 130

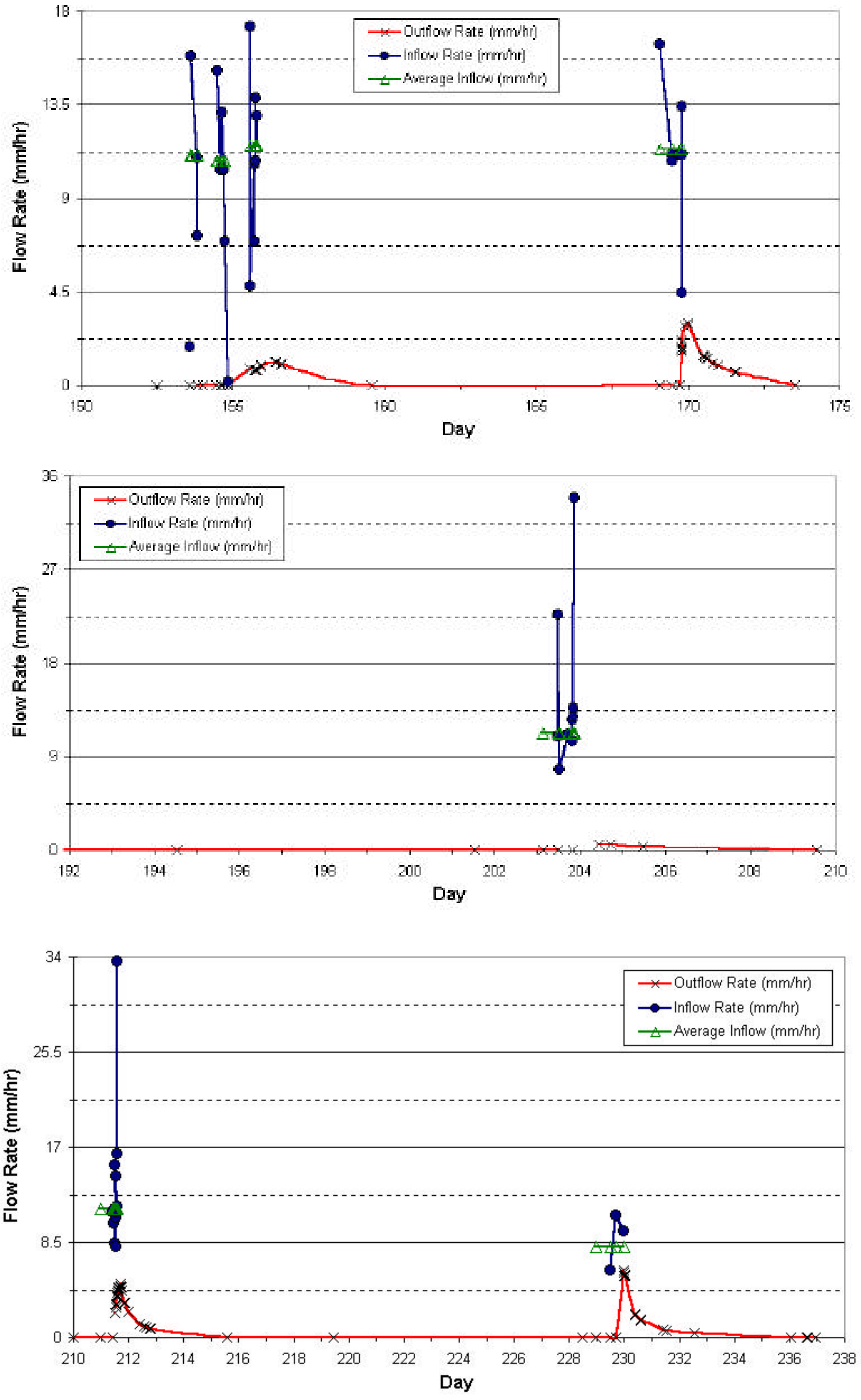


Figure A6.2 - Wet Cell Flow Data : Days 150 to 175; 192 to 210; and 210 to 238

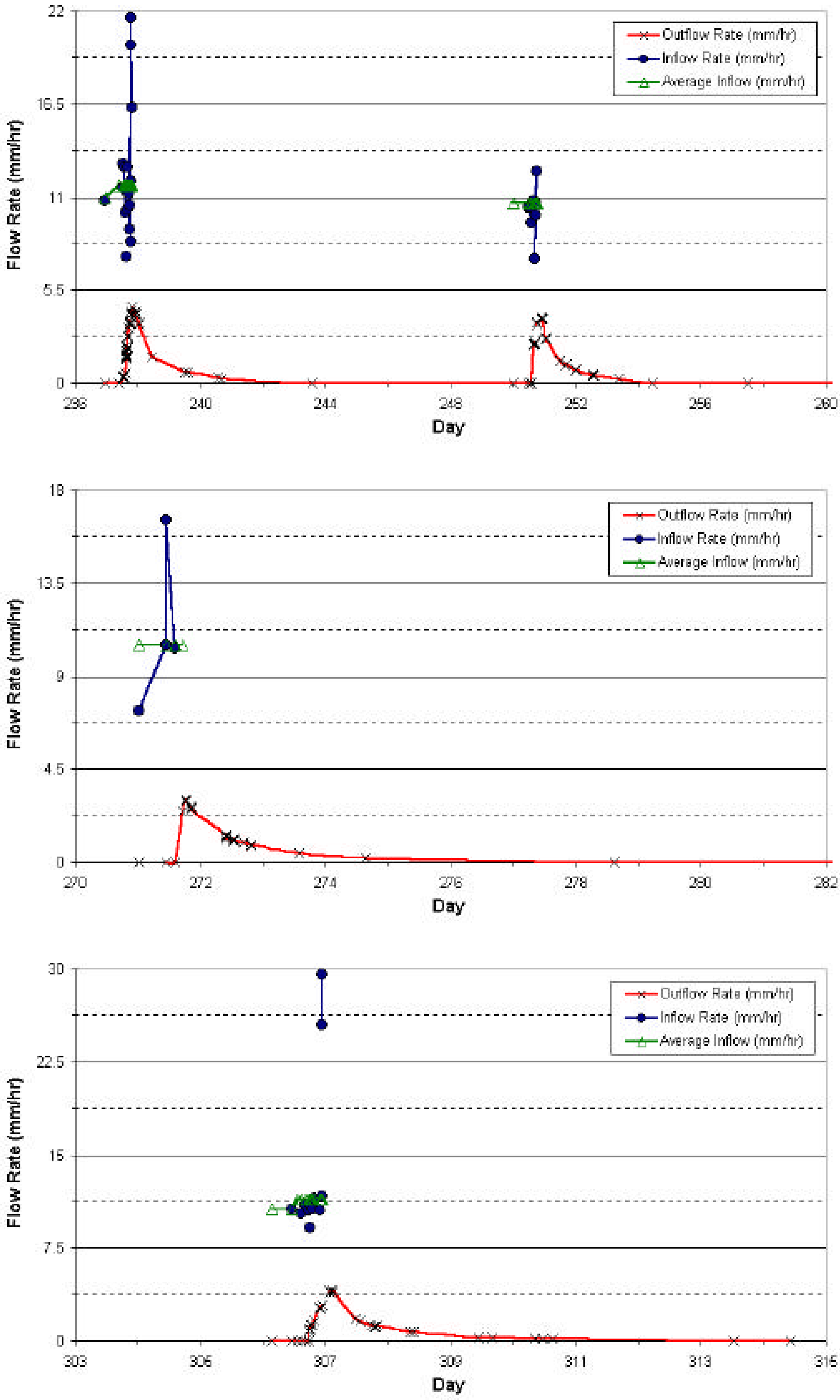


Figure A6.3 - Wet Cell Flow Data : Days 236 to 260; 270 to 282; and 303 to 315

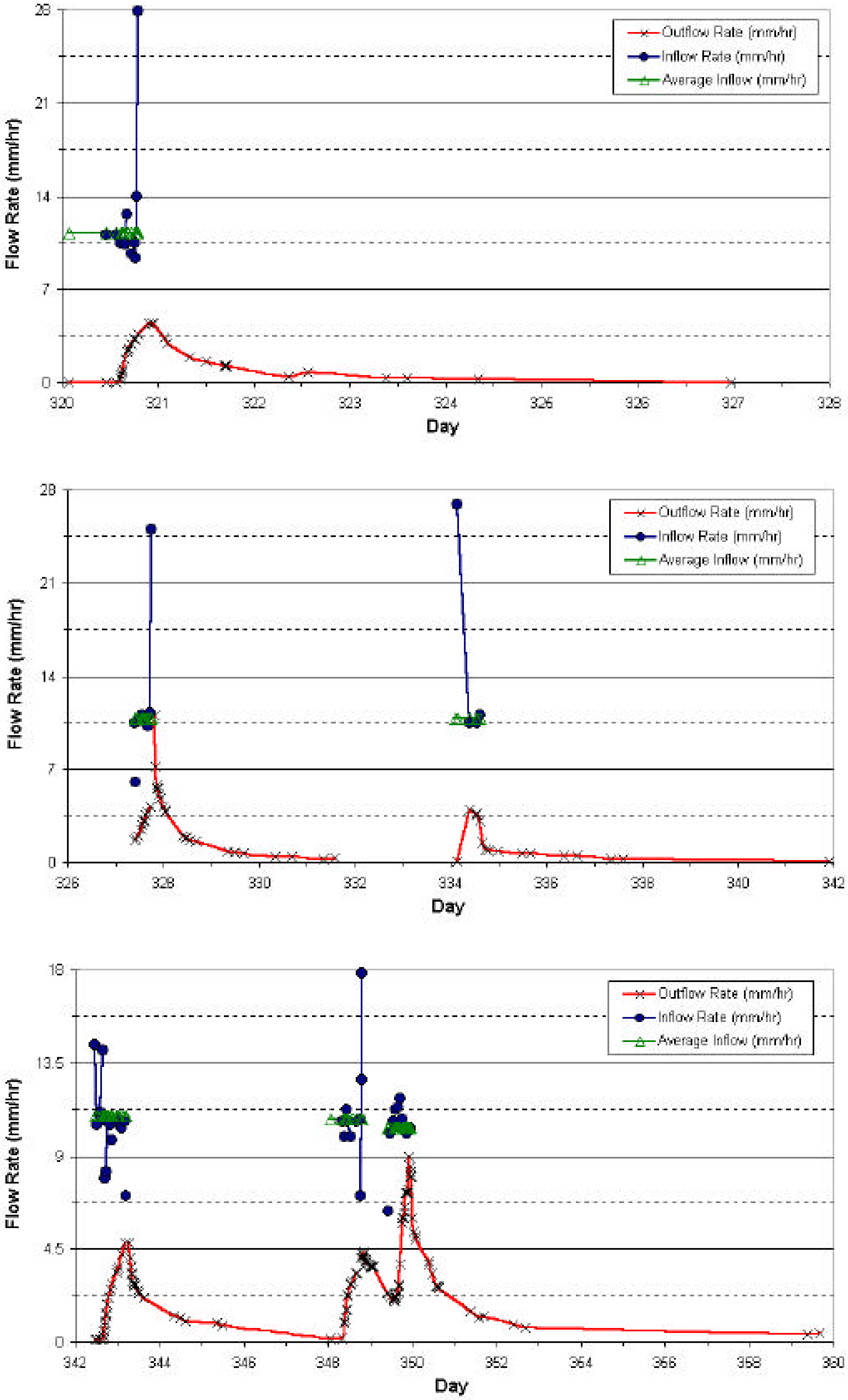
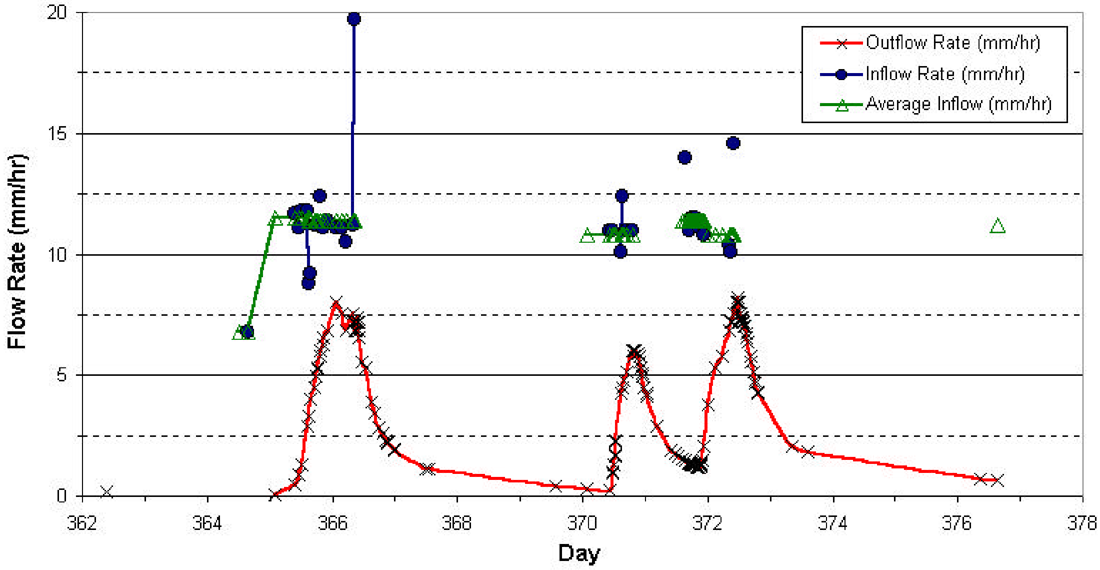


Figure A6.4 - Wet Cell Flow Data : Days 320 to 328; 326 to 342; and 342 to 360



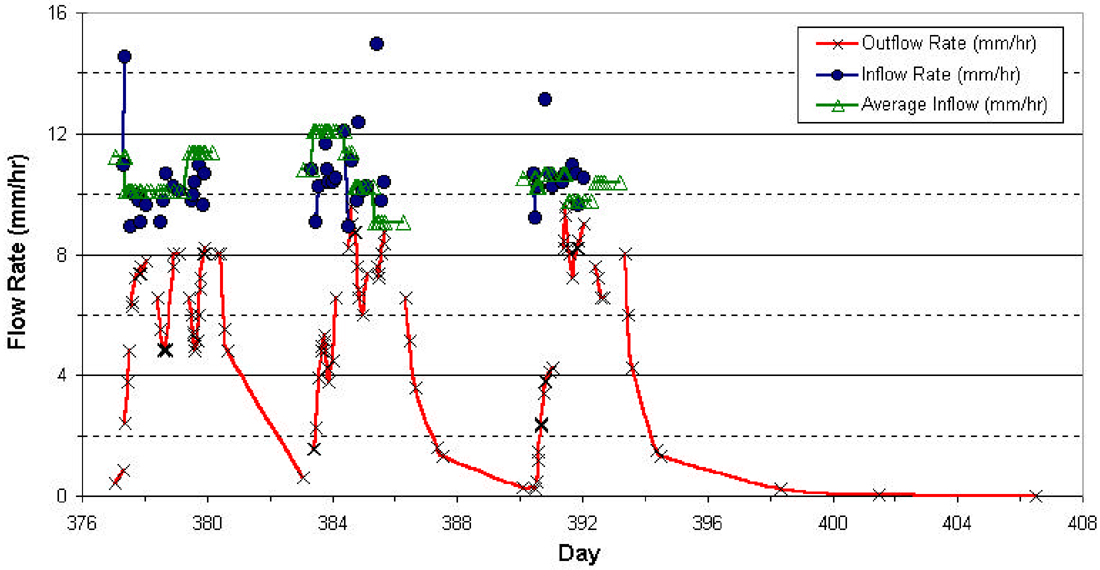


Figure A6.5 - Wet Cell Flow Data : Days 362 to 378; and 376 to 406

Table A6.1 - Wet Cell Inflow Data

Day	Date	Inflow Rate (mm/hr)	Total Inflow (mm)
0	2-Jul-97	0.00	0.0
1	3-Jul-97	0.03	1.2
2	4-Jul-97	0.05	2.0
3	5-Jul-97	0.05	2.0
4	6-Jul-97	0.06	2.4
5	7-Jul-97	0.06	2.4
6	8-Jul-97	0.51	20.4
7	9-Jul-97	0.73	29.2
8	10-Jul-97	0.75	30.0
9	11-Jul-97	0.75	30.0
10	12-Jul-97	0.75	30.0
11	13-Jul-97	0.75	30.0
12	14-Jul-97	0.75	30.0
13	15-Jul-97	0.84	33.6
14	16-Jul-97	0.92	36.8
15	17-Jul-97	0.92	36.8
16	18-Jul-97	0.93	37.2
17	19-Jul-97	0.93	37.2
18	20-Jul-97	0.94	37.6
19	21-Jul-97	0.94	37.6
20	22-Jul-97	2.85	114.0
21	23-Jul-97	2.85	114.0
22	24-Jul-97	2.85	114.0
23	25-Jul-97	2.85	114.0
24	26-Jul-97	2.85	114.0
25	27-Jul-97	2.86	114.4
26	28-Jul-97	2.93	117.2
27	29-Jul-97	2.95	118.0
28	30-Jul-97	2.96	118.4
29	31-Jul-97	2.98	119.2
30	1-Aug-97	2.98	119.2
31	2-Aug-97	2.98	119.2
32	3-Aug-97	2.98	119.2
33	4-Aug-97	2.99	119.6
34	5-Aug-97	2.99	119.6
35	6-Aug-97	2.99	119.6
36	7-Aug-97	7.72	308.8
37	8-Aug-97	7.82	312.8
38	9-Aug-97	7.87	314.8
39	10-Aug-97	7.87	314.8
40	11-Aug-97	8.15	326.0
41	12-Aug-97	8.17	326.8
42	13-Aug-97	8.17	326.8
43	14-Aug-97	8.17	326.8
44	15-Aug-97	8.17	326.8
45	16-Aug-97	8.17	326.8
46	17-Aug-97	8.37	334.8
47	18-Aug-97	8.46	338.4
48	19-Aug-97	8.48	339.2
49	20-Aug-97	8.48	339.2
50	21-Aug-97	8.48	339.2
51	22-Aug-97	8.48	339.2
52	23-Aug-97	8.68	347.2
53	24-Aug-97	9.05	362.0
54	25-Aug-97	9.09	363.6
55	26-Aug-97	9.28	371.2
56	27-Aug-97	10.11	404.4
57	28-Aug-97	12.83	513.2
58	29-Aug-97	12.83	513.2
59	30-Aug-97	12.83	513.2
60	31-Aug-97	12.83	513.2
61	1-Sep-97	12.86	514.4
62	2-Sep-97	13.03	521.2
63	3-Sep-97	13.06	522.4
64	4-Sep-97	13.24	529.6
65	5-Sep-97	13.24	529.6
66	6-Sep-97	13.24	529.6
67	7-Sep-97	13.53	541.2
68	8-Sep-97	13.62	544.8
69	9-Sep-97	13.62	544.8
70	10-Sep-97	13.62	544.8
71	11-Sep-97	15.92	636.8
72	12-Sep-97	17.39	695.6
73	13-Sep-97	17.39	695.6
74	14-Sep-97	17.66	706.4
75	15-Sep-97	17.77	710.8
76	16-Sep-97	17.77	710.8
77	17-Sep-97	17.77	710.8
78	18-Sep-97	22.56	902.4
79	19-Sep-97	22.78	911.2
80	20-Sep-97	22.78	911.2
81	21-Sep-97	22.78	911.2
82	22-Sep-97	22.83	913.2
83	23-Sep-97	22.90	916.0
84	24-Sep-97	22.90	916.0
85	25-Sep-97	22.90	916.0
86	26-Sep-97	22.90	916.0
87	27-Sep-97	22.98	919.2
88	28-Sep-97	22.98	919.2
89	29-Sep-97	22.98	919.2
90	30-Sep-97	22.98	919.2
91	1-Oct-97	23.00	920.0
92	2-Oct-97	23.13	925.2
93	3-Oct-97	23.13	925.2
94	4-Oct-97	23.13	925.2
95	5-Oct-97	23.13	925.2
96	6-Oct-97	23.13	925.2
97	7-Oct-97	23.13	925.2
98	8-Oct-97	23.34	933.6
99	9-Oct-97	23.34	933.6
100	10-Oct-97	23.34	933.6
101	11-Oct-97	23.34	933.6

Table A6.1 (cont'd) - Wet Cell Inflow Data

Day	Date	Inflow Rate (mm/hr)	Total Inflow (mm)
102	12-Oct-97	23.44	937.6
103	13-Oct-97	23.55	942.0
104	14-Oct-97	23.78	951.2
105	15-Oct-97	28.78	1151.2
106	16-Oct-97	28.84	1153.6
107	17-Oct-97	28.93	1157.2
108	18-Oct-97	28.95	1158.0
109	19-Oct-97	28.97	1158.8
110	20-Oct-97	28.97	1158.8
111	21-Oct-97	28.97	1158.8
112	22-Oct-97	28.97	1158.8
113	23-Oct-97	28.97	1158.8
114	24-Oct-97	28.97	1158.8
115	25-Oct-97	28.97	1158.8
116	26-Oct-97	28.97	1158.8
117	27-Oct-97	28.97	1158.8
118	28-Oct-97	28.97	1158.8
119	29-Oct-97	28.97	1158.8
120	30-Oct-97	29.21	1168.4
121	31-Oct-97	29.34	1173.6
122	1-Nov-97	29.41	1176.4
123	2-Nov-97	29.42	1176.8
124	3-Nov-97	33.25	1330.0
125	4-Nov-97	34.42	1376.8
126	5-Nov-97	34.42	1376.8
127	6-Nov-97	34.43	1377.2
128	7-Nov-97	34.43	1377.2
129	8-Nov-97	34.43	1377.2
130	9-Nov-97	34.43	1377.2
131	10-Nov-97	34.74	1389.6
132	11-Nov-97	35.10	1404.0
133	12-Nov-97	35.10	1404.0
134	13-Nov-97	35.10	1404.0
135	14-Nov-97	35.70	1428.0
136	15-Nov-97	35.70	1428.0
137	16-Nov-97	35.91	1436.4
138	17-Nov-97	38.61	1544.4
139	18-Nov-97	40.74	1629.6
140	19-Nov-97	40.74	1629.6
141	20-Nov-97	40.74	1629.6
142	21-Nov-97	40.74	1629.6
143	22-Nov-97	40.74	1629.6
144	23-Nov-97	40.74	1629.6
145	24-Nov-97	40.74	1629.6
146	25-Nov-97	40.74	1629.6
147	26-Nov-97	40.74	1629.6
148	27-Nov-97	40.79	1631.6
149	28-Nov-97	40.79	1631.6
150	29-Nov-97	40.89	1635.6
151	30-Nov-97	40.89	1635.6
152	1-Dec-97	40.89	1635.6
153	2-Dec-97	42.67	1706.8
154	3-Dec-97	44.43	1777.2
155	4-Dec-97	45.90	1836.0
156	5-Dec-97	45.98	1839.2
157	6-Dec-97	45.98	1839.2
158	7-Dec-97	45.98	1839.2
159	8-Dec-97	45.98	1839.2
160	9-Dec-97	45.98	1839.2
161	10-Dec-97	45.98	1839.2
162	11-Dec-97	45.98	1839.2
163	12-Dec-97	45.98	1839.2
164	13-Dec-97	45.98	1839.2
165	14-Dec-97	46.08	1843.2
166	15-Dec-97	46.08	1843.2
167	16-Dec-97	46.08	1843.2
168	17-Dec-97	46.08	1843.2
169	18-Dec-97	50.99	2039.6
170	19-Dec-97	51.22	2048.8
171	20-Dec-97	51.26	2050.4
172	21-Dec-97	51.26	2050.4
173	22-Dec-97	51.26	2050.4
174	23-Dec-97	51.26	2050.4
175	24-Dec-97	51.31	2052.4
176	25-Dec-97	51.31	2052.4
177	26-Dec-97	51.31	2052.4
178	27-Dec-97	51.31	2052.4
179	28-Dec-97	51.31	2052.4
180	29-Dec-97	51.31	2052.4
181	30-Dec-97	51.31	2052.4
182	31-Dec-97	51.31	2052.4
183	1-Jan-98	51.31	2052.4
184	2-Jan-98	51.31	2052.4
185	3-Jan-98	51.31	2052.4
186	4-Jan-98	51.31	2052.4
187	5-Jan-98	51.31	2052.4
188	6-Jan-98	51.31	2052.4
189	7-Jan-98	51.31	2052.4
190	8-Jan-98	51.31	2052.4
191	9-Jan-98	51.31	2052.4
192	10-Jan-98	51.34	2053.6
193	11-Jan-98	51.55	2062.0
194	12-Jan-98	51.55	2062.0
195	13-Jan-98	51.55	2062.0
196	14-Jan-98	51.61	2064.4
197	15-Jan-98	51.74	2069.6
198	16-Jan-98	51.74	2069.6
199	17-Jan-98	51.74	2069.6
200	18-Jan-98	51.74	2069.6
201	19-Jan-98	51.74	2069.6
202	20-Jan-98	51.79	2071.6
203	21-Jan-98	56.76	2270.4

Table A6.1 (cont'd) - Wet Cell Inflow Data

Day	Date	Inflow Rate (mm/hr)	Total Inflow (mm)
204	22-Jan-98	56.76	2270.4
205	23-Jan-98	56.78	2271.2
206	24-Jan-98	56.78	2271.2
207	25-Jan-98	56.95	2278.0
208	26-Jan-98	57.48	2299.2
209	27-Jan-98	57.48	2299.2
210	28-Jan-98	57.61	2304.4
211	29-Jan-98	61.75	2470.0
212	30-Jan-98	61.76	2470.4
213	31-Jan-98	61.76	2470.4
214	1-Feb-98	61.76	2470.4
215	2-Feb-98	61.76	2470.4
216	3-Feb-98	61.77	2470.8
217	4-Feb-98	61.77	2470.8
218	5-Feb-98	61.77	2470.8
219	6-Feb-98	61.84	2473.6
220	7-Feb-98	61.84	2473.6
221	8-Feb-98	62.52	2500.8
222	9-Feb-98	62.52	2500.8
223	10-Feb-98	62.52	2500.8
224	11-Feb-98	62.52	2500.8
225	12-Feb-98	62.62	2504.8
226	13-Feb-98	62.62	2504.8
227	14-Feb-98	62.62	2504.8
228	15-Feb-98	62.80	2512.0
229	16-Feb-98	67.77	2710.8
230	17-Feb-98	68.19	2727.6
231	18-Feb-98	68.19	2727.6
232	19-Feb-98	68.19	2727.6
233	20-Feb-98	68.19	2727.6
234	21-Feb-98	68.20	2728.0
235	22-Feb-98	68.20	2728.0
236	23-Feb-98	70.07	2802.8
237	24-Feb-98	72.98	2919.2
238	25-Feb-98	72.98	2919.2
239	26-Feb-98	72.98	2919.2
240	27-Feb-98	73.00	2920.0
241	28-Feb-98	73.00	2920.0
242	1-Mar-98	73.00	2920.0
243	2-Mar-98	73.00	2920.0
244	3-Mar-98	73.00	2920.0
245	4-Mar-98	73.00	2920.0
246	5-Mar-98	73.00	2920.0
247	6-Mar-98	73.04	2921.6
248	7-Mar-98	73.04	2921.6
249	8-Mar-98	73.12	2924.8
250	9-Mar-98	78.04	3121.6
251	10-Mar-98	78.04	3121.6
252	11-Mar-98	78.04	3121.6
253	12-Mar-98	78.04	3121.6
254	13-Mar-98	78.05	3122.0
255	14-Mar-98	78.09	3123.6
256	15-Mar-98	78.09	3123.6
257	16-Mar-98	78.09	3123.6
258	17-Mar-98	78.09	3123.6
259	18-Mar-98	78.09	3123.6
260	19-Mar-98	78.09	3123.6
261	20-Mar-98	78.09	3123.6
262	21-Mar-98	78.09	3123.6
263	22-Mar-98	78.09	3123.6
264	23-Mar-98	78.14	3125.6
265	24-Mar-98	78.14	3125.6
266	25-Mar-98	78.14	3125.6
267	26-Mar-98	78.14	3125.6
268	27-Mar-98	78.14	3125.6
269	28-Mar-98	78.16	3126.4
270	29-Mar-98	78.16	3126.4
271	30-Mar-98	82.59	3303.6
272	31-Mar-98	82.60	3304.0
273	1-Apr-98	82.60	3304.0
274	2-Apr-98	82.60	3304.0
275	3-Apr-98	82.60	3304.0
276	4-Apr-98	82.62	3304.8
277	5-Apr-98	82.62	3304.8
278	6-Apr-98	82.63	3305.2
279	7-Apr-98	82.63	3305.2
280	8-Apr-98	82.63	3305.2
281	9-Apr-98	82.63	3305.2
282	10-Apr-98	82.63	3305.2
283	11-Apr-98	82.63	3305.2
284	12-Apr-98	82.88	3315.2
285	13-Apr-98	82.97	3318.8
286	14-Apr-98	82.97	3318.8
287	15-Apr-98	82.97	3318.8
288	16-Apr-98	82.97	3318.8
289	17-Apr-98	82.97	3318.8
290	18-Apr-98	82.97	3318.8
291	19-Apr-98	82.97	3318.8
292	20-Apr-98	83.18	3327.2
293	21-Apr-98	83.18	3327.2
294	22-Apr-98	83.18	3327.2
295	23-Apr-98	83.18	3327.2
296	24-Apr-98	83.18	3327.2
297	25-Apr-98	83.18	3327.2
298	26-Apr-98	83.27	3330.8
299	27-Apr-98	83.28	3331.2
300	28-Apr-98	83.28	3331.2
301	29-Apr-98	83.33	3333.2
302	30-Apr-98	83.35	3334.0
303	1-May-98	83.35	3334.0
304	2-May-98	83.35	3334.0
305	3-May-98	83.35	3334.0

Table A6.1 (cont'd) - Wet Cell Inflow Data

Day	Date	Inflow Rate (mm/hr)	Total Inflow (mm)
306	4-May-98	88.23	3529.2
307	5-May-98	88.23	3529.2
308	6-May-98	88.23	3529.2
309	7-May-98	88.24	3529.6
310	8-May-98	88.38	3535.2
311	9-May-98	88.44	3537.6
312	10-May-98	88.45	3538.0
313	11-May-98	88.46	3538.4
314	12-May-98	88.48	3539.2
315	13-May-98	88.49	3539.6
316	14-May-98	88.49	3539.6
317	15-May-98	88.49	3539.6
318	16-May-98	88.50	3540.0
319	17-May-98	88.50	3540.0
320	18-May-98	93.29	3731.6
321	19-May-98	93.29	3731.6
322	20-May-98	93.39	3735.6
323	21-May-98	93.45	3738.0
324	22-May-98	93.46	3738.4
325	23-May-98	93.46	3738.4
326	24-May-98	93.92	3756.8
327	25-May-98	98.83	3953.2
328	26-May-98	98.83	3953.2
329	27-May-98	98.83	3953.2
330	28-May-98	98.83	3953.2
331	29-May-98	98.83	3953.2
332	30-May-98	98.83	3953.2
333	31-May-98	98.83	3953.2
334	1-Jun-98	102.25	4090.0
335	2-Jun-98	102.25	4090.0
336	3-Jun-98	102.25	4090.0
337	4-Jun-98	102.25	4090.0
338	5-Jun-98	102.25	4090.0
339	6-Jun-98	102.29	4091.6
340	7-Jun-98	102.71	4108.4
341	8-Jun-98	102.75	4110.0
342	9-Jun-98	106.20	4248.0
343	10-Jun-98	107.56	4302.4
344	11-Jun-98	107.57	4302.8
345	12-Jun-98	107.57	4302.8
346	13-Jun-98	107.58	4303.2
347	14-Jun-98	107.58	4303.2
348	15-Jun-98	112.51	4500.4
349	16-Jun-98	116.14	4645.6
350	17-Jun-98	116.48	4659.2
351	18-Jun-98	116.48	4659.2
352	19-Jun-98	116.48	4659.2
353	20-Jun-98	116.48	4659.2
354	21-Jun-98	116.48	4659.2
355	22-Jun-98	116.53	4661.2
356	23-Jun-98	116.60	4664.0
357	24-Jun-98	116.77	4670.8
358	25-Jun-98	116.92	4676.8
359	26-Jun-98	116.93	4677.2
360	27-Jun-98	116.93	4677.2
361	28-Jun-98	116.93	4677.2
362	29-Jun-98	116.94	4677.6
363	30-Jun-98	116.94	4677.6
364	1-Jul-98	117.45	4698.0
365	2-Jul-98	123.78	4951.2
366	3-Jul-98	126.26	5050.4
367	4-Jul-98	126.26	5050.4
368	5-Jul-98	126.26	5050.4
369	6-Jul-98	126.37	5054.8
370	7-Jul-98	131.13	5245.2
371	8-Jul-98	133.53	5341.2
372	9-Jul-98	136.45	5458.0
373	10-Jul-98	136.54	5461.6
374	11-Jul-98	136.56	5462.4
375	12-Jul-98	136.56	5462.4
376	13-Jul-98	139.02	5560.8
377	14-Jul-98	145.32	5812.8
378	15-Jul-98	150.09	6003.6
379	16-Jul-98	155.30	6212.0
380	17-Jul-98	156.66	6266.4
381	18-Jul-98	156.66	6266.4
382	19-Jul-98	156.66	6266.4
383	20-Jul-98	161.05	6442.0
384	21-Jul-98	166.62	6664.8
385	22-Jul-98	172.73	6909.2
386	23-Jul-98	173.45	6938.0
387	24-Jul-98	173.46	6938.4
388	25-Jul-98	173.46	6938.4
389	26-Jul-98	173.46	6938.4
390	27-Jul-98	178.16	7126.4
391	28-Jul-98	184.00	7360.0
392	29-Jul-98	189.30	7572.0
393	30-Jul-98	190.39	7615.6
394	31-Jul-98	190.42	7616.8

Table A6.2 - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
7-Jul-97 11:09:36	0.284	18.8
8-Jul-97 15:50:24	0.266	26.4
9-Jul-97 15:48:58	0.308	33.2
14-Jul-97 1:59:31	0.145	57.6
15-Jul-97 15:33:07	0.111	62.4
16-Jul-97 9:46:05	0.128	64.4
18-Jul-97 13:13:26	0.114	70.8
18-Jul-97 13:37:55	0.105	70.8
21-Jul-97 12:04:19	0.073	77.2
21-Jul-97 15:27:22	0.068	77.2
22-Jul-97 10:09:07	0.076	78.4
22-Jul-97 12:54:43	0.082	78.8
25-Jul-97 13:10:34	0.291	92.4
25-Jul-97 13:49:26	0.272	92.4
25-Jul-97 13:56:38	0.300	92.4
1-Aug-97 16:22:05	0.026	120
7-Aug-97 11:54:14	0.926	186.4
7-Aug-97 12:00:00	0.919	186.8
7-Aug-97 14:25:26	1.107	189.2
11-Aug-97 12:20:10	0.253	253.2
11-Aug-97 12:34:34	0.242	253.2
11-Aug-97 16:06:14	0.384	254
11-Aug-97 16:59:31	0.480	254.4
18-Aug-97 13:04:48	0.039	297.2
25-Aug-97 12:50:24	0.432	336.4
25-Aug-97 12:57:36	0.480	336.8
25-Aug-97 15:31:41	0.400	337.6
26-Aug-97 12:08:38	0.576	348
26-Aug-97 13:16:19	0.541	348.4
26-Aug-97 15:38:53	0.533	349.6
26-Aug-97 16:27:50	0.554	350
27-Aug-97 10:01:55	0.576	360
27-Aug-97 11:55:41	0.576	361.2
27-Aug-97 13:03:22	0.586	362
27-Aug-97 22:26:24	0.576	367.2
28-Aug-97 11:03:50	0.766	375.6
28-Aug-97 15:23:02	0.766	379.2
28-Aug-97 15:51:50	0.757	379.6
28-Aug-97 16:06:14	0.720	379.6
28-Aug-97 20:38:24	1.200	384
28-Aug-97 20:42:43	1.241	384
29-Aug-97 10:22:05	2.118	406.8
29-Aug-97 14:48:29	1.895	416
29-Aug-97 14:54:14	1.757	416
29-Aug-97 14:57:07	1.800	416
1-Sep-97 13:30:43	0.432	494.8
1-Sep-97 13:33:36	0.480	494.8
2-Sep-97 16:14:53	0.420	506.8
8-Sep-97 11:42:43	0.265	554.8
8-Sep-97 11:48:29	0.288	554.8
11-Sep-97 14:48:29	0.271	575.6
11-Sep-97 23:11:02	0.242	577.6
12-Sep-97 10:53:46	1.125	585.6
12-Sep-97 11:24:00	1.200	586.4
12-Sep-97 15:50:24	1.800	593.2
12-Sep-97 16:13:26	2.058	593.6
12-Sep-97 20:12:29	2.769	603.6
15-Sep-97 13:43:41	0.618	714.4
15-Sep-97 13:46:34	0.600	714.4
18-Sep-97 0:11:31	0.376	742.8
18-Sep-97 10:14:53	1.309	751.2
18-Sep-97 10:45:07	1.542	752
18-Sep-97 10:55:12	1.662	752.4
18-Sep-97 15:57:36	4.235	767.2
18-Sep-97 16:07:41	4.548	768
18-Sep-97 16:20:38	4.645	768.8
18-Sep-97 18:54:43	5.142	781.6
18-Sep-97 23:31:12	4.645	804
19-Sep-97 8:49:55	2.251	836
19-Sep-97 9:27:22	2.251	837.6
19-Sep-97 12:33:07	1.920	844
19-Sep-97 13:16:19	1.846	845.2
19-Sep-97 16:37:55	1.600	851.2
19-Sep-97 18:46:05	1.500	854.4
22-Sep-97 12:36:00	0.405	917.2
22-Sep-97 12:43:12	0.480	917.2
25-Sep-97 9:00:00	0.036	934.8
29-Sep-97 12:10:05	0.216	947.2
30-Sep-97 8:29:46	0.000	949.6
6-Oct-97 13:30:43	0.000	949.6
7-Oct-97 12:50:24	0.000	949.6
13-Oct-97 13:14:53	0.000	949.6
15-Oct-97 1:03:22	0.000	949.6
15-Oct-97 19:13:26	0.000	949.6
16-Oct-97 0:02:53	3.131	957.2
16-Oct-97 10:35:02	1.757	982.8
16-Oct-97 10:39:22	1.846	982.8
16-Oct-97 10:45:07	1.800	983.2
16-Oct-97 14:44:10	1.469	989.6
16-Oct-97 14:47:02	1.469	989.6
16-Oct-97 15:30:14	1.440	990.8
16-Oct-97 18:27:22	1.263	994.8
16-Oct-97 18:34:34	1.253	994.8
16-Oct-97 23:41:17	1.044	1000.8
16-Oct-97 23:48:29	1.035	1000.8
16-Oct-97 23:52:48	1.028	1000.8
17-Oct-97 10:30:43	0.727	1010.4
17-Oct-97 10:48:00	0.734	1010.4
17-Oct-97 14:41:17	0.655	1013.2
17-Oct-97 14:48:29	0.655	1013.2
20-Oct-97 13:30:43	0.072	1038.8
21-Oct-97 15:00:00	0.000	1040

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
27-Oct-97 13:00:29	0.000	1040
3-Nov-97 16:45:07	0.099	1048.4
3-Nov-97 23:57:07	1.159	1052.8
4-Nov-97 0:00:00	1.174	1052.8
4-Nov-97 0:05:46	1.188	1052.8
4-Nov-97 11:28:19	0.914	1064.8
4-Nov-97 17:41:17	0.760	1070
4-Nov-97 17:45:36	0.749	1070.4
4-Nov-97 17:51:22	0.755	1070.4
5-Nov-97 0:31:41	0.595	1074.8
5-Nov-97 0:36:00	0.595	1074.8
5-Nov-97 10:52:19	0.432	1080
5-Nov-97 10:56:38	0.432	1080
5-Nov-97 11:31:12	0.428	1080.4
5-Nov-97 20:11:02	0.321	1083.6
5-Nov-97 20:16:48	0.321	1083.6
6-Nov-97 11:03:50	0.305	1088.4
6-Nov-97 14:13:55	0.336	1089.2
6-Nov-97 14:18:14	0.334	1089.2
6-Nov-97 14:26:53	0.272	1089.2
10-Nov-97 13:55:12	0.000	1102.4
17-Nov-97 9:47:31	0.118	1112
17-Nov-97 11:06:43	0.148	1112
17-Nov-97 13:42:14	0.163	1112.4
17-Nov-97 15:18:43	0.137	1112.8
17-Nov-97 18:46:05	0.504	1114
17-Nov-97 18:51:50	0.554	1114
17-Nov-97 18:56:10	0.586	1114
17-Nov-97 19:00:29	0.626	1114
17-Nov-97 19:33:36	0.948	1114.4
17-Nov-97 20:31:12	1.565	1115.6
17-Nov-97 20:34:05	1.636	1115.6
17-Nov-97 20:44:10	1.945	1116
17-Nov-97 21:25:55	2.182	1117.6
17-Nov-97 21:33:07	2.150	1117.6
18-Nov-97 0:40:19	1.693	1123.6
18-Nov-97 0:57:36	1.636	1124.4
18-Nov-97 1:01:55	1.675	1124.4
18-Nov-97 10:32:10	1.440	1139.2
18-Nov-97 10:35:02	1.426	1139.2
18-Nov-97 10:39:22	1.411	1139.2
18-Nov-97 10:42:14	1.426	1139.2
18-Nov-97 12:04:19	1.426	1141.2
18-Nov-97 12:07:12	1.411	1141.6
18-Nov-97 12:10:05	1.411	1141.6
18-Nov-97 14:16:48	1.411	1144.4
18-Nov-97 15:27:22	1.800	1146.4
18-Nov-97 15:41:46	1.823	1146.8
18-Nov-97 15:44:38	1.920	1146.8
18-Nov-97 15:48:58	1.973	1147.2
18-Nov-97 16:40:48	2.400	1148.8
18-Nov-97 16:46:34	2.441	1149.2
18-Nov-97 16:55:12	2.483	1149.6
18-Nov-97 16:58:05	2.483	1149.6
18-Nov-97 17:31:12	2.880	1151.2
18-Nov-97 17:35:31	2.880	1151.2
18-Nov-97 17:57:07	3.000	1152.4
18-Nov-97 18:00:00	3.131	1152.4
18-Nov-97 19:12:00	3.600	1156.4
18-Nov-97 19:17:46	3.600	1156.8
18-Nov-97 19:19:12	3.600	1156.8
18-Nov-97 19:48:00	3.892	1158.8
18-Nov-97 19:50:53	3.892	1158.8
18-Nov-97 20:18:14	3.790	1160.8
18-Nov-97 20:21:07	3.692	1160.8
18-Nov-97 20:26:53	3.840	1161.2
18-Nov-97 20:36:58	3.840	1162
18-Nov-97 21:46:05	3.600	1166
18-Nov-97 21:51:50	3.600	1166.4
18-Nov-97 22:07:41	3.512	1167.6
19-Nov-97 0:36:00	3.131	1175.6
19-Nov-97 0:40:19	3.131	1176
19-Nov-97 10:40:48	1.846	1200.8
19-Nov-97 10:46:34	1.846	1200.8
19-Nov-97 10:49:26	1.895	1201.2
19-Nov-97 10:52:19	1.895	1201.2
19-Nov-97 10:55:12	1.895	1201.2
19-Nov-97 13:22:05	1.714	1205.6
19-Nov-97 13:22:05	1.714	1205.6
19-Nov-97 13:52:19	1.675	1206.4
19-Nov-97 13:55:12	1.693	1206.4
19-Nov-97 13:58:05	1.693	1206.8
19-Nov-97 15:34:34	1.565	1209.2
19-Nov-97 15:37:26	1.583	1209.2
19-Nov-97 15:40:19	1.565	1209.6
19-Nov-97 18:05:46	1.485	1213.2
19-Nov-97 18:08:38	1.469	1213.2
19-Nov-97 18:11:31	1.454	1213.2
19-Nov-97 18:12:58	1.447	1213.2
20-Nov-97 9:20:10	0.960	1231.6
20-Nov-97 16:07:41	0.864	1237.6
21-Nov-97 8:21:07	0.618	1249.6
24-Nov-97 12:02:53	0.027	1274
1-Dec-97 12:02:53	0.000	1276.4
2-Dec-97 14:02:24	0.000	1276.4
2-Dec-97 19:33:36	0.000	1276.4
3-Dec-97 0:30:14	0.000	1276.4
3-Dec-97 10:49:26	0.000	1276.4
3-Dec-97 14:02:24	0.000	1276.4
3-Dec-97 14:34:05	0.000	1276.4
3-Dec-97 17:09:36	0.000	1276.4
3-Dec-97 19:56:38	0.000	1276.4

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
4-Dec-97 13:33:36	0.785	1283.2
4-Dec-97 13:36:29	0.785	1283.2
4-Dec-97 13:40:48	0.785	1283.2
4-Dec-97 13:49:26	0.785	1283.6
4-Dec-97 17:05:17	0.757	1286
4-Dec-97 17:34:05	0.752	1286.4
4-Dec-97 18:41:46	0.732	1287.2
4-Dec-97 18:47:31	0.732	1287.2
4-Dec-97 18:51:50	0.732	1287.2
4-Dec-97 22:19:12	0.900	1290
4-Dec-97 22:22:05	0.939	1290.4
4-Dec-97 22:27:50	0.939	1290.4
4-Dec-97 22:30:43	0.939	1290.4
5-Dec-97 9:40:19	1.136	1302
5-Dec-97 9:43:12	1.136	1302
5-Dec-97 9:46:05	1.122	1302
5-Dec-97 9:51:50	1.107	1302
5-Dec-97 9:54:43	1.136	1302
5-Dec-97 13:42:14	1.028	1306.4
5-Dec-97 13:43:41	1.017	1306.4
5-Dec-97 13:46:34	1.005	1306.4
5-Dec-97 13:49:26	1.005	1306.4
5-Dec-97 15:01:26	0.982	1307.6
8-Dec-97 13:45:07	0.000	1342.4
18-Dec-97 2:13:55	0.000	1342.4
18-Dec-97 11:16:48	0.000	1342.4
18-Dec-97 17:19:41	0.000	1342.4
18-Dec-97 18:50:24	1.662	1343.6
18-Dec-97 18:51:50	1.693	1343.6
18-Dec-97 18:54:43	1.800	1343.6
18-Dec-97 19:09:07	1.878	1344
18-Dec-97 19:23:31	2.058	1344.8
18-Dec-97 19:30:43	2.160	1344.8
18-Dec-97 20:26:53	2.880	1347.2
18-Dec-97 20:34:05	2.880	1347.6
18-Dec-97 20:39:50	2.880	1348
19-Dec-97 0:27:22	2.880	1358.8
19-Dec-97 0:27:22	2.979	1358.8
19-Dec-97 0:28:48	2.880	1358.8
19-Dec-97 0:31:41	2.979	1358.8
19-Dec-97 0:33:07	2.979	1359.2
19-Dec-97 11:51:22	1.440	1384
19-Dec-97 11:54:14	1.440	1384
19-Dec-97 11:58:34	1.440	1384.4
19-Dec-97 12:02:53	1.440	1384.4
19-Dec-97 12:47:31	1.417	1385.2
19-Dec-97 13:24:58	1.351	1386.4
19-Dec-97 13:27:50	1.371	1386.4
19-Dec-97 13:32:10	1.351	1386.4
19-Dec-97 14:41:17	1.270	1388
19-Dec-97 14:44:10	1.309	1388
19-Dec-97 14:45:36	1.309	1388
19-Dec-97 19:19:12	1.054	1393.6
19-Dec-97 19:22:05	1.080	1393.6
19-Dec-97 19:26:24	1.080	1393.6
19-Dec-97 19:30:43	1.080	1393.6
19-Dec-97 23:48:29	0.939	1398
19-Dec-97 23:49:55	0.929	1398
19-Dec-97 23:52:48	0.939	1398
19-Dec-97 23:54:14	0.939	1398
20-Dec-97 13:10:34	0.609	1408.4
20-Dec-97 13:13:26	0.609	1408.4
20-Dec-97 13:16:19	0.609	1408.4
22-Dec-97 12:50:24	0.000	1422.8
29-Dec-97 12:50:24	0.000	1422.8
5-Jan-98 12:50:24	0.000	1422.8
12-Jan-98 12:50:24	0.000	1422.8
19-Jan-98 12:50:24	0.000	1422.8
21-Jan-98 2:55:41	0.000	1422.8
21-Jan-98 11:38:24	0.000	1422.8
21-Jan-98 19:33:36	0.000	1422.8
22-Jan-98 10:37:55	0.500	1426.8
22-Jan-98 10:43:41	0.500	1426.8
22-Jan-98 17:12:29	0.492	1430
22-Jan-98 17:21:07	0.487	1430
22-Jan-98 17:28:19	0.485	1430
23-Jan-98 11:03:50	0.327	1437.2
23-Jan-98 11:18:14	0.323	1437.2
23-Jan-98 11:22:34	0.323	1437.2
27-Jan-98 13:20:38	0.000	1453.2
28-Jan-98 0:14:24	0.000	1454.8
28-Jan-98 23:35:31	0.000	1454.8
29-Jan-98 10:17:46	0.000	1454.8
29-Jan-98 12:15:50	2.215	1457.2
29-Jan-98 12:18:43	2.160	1457.2
29-Jan-98 12:18:43	2.160	1457.2
29-Jan-98 12:53:17	2.667	1458.4
29-Jan-98 12:56:10	2.667	1458.4
29-Jan-98 13:17:46	2.880	1459.6
29-Jan-98 13:19:12	3.000	1459.6
29-Jan-98 13:22:05	3.000	1460
29-Jan-98 14:03:50	3.600	1462
29-Jan-98 14:06:43	3.600	1462.4
29-Jan-98 14:09:36	3.692	1462.4
29-Jan-98 14:25:26	3.790	1463.6
29-Jan-98 14:26:53	4.000	1463.6
29-Jan-98 14:29:46	4.000	1463.6
29-Jan-98 14:55:41	4.051	1465.6
29-Jan-98 15:00:00	4.180	1465.6
29-Jan-98 15:02:53	4.363	1466
29-Jan-98 15:05:46	4.363	1466
29-Jan-98 15:07:12	4.500	1466.4

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
29-Jan-98 15:08:38	4.500	1466.4
29-Jan-98 16:53:46	4.800	1474.8
29-Jan-98 16:56:38	4.800	1474.8
29-Jan-98 17:00:58	4.800	1475.2
29-Jan-98 17:22:34	4.645	1476.8
29-Jan-98 17:24:00	4.645	1476.8
29-Jan-98 17:26:53	4.500	1477.2
29-Jan-98 17:29:46	4.500	1477.2
29-Jan-98 17:32:38	4.500	1477.6
29-Jan-98 18:02:53	4.235	1479.6
29-Jan-98 18:02:53	4.235	1480
29-Jan-98 18:05:46	4.235	1480
29-Jan-98 20:21:07	3.131	1488.4
29-Jan-98 20:24:00	3.131	1488.4
29-Jan-98 20:26:53	3.064	1488.4
29-Jan-98 20:29:46	3.131	1488.8
29-Jan-98 20:32:38	3.097	1488.8
29-Jan-98 23:36:58	2.323	1497.2
29-Jan-98 23:38:24	2.285	1497.2
29-Jan-98 23:41:17	2.285	1497.6
30-Jan-98 9:54:43	1.200	1515.2
30-Jan-98 9:57:36	1.210	1515.2
30-Jan-98 10:00:29	1.200	1515.2
30-Jan-98 10:04:48	1.200	1515.6
30-Jan-98 13:35:02	1.028	1519.2
30-Jan-98 13:36:29	1.028	1519.2
30-Jan-98 15:34:34	0.939	1521.2
30-Jan-98 15:37:26	0.939	1521.2
30-Jan-98 18:53:17	0.815	1524
30-Jan-98 18:57:36	0.815	1524.4
30-Jan-98 19:00:29	0.808	1524.4
30-Jan-98 19:06:14	0.815	1524.4
2-Feb-98 13:33:36	0.000	1551.6
6-Feb-98 10:49:26	0.000	1551.6
15-Feb-98 11:18:14	0.000	1551.6
16-Feb-98 11:25:26	0.000	1551.6
16-Feb-98 16:26:24	0.000	1551.6
16-Feb-98 23:42:43	5.760	1572.4
16-Feb-98 23:42:43	5.538	1572.4
16-Feb-98 23:44:10	5.760	1572.4
16-Feb-98 23:45:36	6.000	1572.8
16-Feb-98 23:48:29	6.000	1572.8
16-Feb-98 23:49:55	6.000	1573.2
16-Feb-98 23:51:22	6.000	1573.2
17-Feb-98 0:24:29	5.538	1576.4
17-Feb-98 0:25:55	5.538	1576.4
17-Feb-98 0:27:22	5.648	1576.8
17-Feb-98 9:33:07	2.028	1611.6
17-Feb-98 9:34:34	2.058	1611.6
17-Feb-98 9:36:00	2.058	1611.6
17-Feb-98 14:05:17	1.565	1620

Date & Time	Outflow Rate mm/hr	Total Outflow mm
17-Feb-98 14:08:10	1.565	1620
17-Feb-98 14:09:36	1.532	1620
17-Feb-98 14:12:29	1.565	1620
18-Feb-98 9:31:41	0.744	1642.4
18-Feb-98 9:33:07	0.732	1642.4
18-Feb-98 13:06:14	0.618	1644.8
18-Feb-98 13:09:07	0.609	1644.8
19-Feb-98 13:32:10	0.412	1657.2
19-Feb-98 13:35:02	0.408	1657.2
23-Feb-98 1:30:43	0.000	1674.4
23-Feb-98 14:51:22	0.000	1674.4
23-Feb-98 15:56:10	0.000	1674.4
23-Feb-98 22:48:00	0.000	1674.4
24-Feb-98 9:25:55	0.000	1674.4
24-Feb-98 12:51:50	0.408	1675.2
24-Feb-98 12:57:36	0.333	1675.2
24-Feb-98 13:01:55	0.363	1675.2
24-Feb-98 13:04:48	0.366	1675.2
24-Feb-98 13:35:02	0.415	1675.2
24-Feb-98 14:08:10	0.576	1675.6
24-Feb-98 15:08:38	1.440	1676.4
24-Feb-98 15:10:05	1.516	1676.8
24-Feb-98 15:12:58	1.529	1676.8
24-Feb-98 15:12:58	1.585	1676.8
24-Feb-98 15:15:50	1.600	1676.8
24-Feb-98 15:17:17	1.646	1676.8
24-Feb-98 15:20:10	1.693	1676.8
24-Feb-98 15:31:41	1.858	1677.2
24-Feb-98 15:31:41	1.899	1677.2
24-Feb-98 15:33:07	1.920	1677.2
24-Feb-98 15:36:00	1.964	1677.2
24-Feb-98 15:44:38	2.187	1677.6
24-Feb-98 15:44:38	2.082	1677.6
24-Feb-98 15:47:31	2.133	1677.6
24-Feb-98 15:50:24	2.107	1678
24-Feb-98 16:30:43	2.786	1679.6
24-Feb-98 16:32:10	2.700	1679.6
24-Feb-98 17:13:55	3.273	1681.6
24-Feb-98 17:16:48	3.273	1681.6
24-Feb-98 17:36:58	3.429	1682.8
24-Feb-98 17:39:50	3.512	1683.2
24-Feb-98 17:42:43	3.600	1683.2
24-Feb-98 17:47:02	3.512	1683.6
24-Feb-98 17:54:14	3.692	1684
24-Feb-98 17:57:07	3.692	1684
24-Feb-98 18:25:55	4.114	1686
24-Feb-98 18:27:22	4.000	1686
24-Feb-98 18:30:14	4.056	1686.4
24-Feb-98 18:54:43	4.235	1688
24-Feb-98 18:57:36	4.235	1688
24-Feb-98 19:24:58	4.500	1690.4

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
24-Feb-98 19:26:24	4.500	1690.4
24-Feb-98 19:27:50	4.500	1690.4
24-Feb-98 22:14:53	4.000	1702
24-Feb-98 22:16:19	4.114	1702.4
24-Feb-98 22:17:46	4.114	1702.4
24-Feb-98 22:20:38	4.235	1702.4
24-Feb-98 22:20:38	4.114	1702.8
25-Feb-98 0:44:38	3.600	1712
25-Feb-98 0:44:38	3.429	1712
25-Feb-98 0:46:05	3.429	1712
25-Feb-98 10:23:31	1.565	1736
25-Feb-98 10:24:58	1.565	1736
25-Feb-98 10:26:24	1.583	1736
25-Feb-98 10:29:17	1.565	1736
26-Feb-98 11:45:36	0.675	1764.4
26-Feb-98 14:31:12	0.655	1766.4
27-Feb-98 13:17:46	0.318	1777.2
27-Feb-98 15:47:31	0.261	1778
2-Mar-98 13:30:43	0.000	1787.2
8-Mar-98 23:42:43	0.000	1787.2
9-Mar-98 11:34:05	0.000	1787.2
9-Mar-98 12:48:58	0.000	1787.2
9-Mar-98 13:32:10	0.000	1787.2
9-Mar-98 15:56:10	2.251	1790
9-Mar-98 16:01:55	2.323	1790
9-Mar-98 16:04:48	2.360	1790
9-Mar-98 16:10:34	2.400	1790.4
9-Mar-98 18:07:12	3.429	1796
9-Mar-98 18:08:38	3.429	1796
9-Mar-98 18:10:05	3.600	1796.4
9-Mar-98 21:38:53	3.790	1809.2
9-Mar-98 21:40:19	3.892	1809.2
9-Mar-98 21:41:46	3.790	1809.2
9-Mar-98 21:54:43	3.790	1810
10-Mar-98 1:09:07	2.618	1820.4
10-Mar-98 1:12:00	2.667	1820.4
10-Mar-98 1:12:00	2.618	1820.8
10-Mar-98 1:14:53	2.667	1820.8
10-Mar-98 11:25:26	1.309	1840.8
10-Mar-98 11:31:12	1.309	1841.2
10-Mar-98 11:32:38	1.309	1841.2
10-Mar-98 16:19:12	1.058	1846.8
10-Mar-98 16:20:38	1.074	1846.8
10-Mar-98 16:23:31	1.074	1846.8
10-Mar-98 16:24:58	1.074	1846.8
10-Mar-98 23:47:02	0.775	1853.6
10-Mar-98 23:54:14	0.782	1853.6
10-Mar-98 23:57:07	0.782	1854
11-Mar-98 0:00:00	0.775	1854
11-Mar-98 0:02:53	0.775	1854
11-Mar-98 13:10:34	0.477	1862
11-Mar-98 13:14:53	0.490	1862
11-Mar-98 13:19:12	0.484	1862
11-Mar-98 13:22:05	0.484	1862.4
11-Mar-98 13:26:24	0.484	1862.4
12-Mar-98 8:32:38	0.279	1869.6
13-Mar-98 10:30:43	0.000	1873.2
16-Mar-98 11:29:46	0.000	1873.2
23-Mar-98 11:35:31	0.000	1873.2
30-Mar-98 0:04:19	0.000	1873.2
30-Mar-98 10:43:41	0.000	1873.2
30-Mar-98 14:16:48	0.000	1873.2
30-Mar-98 16:53:46	2.468	1876.4
30-Mar-98 16:55:12	2.468	1876.4
30-Mar-98 16:56:38	2.468	1876.4
30-Mar-98 18:18:43	2.979	1880.4
30-Mar-98 18:20:10	3.031	1880.4
30-Mar-98 18:21:36	2.929	1880.4
30-Mar-98 18:21:36	3.031	1880.4
30-Mar-98 18:23:02	3.031	1880.4
30-Mar-98 18:27:22	2.929	1880.8
30-Mar-98 18:28:48	2.979	1880.8
30-Mar-98 20:19:41	2.700	1886
30-Mar-98 20:19:41	2.700	1886
30-Mar-98 20:21:07	2.618	1886
30-Mar-98 20:22:34	2.579	1886
31-Mar-98 9:40:19	1.136	1912
31-Mar-98 9:43:12	1.200	1912
31-Mar-98 12:41:46	1.005	1915.2
31-Mar-98 12:43:12	1.054	1915.2
31-Mar-98 12:44:38	1.136	1915.2
31-Mar-98 12:47:31	1.136	1915.2
31-Mar-98 12:50:24	1.054	1915.2
31-Mar-98 16:20:38	0.960	1918.8
31-Mar-98 16:22:05	0.939	1918.8
31-Mar-98 16:26:24	0.982	1918.8
31-Mar-98 16:27:50	0.939	1918.8
31-Mar-98 19:26:24	0.847	1921.6
31-Mar-98 19:27:50	0.831	1921.6
31-Mar-98 19:29:17	0.815	1921.6
31-Mar-98 19:35:02	0.831	1921.6
1-Apr-98 14:00:58	0.451	1933.6
2-Apr-98 15:18:43	0.192	1941.6
6-Apr-98 14:35:31	0.000	1950.8
13-Apr-98 14:35:31	0.000	1950.8
14-Apr-98 14:35:31	0.000	1950.8
15-Apr-98 14:35:31	0.000	1950.8
20-Apr-98 11:29:46	0.000	1950.8
27-Apr-98 10:00:29	0.000	1950.8
4-May-98 3:08:38	0.000	1950.8
4-May-98 11:03:50	0.000	1950.8
4-May-98 13:03:22	0.000	1950.8

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
4-May-98 14:31:12	0.000	1950.8
4-May-98 16:13:26	0.000	1950.8
4-May-98 17:32:38	0.000	1950.8
4-May-98 17:41:17	0.801	1950.8
4-May-98 17:42:43	0.815	1950.8
4-May-98 17:44:10	0.831	1950.8
4-May-98 17:48:29	0.847	1950.8
4-May-98 17:54:14	0.900	1951.2
4-May-98 17:58:34	0.960	1951.2
4-May-98 18:36:00	1.234	1952
4-May-98 18:37:26	1.270	1952
4-May-98 18:38:53	1.309	1952
4-May-98 19:35:02	1.600	1953.2
4-May-98 19:35:02	1.600	1953.2
4-May-98 19:36:29	1.630	1953.2
4-May-98 21:57:36	2.700	1958.4
4-May-98 21:57:36	2.618	1958.4
4-May-98 21:59:02	2.618	1958.4
4-May-98 22:27:50	2.880	1959.6
4-May-98 22:29:17	2.880	1960
4-May-98 22:30:43	2.880	1960
5-May-98 1:23:31	4.114	1970
5-May-98 1:24:58	3.927	1970
5-May-98 1:26:24	4.114	1970
5-May-98 1:27:50	4.114	1970.4
5-May-98 2:48:29	3.927	1975.6
5-May-98 2:51:22	3.927	1976
5-May-98 2:52:48	4.114	1976
5-May-98 2:52:48	4.114	1976
5-May-98 11:32:38	1.800	2001.6
5-May-98 11:34:05	1.800	2001.6
5-May-98 11:35:31	1.728	2001.6
5-May-98 11:36:58	1.800	2001.6
5-May-98 13:12:00	1.630	2004.4
5-May-98 13:12:00	1.630	2004.4
5-May-98 13:13:26	1.630	2004.4
5-May-98 17:32:38	1.270	2010.8
5-May-98 17:34:05	1.270	2010.8
5-May-98 17:36:58	1.270	2010.8
5-May-98 18:53:17	1.168	2012.4
5-May-98 18:56:10	1.168	2012.4
5-May-98 20:08:10	1.270	2014
5-May-98 20:08:10	1.270	2014
6-May-98 8:38:24	0.697	2026
6-May-98 8:41:17	0.708	2026.4
6-May-98 8:42:43	0.697	2026.4
6-May-98 9:53:17	0.678	2027.2
6-May-98 9:54:43	0.678	2027.2
6-May-98 9:56:10	0.675	2027.2
7-May-98 10:17:46	0.308	2039.2
7-May-98 15:47:31	0.262	2040.8

Date & Time	Outflow Rate mm/hr	Total Outflow mm
8-May-98 8:12:29	0.180	2044.4
8-May-98 11:12:29	0.206	2044.8
8-May-98 15:02:53	0.160	2045.6
11-May-98 12:30:14	0.000	2051.2
12-May-98 10:00:29	0.000	2051.2
18-May-98 1:45:07	0.000	2051.2
18-May-98 11:02:24	0.000	2051.2
18-May-98 13:30:43	0.000	2051.2
18-May-98 14:26:53	0.279	2051.2
18-May-98 14:41:17	0.485	2051.2
18-May-98 14:55:41	0.683	2051.6
18-May-98 15:01:26	0.825	2051.6
18-May-98 15:05:46	1.005	2051.6
18-May-98 15:07:12	1.017	2051.6
18-May-98 15:31:41	1.728	2052
18-May-98 16:07:41	2.274	2053.2
18-May-98 16:07:41	2.274	2053.6
18-May-98 16:30:43	2.468	2054.4
18-May-98 16:32:10	2.542	2054.4
18-May-98 17:13:55	2.880	2056.4
18-May-98 17:13:55	2.880	2056.4
18-May-98 18:10:05	3.200	2059.2
18-May-98 18:10:05	3.273	2059.2
18-May-98 18:57:36	3.600	2061.6
18-May-98 18:59:02	3.600	2062
18-May-98 21:40:19	4.500	2072.8
18-May-98 21:41:46	4.500	2072.8
18-May-98 22:26:24	4.500	2076.4
18-May-98 22:27:50	4.500	2076.4
18-May-98 22:50:53	4.363	2078
18-May-98 22:50:53	4.363	2078
19-May-98 1:27:50	3.349	2088
19-May-98 1:29:17	3.349	2088.4
19-May-98 2:16:48	3.000	2090.8
19-May-98 2:18:14	3.000	2090.8
19-May-98 7:45:07	1.878	2104
19-May-98 12:02:53	1.542	2111.6
19-May-98 12:02:53	1.542	2111.6
19-May-98 16:39:22	1.234	2118
19-May-98 16:40:48	1.234	2118
19-May-98 16:52:19	1.234	2118
19-May-98 17:16:48	1.200	2118.8
19-May-98 17:18:14	1.200	2118.8
20-May-98 8:31:12	0.432	2131.2
20-May-98 13:30:43	0.720	2134
21-May-98 9:01:26	0.360	2144.4
21-May-98 14:16:48	0.320	2146.4
22-May-98 8:11:02	0.274	2151.6
24-May-98 23:18:14	0.027	2161.2
25-May-98 9:48:58	1.662	2170
25-May-98 9:51:50	1.693	2170

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
25-May-98 9:53:17	1.693	2170
25-May-98 11:16:48	1.964	2172.8
25-May-98 11:18:14	1.964	2172.8
25-May-98 12:36:00	2.483	2175.6
25-May-98 12:36:00	2.483	2175.6
25-May-98 13:13:26	2.769	2177.2
25-May-98 13:14:53	2.769	2177.2
25-May-98 14:13:55	3.131	2180
25-May-98 14:15:22	3.131	2180.4
25-May-98 15:12:58	3.512	2183.6
25-May-98 15:14:24	3.512	2183.6
25-May-98 16:06:14	3.790	2186.8
25-May-98 16:07:41	3.790	2186.8
25-May-98 17:11:02	4.235	2190.8
25-May-98 17:12:29	4.235	2191.2
25-May-98 19:20:38	11.076	2207.6
25-May-98 19:22:05	11.076	2207.6
25-May-98 19:59:31	7.200	2213.2
25-May-98 19:59:31	7.200	2213.6
25-May-98 20:25:26	5.760	2216
25-May-98 20:26:53	5.538	2216.4
25-May-98 20:26:53	5.760	2216.4
25-May-98 20:49:55	5.538	2218.4
25-May-98 20:51:22	5.538	2218.8
25-May-98 21:33:07	5.142	2222.4
25-May-98 21:34:34	5.142	2222.4
25-May-98 22:10:34	4.800	2225.6
25-May-98 22:12:00	4.800	2225.6
25-May-98 23:47:02	4.235	2232.8
25-May-98 23:48:29	4.235	2232.8
26-May-98 1:01:55	3.892	2237.6
26-May-98 1:01:55	3.790	2238
26-May-98 1:03:22	3.892	2238
26-May-98 9:53:17	2.000	2264
26-May-98 9:54:43	2.000	2264
26-May-98 11:32:38	1.878	2267.2
26-May-98 11:34:05	1.800	2267.2
26-May-98 11:34:05	1.839	2267.2
26-May-98 13:04:48	1.662	2269.6
26-May-98 13:04:48	1.662	2270
26-May-98 16:35:02	1.600	2275.6
27-May-98 8:21:07	0.847	2294.8
27-May-98 11:41:17	0.775	2297.6
27-May-98 16:01:55	0.639	2300.4
28-May-98 8:00:58	0.432	2309.2
28-May-98 16:01:55	0.384	2312.4
29-May-98 8:02:24	0.274	2317.6
29-May-98 13:32:10	0.320	2319.2
1-Jun-98 3:18:43	0.071	2331.2
1-Jun-98 9:24:29	3.927	2343.6
1-Jun-98 9:25:55	3.927	2343.6
1-Jun-98 12:54:43	3.600	2356.8
1-Jun-98 12:56:10	3.600	2356.8
1-Jun-98 15:00:00	3.131	2363.6
1-Jun-98 15:01:26	3.131	2364
1-Jun-98 16:10:34	1.489	2366.4
1-Jun-98 16:12:00	1.489	2366.4
1-Jun-98 17:32:38	1.005	2368
1-Jun-98 18:30:14	0.939	2369.2
1-Jun-98 18:31:41	0.939	2369.2
1-Jun-98 23:47:02	0.785	2373.6
1-Jun-98 23:48:29	0.785	2373.6
2-Jun-98 11:35:31	0.685	2382.4
2-Jun-98 11:36:58	0.685	2382.4
2-Jun-98 16:07:41	0.635	2385.2
3-Jun-98 8:41:17	0.524	2394.8
3-Jun-98 15:31:41	0.461	2398.4
4-Jun-98 8:18:14	0.225	2404
4-Jun-98 14:32:38	0.276	2405.6
8-Jun-98 21:59:02	0.082	2424.4
9-Jun-98 11:15:22	0.102	2425.6
9-Jun-98 12:40:19	0.105	2425.6
9-Jun-98 14:13:55	0.101	2425.6
9-Jun-98 15:25:55	0.120	2426
9-Jun-98 16:00:29	0.240	2426
9-Jun-98 16:23:31	0.520	2426
9-Jun-98 16:42:14	0.772	2426.4
9-Jun-98 16:56:38	0.982	2426.4
9-Jun-98 17:19:41	1.270	2426.8
9-Jun-98 17:36:58	1.394	2427.2
9-Jun-98 18:12:58	1.800	2428.4
9-Jun-98 18:56:10	2.160	2429.6
9-Jun-98 19:59:31	2.542	2432.4
9-Jun-98 20:00:58	2.542	2432.4
9-Jun-98 20:47:02	2.824	2434.4
9-Jun-98 20:48:29	2.824	2434.4
9-Jun-98 22:56:38	3.349	2441.2
9-Jun-98 22:58:05	3.349	2441.2
9-Jun-98 23:31:12	3.429	2442.8
9-Jun-98 23:32:38	3.429	2443.2
10-Jun-98 0:14:24	3.600	2445.6
10-Jun-98 0:15:50	3.600	2445.6
10-Jun-98 2:26:53	4.235	2454
10-Jun-98 2:26:53	4.235	2454
10-Jun-98 4:20:38	4.800	2462.8
10-Jun-98 4:20:38	4.800	2462.8
10-Jun-98 6:46:05	4.800	2474.4
10-Jun-98 6:47:31	4.800	2474.4
10-Jun-98 7:14:53	4.114	2476.4
10-Jun-98 7:14:53	4.114	2476.4
10-Jun-98 7:42:14	3.600	2478.4
10-Jun-98 7:43:41	3.600	2478.4

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
10-Jun-98 8:11:02	3.273	2480
10-Jun-98 8:12:29	3.273	2480
10-Jun-98 8:44:10	3.000	2481.6
10-Jun-98 8:45:36	3.000	2481.6
10-Jun-98 9:18:43	2.880	2483.2
10-Jun-98 9:20:10	2.824	2483.6
10-Jun-98 9:59:02	2.769	2485.2
10-Jun-98 10:00:29	2.717	2485.2
10-Jun-98 11:21:07	2.483	2488.8
10-Jun-98 11:22:34	2.483	2488.8
10-Jun-98 12:08:38	2.400	2490.8
10-Jun-98 12:10:05	2.400	2490.8
10-Jun-98 14:41:17	2.150	2496.4
10-Jun-98 14:41:17	2.118	2496.4
11-Jun-98 8:31:12	1.263	2526.8
11-Jun-98 11:45:36	1.143	2530.4
11-Jun-98 14:45:36	1.028	2533.6
12-Jun-98 8:47:02	0.900	2551.2
12-Jun-98 11:47:02	0.775	2553.6
15-Jun-98 1:17:46	0.147	2582
15-Jun-98 8:06:43	0.186	2583.2
15-Jun-98 9:17:17	0.919	2583.6
15-Jun-98 9:17:17	0.939	2583.6
15-Jun-98 9:30:14	1.107	2584
15-Jun-98 9:31:41	1.093	2584
15-Jun-98 10:07:41	1.542	2584.8
15-Jun-98 10:09:07	1.600	2584.8
15-Jun-98 11:19:41	2.274	2587.2
15-Jun-98 11:21:07	2.215	2587.2
15-Jun-98 13:12:00	2.769	2591.6
15-Jun-98 13:12:00	2.796	2592
15-Jun-98 13:53:46	2.939	2593.6
15-Jun-98 13:53:46	2.939	2594
15-Jun-98 16:06:14	3.349	2600.8
15-Jun-98 16:07:41	3.273	2600.8
15-Jun-98 18:36:00	4.114	2610
15-Jun-98 18:37:26	4.114	2610
15-Jun-98 19:20:38	4.114	2613.2
15-Jun-98 19:22:05	4.235	2613.2
15-Jun-98 20:18:14	4.363	2617.2
15-Jun-98 20:19:41	4.235	2617.2
15-Jun-98 20:34:05	4.114	2618.4
15-Jun-98 20:52:48	4.000	2619.6
15-Jun-98 20:54:14	3.892	2619.6
15-Jun-98 21:12:58	4.000	2620.8
15-Jun-98 21:14:24	3.892	2620.8
15-Jun-98 21:34:34	3.790	2622
15-Jun-98 21:36:00	3.892	2622.4
15-Jun-98 21:56:10	3.790	2623.6
15-Jun-98 21:57:36	3.790	2623.6
15-Jun-98 22:45:07	3.790	2626.8
15-Jun-98 22:46:34	3.790	2626.8
15-Jun-98 23:35:31	3.740	2630
15-Jun-98 23:36:58	3.740	2630
16-Jun-98 0:10:05	3.646	2632
16-Jun-98 0:11:31	3.600	2632
16-Jun-98 1:30:43	3.600	2636.8
16-Jun-98 1:30:43	3.646	2636.8
16-Jun-98 9:36:00	2.400	2661.2
16-Jun-98 9:36:00	2.400	2661.2
16-Jun-98 10:20:38	2.323	2663.2
16-Jun-98 10:22:05	2.323	2663.2
16-Jun-98 11:41:17	2.182	2666
16-Jun-98 11:42:43	2.182	2666
16-Jun-98 13:07:41	2.028	2669.2
16-Jun-98 13:09:07	2.118	2669.2
16-Jun-98 13:09:07	2.058	2669.2
16-Jun-98 13:45:07	1.945	2670.4
16-Jun-98 13:46:34	1.945	2670.4
16-Jun-98 14:42:43	2.199	2672.4
16-Jun-98 14:44:10	2.150	2672.4
16-Jun-98 14:44:10	2.150	2672.4
16-Jun-98 15:18:43	2.285	2673.6
16-Jun-98 15:20:10	2.285	2673.6
16-Jun-98 15:38:53	2.400	2674.4
16-Jun-98 15:40:19	2.400	2674.4
16-Jun-98 16:09:07	2.717	2675.6
16-Jun-98 16:09:07	2.769	2675.6
16-Jun-98 16:48:00	3.790	2678
16-Jun-98 16:49:26	3.790	2678
16-Jun-98 18:08:38	5.760	2684.4
16-Jun-98 18:10:05	5.760	2684.4
16-Jun-98 18:28:48	6.000	2686.4
16-Jun-98 18:30:14	6.000	2686.4
16-Jun-98 19:00:29	6.000	2689.2
16-Jun-98 19:01:55	6.000	2689.6
16-Jun-98 19:20:38	6.261	2691.6
16-Jun-98 19:22:05	6.261	2691.6
16-Jun-98 19:40:48	6.545	2693.6
16-Jun-98 19:40:48	6.545	2693.6
16-Jun-98 20:08:10	7.200	2696.8
16-Jun-98 20:09:36	7.200	2696.8
16-Jun-98 20:52:48	7.200	2702
16-Jun-98 20:52:48	7.200	2702
16-Jun-98 21:18:43	7.200	2705.2
16-Jun-98 21:18:43	7.384	2705.2
16-Jun-98 21:44:38	9.000	2708.8
16-Jun-98 21:44:38	9.000	2708.8
16-Jun-98 22:36:29	8.001	2716
16-Jun-98 22:36:29	8.470	2716
16-Jun-98 22:37:55	8.228	2716.4
16-Jun-98 22:59:31	8.001	2719.2

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
16-Jun-98 23:00:58	8.001	2719.2
16-Jun-98 23:48:29	6.000	2724.8
16-Jun-98 23:49:55	6.000	2724.8
17-Jun-98 0:37:26	5.334	2729.6
17-Jun-98 0:38:53	5.334	2729.6
17-Jun-98 1:53:46	5.142	2736
17-Jun-98 1:53:46	4.965	2736.4
17-Jun-98 9:14:24	3.892	2768.8
17-Jun-98 9:15:50	3.790	2768.8
17-Jun-98 11:00:58	3.273	2774.8
17-Jun-98 11:00:58	3.273	2775.2
17-Jun-98 13:59:31	2.691	2784
17-Jun-98 14:00:58	2.717	2784
17-Jun-98 14:42:43	2.618	2785.6
17-Jun-98 14:44:10	2.642	2786
17-Jun-98 14:47:02	2.645	2786
17-Jun-98 14:49:55	2.592	2786
18-Jun-98 9:01:26	1.469	2823.2
18-Jun-98 13:50:53	1.143	2829.2
18-Jun-98 16:26:24	1.200	2832.4
19-Jun-98 9:15:50	0.837	2849.6
19-Jun-98 16:22:05	0.713	2855.2
26-Jun-98 9:01:26	0.384	2943.2
26-Jun-98 16:00:29	0.412	2946
29-Jun-98 9:02:53	0.199	2965.6
2-Jul-98 1:36:29	0.063	2974.4
2-Jul-98 9:46:05	0.455	2976.4
2-Jul-98 11:15:22	0.900	2977.2
2-Jul-98 11:16:48	0.900	2977.2
2-Jul-98 12:08:38	1.270	2978.4
2-Jul-98 12:10:05	1.270	2978.4
2-Jul-98 14:22:34	2.880	2982.8
2-Jul-98 14:24:00	2.880	2982.8
2-Jul-98 14:48:29	3.324	2984.4
2-Jul-98 14:49:55	3.324	2984.4
2-Jul-98 15:46:05	4.000	2987.6
2-Jul-98 15:47:31	4.000	2988
2-Jul-98 16:56:38	4.500	2992.8
2-Jul-98 16:56:38	4.500	2992.8
2-Jul-98 17:55:41	4.965	2997.2
2-Jul-98 17:55:41	4.965	2997.6
2-Jul-98 18:30:14	5.334	3000.4
2-Jul-98 18:31:41	5.236	3000.4
2-Jul-98 19:29:17	6.000	3006
2-Jul-98 19:29:17	5.760	3006
2-Jul-98 19:30:43	6.000	3006
2-Jul-98 20:29:46	6.261	3012
2-Jul-98 20:31:12	6.545	3012
2-Jul-98 20:31:12	6.545	3012.4
2-Jul-98 21:56:10	6.857	3021.6
2-Jul-98 21:57:36	6.857	3022
3-Jul-98 1:09:07	8.001	3045.6
3-Jul-98 1:10:34	8.001	3045.6
3-Jul-98 3:34:34	7.579	3064.4
3-Jul-98 3:34:34	7.579	3064.4
3-Jul-98 5:26:53	6.857	3078
3-Jul-98 5:26:53	6.857	3078
3-Jul-98 7:50:53	7.579	3095.2
3-Jul-98 7:52:19	7.200	3095.6
3-Jul-98 8:35:31	7.200	3100.8
3-Jul-98 8:35:31	6.857	3100.8
3-Jul-98 8:36:58	6.857	3100.8
3-Jul-98 9:08:38	6.857	3104.4
3-Jul-98 9:08:38	6.857	3104.4
3-Jul-98 9:41:46	7.384	3108.4
3-Jul-98 9:43:12	7.200	3108.4
3-Jul-98 10:10:34	7.200	3111.6
3-Jul-98 10:10:34	6.545	3112
3-Jul-98 10:10:34	6.857	3112
3-Jul-98 11:26:53	5.538	3119.6
3-Jul-98 11:28:19	5.538	3120
3-Jul-98 12:47:31	5.334	3127.2
3-Jul-98 12:48:58	5.334	3127.2
3-Jul-98 15:10:05	3.892	3138
3-Jul-98 15:11:31	3.892	3138
3-Jul-98 16:07:41	3.429	3141.6
3-Jul-98 16:09:07	3.429	3141.6
3-Jul-98 17:34:05	2.824	3146
3-Jul-98 17:34:05	2.824	3146
3-Jul-98 19:13:26	2.618	3150.4
3-Jul-98 19:14:53	2.572	3150.8
3-Jul-98 20:32:38	2.323	3153.6
3-Jul-98 20:34:05	2.323	3154
3-Jul-98 20:57:07	2.182	3154.8
3-Jul-98 20:57:07	2.251	3154.8
4-Jul-98 0:00:00	1.945	3161.2
4-Jul-98 0:00:00	1.895	3161.2
4-Jul-98 11:44:10	1.125	3178.8
4-Jul-98 11:45:36	1.125	3178.8
4-Jul-98 12:56:10	1.092	3180
4-Jul-98 12:57:36	1.092	3180
6-Jul-98 13:32:10	0.390	3216
7-Jul-98 1:40:48	0.288	3220.4
7-Jul-98 10:09:07	0.262	3222.8
7-Jul-98 11:39:50	0.960	3223.6
7-Jul-98 11:42:43	0.994	3223.6
7-Jul-98 12:00:00	1.270	3224
7-Jul-98 12:00:00	1.309	3224
7-Jul-98 12:01:26	1.309	3224
7-Jul-98 12:21:36	1.693	3224.4
7-Jul-98 12:23:02	1.662	3224.4
7-Jul-98 12:44:38	2.215	3225.2

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
7-Jul-98 12:44:38	2.274	3225.2
7-Jul-98 14:44:10	4.235	3231.6
7-Jul-98 14:45:36	4.235	3231.6
7-Jul-98 15:21:36	4.500	3234.4
7-Jul-98 15:23:02	4.500	3234.4
7-Jul-98 15:51:50	4.800	3236.8
7-Jul-98 15:51:50	4.800	3236.8
7-Jul-98 17:06:43	5.142	3242.8
7-Jul-98 17:06:43	5.142	3242.8
7-Jul-98 19:17:46	6.000	3255.2
7-Jul-98 19:17:46	6.000	3255.2
7-Jul-98 19:43:41	5.760	3257.6
7-Jul-98 19:45:07	6.000	3257.6
7-Jul-98 20:22:34	6.000	3261.6
7-Jul-98 20:24:00	6.000	3261.6
7-Jul-98 21:07:12	5.878	3266
7-Jul-98 21:08:38	5.878	3266
7-Jul-98 21:08:38	5.878	3266
7-Jul-98 21:38:53	5.538	3268.8
7-Jul-98 21:38:53	5.760	3268.8
7-Jul-98 22:06:14	5.538	3271.6
7-Jul-98 22:07:41	5.538	3271.6
7-Jul-98 22:33:36	5.334	3274
7-Jul-98 22:33:36	5.334	3274
7-Jul-98 23:09:36	5.053	3277.2
7-Jul-98 23:09:36	4.965	3277.2
7-Jul-98 23:32:38	4.500	3278.8
7-Jul-98 23:34:05	4.500	3279.2
8-Jul-98 0:24:29	4.114	3282.8
8-Jul-98 0:25:55	4.235	3282.8
8-Jul-98 4:12:00	2.880	3296
8-Jul-98 4:13:26	2.880	3296.4
8-Jul-98 10:06:14	1.895	3310.4
8-Jul-98 10:07:41	1.895	3310.4
8-Jul-98 11:28:19	1.757	3312.8
8-Jul-98 11:29:46	1.757	3312.8
8-Jul-98 12:48:58	1.636	3315.2
8-Jul-98 12:50:24	1.636	3315.2
8-Jul-98 14:15:22	1.516	3317.2
8-Jul-98 14:15:22	1.532	3317.2
8-Jul-98 15:14:24	1.485	3318.8
8-Jul-98 15:15:50	1.469	3318.8
8-Jul-98 16:39:22	1.385	3320.8
8-Jul-98 16:39:22	1.385	3320.8
8-Jul-98 17:15:22	1.371	3321.6
8-Jul-98 17:15:22	1.394	3321.6
8-Jul-98 17:39:50	1.309	3322.4
8-Jul-98 17:39:50	1.329	3322.4
8-Jul-98 18:07:12	1.270	3322.8
8-Jul-98 18:07:12	1.270	3322.8
8-Jul-98 18:44:38	1.270	3323.6

Date & Time	Outflow Rate mm/hr	Total Outflow mm
8-Jul-98 18:46:05	1.270	3323.6
8-Jul-98 19:12:00	1.270	3324
8-Jul-98 19:13:26	1.270	3324.4
8-Jul-98 19:35:02	1.234	3324.8
8-Jul-98 19:36:29	1.234	3324.8
8-Jul-98 20:00:58	1.200	3325.2
8-Jul-98 20:02:24	1.168	3325.2
8-Jul-98 20:54:14	1.200	3326.4
8-Jul-98 20:55:41	1.200	3326.4
8-Jul-98 21:17:17	1.234	3326.8
8-Jul-98 21:17:17	1.270	3326.8
8-Jul-98 21:33:07	1.351	3327.2
8-Jul-98 21:34:34	1.371	3327.2
8-Jul-98 21:56:10	1.489	3327.6
8-Jul-98 22:45:07	2.058	3329.2
9-Jul-98 0:17:17	3.790	3333.6
9-Jul-98 0:18:43	3.790	3333.6
9-Jul-98 2:45:36	5.334	3344.8
9-Jul-98 2:47:02	5.334	3344.8
9-Jul-98 5:22:34	5.760	3359.2
9-Jul-98 5:24:00	5.760	3359.6
9-Jul-98 8:09:36	6.857	3376.8
9-Jul-98 8:11:02	6.857	3377.2
9-Jul-98 8:47:02	7.200	3381.2
9-Jul-98 8:48:29	7.200	3381.2
9-Jul-98 9:21:36	7.200	3385.6
9-Jul-98 9:23:02	7.200	3385.6
9-Jul-98 9:57:36	7.579	3389.6
9-Jul-98 9:57:36	7.579	3390
9-Jul-98 10:53:46	8.001	3397.2
9-Jul-98 10:53:46	7.579	3397.2
9-Jul-98 11:22:34	8.228	3400.8
9-Jul-98 11:24:00	8.001	3401.2
9-Jul-98 11:39:50	8.001	3403.2
9-Jul-98 11:41:17	8.001	3403.2
9-Jul-98 12:05:46	8.001	3406.8
9-Jul-98 12:07:12	8.001	3406.8
9-Jul-98 12:25:55	7.200	3409.2
9-Jul-98 12:27:22	7.579	3409.2
9-Jul-98 12:44:38	7.384	3411.6
9-Jul-98 12:46:05	7.579	3411.6
9-Jul-98 13:10:34	7.200	3414.8
9-Jul-98 13:10:34	7.384	3414.8
9-Jul-98 13:27:50	7.200	3416.8
9-Jul-98 13:29:17	7.200	3416.8
9-Jul-98 13:59:31	7.200	3420.4
9-Jul-98 13:59:31	7.024	3420.4
9-Jul-98 14:18:14	7.024	3422.8
9-Jul-98 14:19:41	7.024	3422.8
9-Jul-98 14:39:50	6.697	3425.2
9-Jul-98 14:41:17	6.697	3425.6

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
9-Jul-98 15:07:12	6.545	3428.4
9-Jul-98 15:08:38	6.545	3428.4
9-Jul-98 15:28:48	6.399	3430.8
9-Jul-98 15:30:14	6.399	3430.8
9-Jul-98 16:23:31	5.538	3436
9-Jul-98 16:24:58	5.760	3436.4
9-Jul-98 17:26:53	5.142	3442
9-Jul-98 17:28:19	5.142	3442
9-Jul-98 18:17:17	4.800	3446
9-Jul-98 18:18:43	4.645	3446
9-Jul-98 19:06:14	4.235	3449.6
9-Jul-98 19:07:41	4.298	3449.6
10-Jul-98 8:21:07	2.058	3491.6
10-Jul-98 14:21:07	1.800	3503.2
13-Jul-98 8:31:12	0.720	3586.8
13-Jul-98 15:01:26	0.639	3591.2
14-Jul-98 1:14:53	0.420	3596.4
14-Jul-98 7:16:19	0.847	3600.4
14-Jul-98 9:07:12	2.400	3603.2
14-Jul-98 9:07:12	2.400	3603.6
14-Jul-98 10:42:14	3.790	3608.4
14-Jul-98 12:23:02	4.800	3615.6
14-Jul-98 14:19:41	6.261	3626.4
14-Jul-98 14:21:07	6.399	3626.4
14-Jul-98 16:30:43	7.200	3641.2
14-Jul-98 16:30:43	7.200	3641.2
14-Jul-98 19:40:48	7.384	3664
14-Jul-98 19:40:48	7.384	3664.4
14-Jul-98 20:34:05	7.579	3670.8
14-Jul-98 20:35:31	7.384	3670.8
15-Jul-98 1:12:00	7.783	3706
15-Jul-98 1:13:26	7.783	3706
15-Jul-98 1:13:26	7.783	3706.4
15-Jul-98 10:16:19	6.545	3770.8
15-Jul-98 10:17:46	6.545	3771.2
15-Jul-98 12:17:17	5.538	3783.2
15-Jul-98 12:18:43	5.538	3783.2
15-Jul-98 14:47:02	4.800	3796
15-Jul-98 14:48:29	4.882	3796
15-Jul-98 16:30:43	4.800	3804.4
15-Jul-98 16:30:43	4.882	3804.4
15-Jul-98 22:04:48	7.579	3839.2
15-Jul-98 22:04:48	8.001	3839.2
15-Jul-98 22:06:14	8.001	3839.2
16-Jul-98 2:26:53	8.001	3874
16-Jul-98 2:28:19	8.001	3874.4
16-Jul-98 10:22:05	6.545	3931.6
16-Jul-98 10:23:31	6.545	3932
16-Jul-98 11:44:10	6.000	3940.4
16-Jul-98 11:45:36	6.000	3940.4
16-Jul-98 12:51:50	5.334	3946.8
16-Jul-98 12:53:17	5.435	3946.8
16-Jul-98 14:06:43	4.965	3953.2
16-Jul-98 14:08:10	4.965	3953.2
16-Jul-98 14:52:48	4.800	3956.8
16-Jul-98 14:52:48	4.800	3956.8
16-Jul-98 16:52:19	5.142	3966.8
16-Jul-98 16:53:46	5.142	3966.8
16-Jul-98 16:53:46	5.142	3967.2
16-Jul-98 16:56:38	5.142	3967.2
16-Jul-98 18:11:31	6.000	3974.4
16-Jul-98 18:12:58	6.000	3974.4
16-Jul-98 19:13:26	7.200	3980.8
16-Jul-98 19:13:26	6.857	3980.8
16-Jul-98 19:14:53	7.200	3981.2
16-Jul-98 20:29:46	8.001	3990.4
16-Jul-98 20:29:46	8.001	3990.8
16-Jul-98 22:01:55	8.001	4002.8
16-Jul-98 22:03:22	8.228	4003.2
17-Jul-98 8:25:26	8.001	4087.2
17-Jul-98 10:35:02	8.001	4104.4
17-Jul-98 13:30:43	5.538	4124.4
17-Jul-98 16:00:29	4.800	4137.2
20-Jul-98 1:43:41	0.600	4293.2
20-Jul-98 9:46:05	1.571	4301.6
20-Jul-98 9:47:31	1.571	4302
20-Jul-98 11:24:00	2.274	4304.8
20-Jul-98 11:25:26	2.274	4304.8
20-Jul-98 13:33:36	3.927	4311.6
20-Jul-98 13:33:36	3.927	4311.6
20-Jul-98 15:15:50	4.800	4318.8
20-Jul-98 15:15:50	4.938	4319.2
20-Jul-98 15:15:50	4.800	4319.2
20-Jul-98 17:26:53	5.334	4330
20-Jul-98 17:26:53	5.142	4330
20-Jul-98 17:26:53	5.334	4330
20-Jul-98 18:37:26	4.800	4336
20-Jul-98 18:38:53	4.800	4336
20-Jul-98 19:56:38	4.235	4342
20-Jul-98 19:58:05	4.235	4342
20-Jul-98 21:05:46	3.790	4346.8
20-Jul-98 21:07:12	3.790	4346.8
21-Jul-98 0:08:38	4.500	4359.2
21-Jul-98 0:08:38	4.500	4359.2
21-Jul-98 2:16:48	6.545	4370.8
21-Jul-98 2:16:48	6.545	4371.2
21-Jul-98 12:34:34	8.228	4447.2
21-Jul-98 12:36:00	8.228	4447.2
21-Jul-98 14:25:26	9.000	4462.8
21-Jul-98 14:25:26	9.600	4463.2
21-Jul-98 14:25:26	9.000	4463.2
21-Jul-98 15:17:17	9.600	4471.2

Table A6.2 (cont'd) - Wet Cell Outflow Data

Date & Time	Outflow Rate mm/hr	Total Outflow mm
21-Jul-98 15:18:43	9.000	4471.2
21-Jul-98 17:29:46	8.728	4490.8
21-Jul-98 17:31:12	8.728	4490.8
21-Jul-98 19:20:38	7.579	4505.6
21-Jul-98 19:20:38	7.579	4505.6
21-Jul-98 20:22:34	6.545	4513.2
21-Jul-98 20:24:00	6.857	4513.2
21-Jul-98 20:24:00	6.857	4513.2
21-Jul-98 23:32:38	6.000	4533.6
21-Jul-98 23:34:05	6.000	4533.6
22-Jul-98 3:00:00	7.384	4556.4
22-Jul-98 3:01:26	7.384	4556.8
22-Jul-98 10:07:41	7.579	4610
22-Jul-98 10:09:07	7.579	4610
22-Jul-98 11:57:07	7.384	4623.6
22-Jul-98 11:57:07	7.200	4623.6
22-Jul-98 11:58:34	7.200	4623.6
22-Jul-98 13:17:46	8.001	4633.6
22-Jul-98 13:19:12	8.001	4634
22-Jul-98 15:54:43	8.728	4655.6
22-Jul-98 15:54:43	8.728	4655.6
22-Jul-98 15:56:10	8.348	4655.6
22-Jul-98 15:57:36	8.348	4656
22-Jul-98 15:57:36	8.728	4656
23-Jul-98 8:09:36	6.545	4779.6
23-Jul-98 12:00:00	5.142	4802
23-Jul-98 16:00:29	3.600	4819.6
24-Jul-98 8:05:17	1.600	4861.6
24-Jul-98 12:25:55	1.309	4867.6
27-Jul-98 1:36:29	0.307	4917.2
27-Jul-98 10:39:22	0.268	4919.6
27-Jul-98 11:21:07	0.256	4920
27-Jul-98 13:09:07	0.480	4920.8
27-Jul-98 14:08:10	1.200	4921.6
27-Jul-98 14:35:31	1.464	4922
27-Jul-98 16:33:36	2.304	4925.6
27-Jul-98 16:33:36	2.336	4926
27-Jul-98 16:36:29	2.400	4926
27-Jul-98 16:37:55	2.367	4926
27-Jul-98 18:30:14	3.388	4931.2
27-Jul-98 18:30:14	3.388	4931.2
27-Jul-98 19:10:34	3.757	4933.6
27-Jul-98 19:10:34	3.840	4933.6
27-Jul-98 23:21:07	4.114	4950.4
27-Jul-98 23:22:34	4.114	4950.4
28-Jul-98 0:47:31	4.235	4956.4
28-Jul-98 0:48:58	4.235	4956.4
28-Jul-98 9:47:31	8.470	5013.6
28-Jul-98 9:47:31	8.228	5013.6
28-Jul-98 9:47:31	8.470	5013.6
28-Jul-98 10:58:05	9.291	5024
28-Jul-98 10:58:05	9.600	5024
28-Jul-98 10:59:31	9.600	5024
28-Jul-98 12:46:05	8.228	5040
28-Jul-98 12:46:05	8.228	5040
28-Jul-98 14:39:50	8.001	5055.6
28-Jul-98 14:41:17	8.001	5055.6
28-Jul-98 16:20:38	7.200	5068
28-Jul-98 16:20:38	7.200	5068
28-Jul-98 19:53:46	8.228	5095.6
28-Jul-98 19:53:46	8.228	5095.6
28-Jul-98 21:08:38	8.228	5105.6
28-Jul-98 21:08:38	8.470	5106
28-Jul-98 21:08:38	8.228	5106
29-Jul-98 0:47:31	9.000	5137.2
29-Jul-98 0:48:58	9.000	5137.6
29-Jul-98 9:34:34	7.579	5210
29-Jul-98 9:36:00	7.579	5210.4
29-Jul-98 12:34:34	7.200	5232.4
29-Jul-98 13:59:31	6.545	5242
29-Jul-98 15:54:43	6.545	5254.8
30-Jul-98 9:00:00	8.001	5378.8
30-Jul-98 11:15:22	6.000	5394.8
30-Jul-98 14:29:46	4.235	5411.2
31-Jul-98 8:51:22	1.500	5464
31-Jul-98 12:01:26	1.333	5468.4
4-Aug-98 8:32:38	0.230	5540.8
7-Aug-98 12:04:19	0.060	5551.6
12-Aug-98 12:00:00	0.000	5555.2

Table A6.3 - Wet Cell Leachate Quality : Trace Elements (minor) (mg/L)

Date	Cd	Cr	Co	Cu	Pb	Hg	Ni	Sn	Zn
07-07-97	<0.001	<0.01	0.01	<0.01	<0.01	<0.001	<0.01	<0.01	<0.01
18-07-97	<0.001	<0.01	-	0.06	<0.01	<0.001	<0.01	0.02	0.01
25-07-97	<0.001	<0.01	-	<0.01	<0.01	<0.001	<0.01	<0.01	<0.01
04-08-97	<0.001	<0.01	<0.01	<0.01	-	<0.001	<0.01	<0.01	-
07-08-97	<0.001	<0.01	-	<0.01	<0.01	<0.001	<0.01	<0.01	<0.01
11-08-97	<0.001	<0.01	-	<0.01	<0.01	<0.001	<0.01	<0.01	<0.01
18-08-97	-	<0.01	-	<0.01	-	<0.001	-	-	-
25-08-97	<0.001	0.05	<0.01	<0.01	<0.01	<0.001	0.02	0.01	<0.01
01-09-97	-	<0.01	-	<0.01		<0.001	-	-	-
08-09-97	<0.001	<0.01	<0.01	0.01	<0.01	<0.001	<0.01	<0.01	0.02
15-09-97	-	<0.01	-	<0.01	-	<0.001	-	-	-
22-09-97	-	-	-	0.05	-	-	-	-	-
29-09-97	-	-	-	<0.01	-	-	-	-	-
20-10-97	-	-	-	<0.01	-	-	-	-	-
27-10-97	-	-	-	-	-	-	-	-	-
04-11-97	<0.001	<0.01	<0.01	<0.01		<0.001	<0.01		
10-11-97	-	0.01	-	<0.01	-	<0.001	-	-	-
17-11-97	-	<0.01	-	<0.01	-	<0.001	-	-	-
24-11-97	-	-	-	<0.01	-	-	-	-	-
01-12-97	-	-	-	<0.01	-	<0.001	-	-	-
08-12-97	-	-	-	<0.01	-	-	-	-	<0.01
23-12-97	-	-	-	<0.01	-	-	-	-	-
27-01-98	<0.001	0.01	<0.01	<0.01	<0.01	<0.001	<0.01	<0.01	0.02
02-02-98	-	-	-	<0.01	-	-	-	-	-
02-02-98	<0.001	<0.01	<0.01	<0.01	-	<0.001	<0.01	<0.01	-
23-02-98	-	-	-	<0.01	-	-	-	-	-
02-03-98	-	-	-	<0.01	-	-	-	-	-
10-03-98	-	-	-	<0.01	-	-	-	-	-
17-03-98	-	-	-	<0.01	-	-	-	-	-
23-03-98	-	-	-	<0.01	-	-	-	-	-
07-04-98	-	-	-	<0.01	-	-	-	-	-
15-04-98	-	-	-	<0.01	-	-	-	-	-
04-05-98	<0.001	0.01	<0.01	<0.01	-	<0.001	<0.01	-	-
18-05-98	-	-	-	<0.01	-	-	-	-	-
19-05-98	-	-	-	<0.01	-	-	-	-	-
25-05-98	-	0.01	-	<0.01	-	<0.001	-	-	-
01-06-98	<0.001	<0.01	-	<0.01	<0.01	-	<0.01	-	<0.01
15-06-98	-	-	-	<0.01	-	-	-	-	-
17-06-98	-	0.02	-	<0.01	-	<0.001	-	-	-
22-06-98	-	-	-	<0.01	-	-	-	-	-
29-06-98	-	-	-	0.03	-	-	-	-	-
06-07-98	-	-	-	0.01	-	-	-	-	-
13-07-98	-	-	-	<0.01	-	-	-	-	-
16-07-98	-	-	-	<0.01	-	-	<0.01	-	-
21-07-98	-	-	-	<0.01	-	-	-	-	-
22-07-98	-	-	-	<0.01	-	-	-	-	-
27-07-98	-	-	-	<0.01	-	-	-	-	-
29-07-98	-	-	-	<0.01	-	-	-	-	-

Appendix A7 - Laboratory Leaching Columns

Flow Monitoring Data

Tables

Table A7.1 - Large Column Inflow Data

Time (days)	Inflow Total (mm)	Inflow Rate (mm/hr)
0.000	0.0	0.00
0.002	1.6	32.45
0.012	8.9	31.03
0.015	11.0	31.83
0.075	57.7	32.19
0.100	76.9	32.04
0.108	83.3	31.83
0.115	88.1	32.45
0.197	151.4	32.18
0.208	160.5	32.16
0.217	166.8	31.20
0.222	171.1	32.76
0.751	574.4	31.80
0.759	580.8	31.83
0.767	587.3	32.45
0.779	596.2	31.72
0.794	608.1	32.34
0.806	617.1	31.72
0.826	632.2	32.36
0.892	683.6	32.14
0.897	686.7	31.20
0.915	701.2	32.17
0.927	710.3	32.16
0.940	719.9	32.04
0.946	724.8	32.45
0.985	754.8	32.10
1.006	770.9	32.20
1.018	780.5	32.04
1.025	785.8	32.20
1.034	789.8	18.43
1.056	799.3	18.36
1.069	805.4	18.35
1.113	824.3	18.24
1.138	835.3	18.31
1.156	840.3	11.52
1.194	850.6	11.30
1.202	852.9	11.23
1.802	1015.0	11.26
1.827	1021.6	11.03
1.868	1032.7	11.30
1.883	1036.6	11.06
1.897	1040.6	11.98
1.932	1049.9	11.01
1.945	1053.6	11.43
2.042	1079.7	11.26
2.046	1080.8	11.23
2.085	1091.4	11.17
2.129	1102.9	10.94
2.138	1105.7	13.25
2.812	1286.5	11.18
2.839	1293.7	11.14
2.877	1304.1	11.30
2.888	1307.1	11.23
2.912	1313.3	11.01
2.940	1321.0	11.32
2.944	1322.2	11.23
3.200	1390.9	11.21
3.212	1394.4	12.33
3.893	1576.9	11.16
3.900	1578.8	11.23
3.914	1582.5	11.23
3.928	1586.7	11.77
3.975	1598.6	10.73
3.975	1598.6	
3.982	1600.4	10.48
3.994	1603.5	11.01
4.047	1617.6	11.13
4.060	1621.3	11.23
4.087	1628.5	11.23
4.099	1631.8	11.23
4.113	1635.3	11.04
4.872	1838.9	11.18
4.901	1846.6	10.80
4.914	1850.3	12.07
4.946	1860.1	12.86
4.952	1861.6	9.99
5.070	1892.8	11.01
5.086	1897.4	12.05
5.936	2123.9	11.10
5.960	2130.1	11.01
5.969	2132.3	9.63
5.972	2133.2	13.11
6.179	2187.8	10.98
6.181	2187.8	
6.859	2187.8	
6.861	2187.9	2.50
6.864	2188.8	13.11
6.870	2192.4	24.13
6.890	2196.7	9.36
6.917	2202.4	8.64
6.920	2203.4	11.98
6.981	2219.6	11.06
6.993	2221.3	6.17
7.003	2223.8	10.70
7.023	2229.2	11.10
7.878	2437.6	10.16
7.899	2443.3	10.87
7.938	2453.4	11.03
7.950	2456.6	10.82
7.976	2463.4	10.93
8.040	2480.2	10.87
8.064	2486.4	11.01

Table A7.1 (cont'd) - Large Column Inflow Data

Time (days)	Inflow Total (mm)	Inflow Rate (mm/hr)
8.103	2496.6	10.83
9.003	2730.8	10.85
9.011	2733.1	11.23
9.078	2750.6	10.81
9.094	2754.8	11.07
9.144	2767.7	10.71
9.157	2771.0	11.23
9.885	2959.0	10.75
9.938	2972.6	10.74
9.950	2975.6	10.57
9.973	2981.6	10.89
10.820	3199.9	10.74
10.831	3202.8	10.77
10.843	3205.8	10.57
10.924	3226.8	10.82
10.989	3243.6	10.79
11.016	3250.7	10.95
11.044	3258.1	11.05
11.104	3273.8	10.85
11.786	3451.5	10.86
11.841	3465.7	10.81
11.933	3489.7	10.81
11.967	3498.4	10.92
12.752	3700.6	10.73
13.599	3917.3	10.67
13.617	3921.9	10.66
13.620	3922.8	10.48
14.294	4095.4	10.67
14.307	4098.6	10.40
14.983	4271.5	10.67
14.990	4273.3	10.48
15.005	4277.2	10.55
15.047	4287.8	10.61
15.108	4303.5	10.60
15.817	4482.4	10.52
15.843	4489.0	10.45
15.910	4506.0	10.50
15.977	4522.8	10.53
16.022	4534.2	10.48
16.025	4534.9	11.23
32.097	4534.9	
32.101	4535.9	9.99
32.111	4538.0	9.09
32.121	4541.0	12.84
32.753	4745.1	13.46
32.760	4747.3	13.48
32.766	4749.5	14.15
32.796	4759.2	13.58
32.858	4779.3	13.55
32.874	4784.8	13.73
32.915	4798.0	13.69
33.656	5039.8	13.58
33.664	5042.3	13.62
33.672	5043.9	8.85
33.679	5045.5	8.85
34.761	5273.2	8.77
34.769	5274.9	8.74
34.808	5282.9	8.71
35.767	5483.3	8.70
35.826	5495.5	8.63
35.885	5507.7	8.63
35.957	5522.6	8.65
35.994	5532.2	10.88
36.028	5541.2	11.00
36.075	5553.8	11.12
36.769	5735.5	10.90
36.781	5738.4	10.77
36.840	5753.9	10.92
36.907	5771.6	10.96
36.965	5786.7	10.92
37.024	5802.3	11.01
37.028	5802.3	
37.052	5808.4	10.79
37.774	5999.0	11.00
37.799	6005.4	10.91
37.852	6019.5	10.99
37.857	6019.5	
37.861	6019.5	
37.867	6021.2	11.65
37.872	6022.5	10.70
37.889	6027.0	11.39
37.917	6034.4	11.14
37.933	6038.9	11.23
37.983	6052.4	11.23
38.199	6110.6	11.22
38.224	6117.3	11.13
38.766	6261.3	11.08
38.901	6325.4	19.74
38.910	6327.4	9.99
38.974	6344.2	10.91
39.769	6552.2	10.90
39.830	6568.2	10.89
39.868	6578.3	11.03
39.918	6591.4	10.92
40.776	6817.8	10.99
40.788	6820.8	11.23
41.738	7072.3	11.03
41.757	7077.3	10.70
42.700	7326.6	11.01
42.776	7346.7	10.96
42.843	7364.3	11.00
42.874	7372.5	10.98

Table A7.1 (cont'd) - Large Column Inflow Data

Time (days)	Inflow Total (mm)	Inflow Rate (mm/hr)
42.919	7388.4	14.86
42.992	7414.7	14.91
43.012	7421.6	14.71
43.061	7439.3	14.98
43.732	7677.3	14.78
43.821	7708.6	14.69
43.867	7724.9	14.75
43.897	7735.6	14.64
43.951	7748.2	9.82
44.174	7748.2	
44.181	7750.0	9.87
44.182	7750.2	11.23
44.190	7750.2	
44.195	7751.6	10.30
44.203	7753.6	10.30
44.708	7878.4	10.30
44.765	7892.4	10.23
44.778	7895.5	10.40
44.812	7903.8	10.16
44.836	7909.8	10.27
44.867	7917.3	10.30
44.933	7933.6	10.25
45.202	7933.6	
45.210	7935.9	11.86
45.215	7937.6	16.23
45.738	8178.0	19.15
45.741	8179.7	20.97
45.744	8179.7	
45.748	8180.9	14.98
45.847	8240.0	24.77
45.850	8241.6	24.34
45.874	8255.6	24.67
45.952	8301.9	24.59
45.958	8303.4	11.23
46.222	8330.5	4.27
46.227	8331.2	6.42
46.775	8430.2	7.53
46.811	8436.4	7.20
46.853	8443.9	7.37
46.859	8445.1	8.43
47.690	8594.5	7.49
47.694	8595.1	7.49
48.752	8785.6	7.50
48.756	8786.3	7.49
49.738	8993.6	8.80
49.749	8996.0	8.89
49.753	8997.6	16.23
49.822	9008.5	6.52
49.824	9008.6	3.74
49.844	9034.1	52.68
49.891	9053.5	17.18
51.040	9053.5	
51.043	9054.7	16.85
51.047	9056.2	17.97
51.078	9069.8	18.14
51.735	9246.6	11.21
51.739	9247.5	10.48
51.742	9249.1	24.34
51.790	9277.7	24.85
51.794	9280.2	24.96
51.839	9307.2	24.89
51.882	9332.9	24.88
51.897	9341.6	24.96
51.949	9372.7	24.86
51.973	9387.2	24.82
52.163	9499.9	24.77
52.201	9522.5	24.65
52.205	9525.0	24.96
52.747	9778.0	19.46
52.755	9781.8	19.35

Table A7.2 - Large Column Outflow Data

Day	Outflow Total (mm)	Outflow Rate (mm/hr)
0.000	0.0	0.00
0.763	115.5	
0.766	118.1	37.97
0.930	231.5	28.85
0.935	245.3	118.32
1.037	323.8	32.02
1.044	330.5	40.44
1.194	494.7	45.38
1.199	496.8	18.65
1.802	664.5	11.59
1.933	700.9	11.61
2.133	754.7	11.21
2.135	754.7	0.06
2.814	938.0	11.26
2.836	942.4	8.36
3.201	1039.7	11.12
3.209	1044.3	22.75
4.047	1269.1	11.19
4.101	1283.5	10.89
4.928	1510.5	11.45
5.069	1549.2	11.40
5.960	1785.9	11.07
5.977	1785.9	0.04
6.859	1894.1	5.11
6.890	1894.1	0.00
7.003	1894.1	0.00
7.024	1894.1	0.00
7.880	2097.2	9.88
7.978	2123.1	10.94
8.104	2155.9	10.86
8.106	2156.4	11.76
9.003	2385.4	10.64
9.094	2409.0	10.72
9.886	2611.9	10.68
9.984	2637.0	10.70
10.822	2852.7	10.73
10.950	2886.6	11.00
11.105	2927.4	10.98
11.107	2928.1	14.05
11.788	3104.7	10.80
11.845	3119.3	10.66
12.752	3350.7	10.63
12.758	3352.1	10.50
13.599	3565.2	10.56
13.619	3570.2	10.31
14.294	3743.8	10.70
14.304	3746.3	10.68
14.981	3918.3	10.58
15.047	3934.8	10.45
15.910	4151.8	10.47
16.022	4179.7	10.40
16.094	4198.1	10.61
16.226	4219.6	6.79
16.910	4264.3	2.73
17.000	4267.1	1.31
18.815	4290.9	0.55
22.849	4298.2	0.08
25.939	4299.5	0.02
26.017	4299.6	0.04
29.930	4299.9	0.00
32.093	4300.4	0.01
32.753	4391.9	5.78
32.856	4424.8	13.34
32.911	4442.8	13.53
32.913	4443.3	13.52
33.656	4684.2	13.50
33.673	4689.6	13.39
34.761	4928.5	9.15
34.808	4938.1	8.64
35.767	5135.9	8.59
35.958	5175.5	8.68
36.031	5191.1	8.89
36.074	5201.1	9.53
36.772	5380.7	10.73
36.901	5414.6	10.92
37.775	5637.0	10.61
37.873	5661.0	10.23
38.198	5748.8	11.25
38.213	5752.9	11.21
38.821	5903.5	10.33
38.934	5944.6	15.12
39.769	6160.6	10.78
39.868	6186.1	10.71
40.776	6418.9	10.67
40.786	6421.4	10.71
41.738	6659.9	10.45
41.756	6664.7	11.20
42.700	6913.5	10.97
42.781	6934.5	10.81
43.010	6998.0	11.57
43.060	7015.1	14.08
43.732	7261.8	15.31
43.820	7292.7	14.58
44.092	7375.7	12.75
44.167	7386.0	5.64
44.707	7466.7	6.23
44.860	7503.4	10.01
45.196	7571.5	8.45
45.213	7573.7	5.41
45.738	7754.4	14.35
45.838	7799.9	18.80
45.846	7807.7	42.69
45.953	7869.4	23.90
45.956	7873.4	60.00

Table A7.2 (cont'd) - Large Column Outflow Data

Day	Outflow Total (mm)	Outflow Rate (mm/hr)
46.222	7947.2	11.55
46.226	7947.6	5.71
46.775	8035.8	6.69
46.894	8049.8	4.88
47.690	8201.5	7.94
47.693	8202.0	7.21
48.752	8393.0	7.52
48.756	8394.0	9.86
49.738	8597.3	8.63
49.819	8605.5	4.20
49.912	8641.8	16.33
49.954	8658.5	16.44
50.778	8733.6	3.80
50.824	8737.2	3.23
51.044	8745.0	1.49
51.078	8746.1	1.27
51.735	8848.7	6.51
51.790	8863.4	11.29
51.883	8908.2	20.08
51.943	8945.5	25.73
51.971	8962.1	24.90
52.201	9098.4	24.70
52.203	9100.0	24.69
52.746	9350.9	19.27
52.790	9371.3	19.12
52.950	9414.9	11.37
53.019	9423.6	5.24
53.140	9437.2	4.73
53.222	9444.6	3.71
53.906	9478.4	2.06
53.910	9478.5	1.17
54.779	9493.0	0.69
54.781	9493.0	0.50
55.101	9496.1	0.40
55.736	9500.2	0.27
56.768	9503.4	0.13
57.929	9505.2	0.07
58.831	9505.6	0.02
59.769	9505.7	0.01

Table A7.3 - Medium Column Inflow Data

Time (days)	Inflow Total (mm)	Inflow Rate (mm/hr)
0.000	0.00	
0.003	1.00	14.98
0.008	2.25	10.70
0.013	3.68	10.77
0.076	20.47	11.07
0.131	35.01	11.04
0.138	36.88	11.23
0.151	40.38	11.04
0.199	52.92	11.07
0.280	74.45	11.04
0.738	194.46	10.93
0.767	202.26	10.89
0.791	208.44	10.90
0.861	226.79	10.90
0.965	254.00	10.88
0.978	257.31	11.03
0.994	257.31	
1.005	260.11	10.53
1.778	460.38	10.80
2.101	544.32	10.81
2.117	548.25	10.72
2.737	708.95	10.80
2.753	713.26	10.77
3.053	790.77	10.79
3.777	975.93	10.65
3.917	1014.06	11.33
4.219	1092.07	10.76
4.274	1106.24	10.76
4.710	1218.45	10.72
4.952	1280.73	10.74
5.833	1507.70	10.74
5.846	1511.14	10.84
24.026	1511.14	
24.031	1512.07	8.02
24.057	1518.38	9.95
24.808	1705.66	10.39
24.821	1708.91	10.24
25.004	1754.53	10.36
25.016	1757.46	10.35
25.093	1776.62	10.36
25.112	1781.30	10.40
25.865	1956.30	9.86
26.145	2022.60	9.87
26.774	2215.33	12.79
26.804	2224.73	13.11
26.992	2325.18	22.32
26.998	2328.14	22.14
27.255	2462.67	21.82
27.267	2469.23	21.91
27.747	2651.45	15.82
27.771	2664.12	22.36
27.953	2758.79	21.68

Table A7.4 - Medium Column Outflow Data

Day	Outflow Total (mm)	Outflow Rate (mm/hr)
0.000	0.00	0.00
0.281	0.00	0.00
0.966	0.00	9.18
1.778	178.90	10.15
1.787	181.10	10.54
2.111	263.13	11.22
2.115	264.06	10.46
2.747	422.86	13.95
2.753	424.72	10.48
3.063	502.78	9.62
3.066	503.42	10.47
3.778	682.32	11.97
3.785	684.31	10.38
4.279	807.49	10.62
4.285	808.90	10.55
4.960	979.97	10.01
4.988	986.48	10.47
5.840	1200.71	5.15
5.845	1201.31	0.94
6.785	1222.42	0.00
6.786	1222.42	0.20
7.012	1223.51	0.00
7.793	1223.51	0.01
9.029	1223.69	0.00
10.792	1223.69	0.00
24.057	1223.69	8.03
24.823	1371.32	10.42
24.831	1373.23	9.94
25.106	1438.98	9.80
25.126	1443.72	9.61
25.853	1611.47	10.17
25.859	1612.82	9.89
26.155	1683.04	9.75
26.158	1683.69	12.50
26.792	1873.91	11.83
26.799	1876.08	19.22
26.987	1962.56	23.46
26.99	1964.13	21.83
27.269	2110.36	22.17
27.273	2112.58	16.18
27.746	2296.26	15.70
27.755	2299.66	20.85
27.964	2404.25	18.50
27.967	2405.79	1.38
28.801	2433.51	0.04
30.89	2435.28	0.00
32.93	2435.41	0.00

Table A7.5 - Small Column Inflow Data

Time (days)	Inflow Total (mm)	Inflow Rate (mm/hr)
0.000	0.00	
0.003	1.00	14.978
0.008	2.25	10.698
0.013	3.68	10.765
0.076	20.47	11.069
0.131	35.01	11.044
0.138	36.88	11.233
0.151	40.38	11.036
0.199	52.92	11.068
0.280	74.45	11.041
0.738	194.46	10.927
0.767	202.26	10.885
0.791	208.44	10.903
0.861	226.79	10.900
0.965	254.00	10.884
0.978	257.31	11.025
0.994	257.31	
1.005	260.11	10.531
1.778	460.38	10.796
2.101	544.32	10.807
2.117	548.25	10.723
2.737	708.95	10.797
2.753	713.26	10.765
3.053	790.77	10.790
3.769	975.93	10.765
3.917	1014.06	10.741
4.219	1092.07	10.760
4.274	1106.24	10.759
4.710	1218.45	10.721
4.952	1280.73	10.738
5.833	1507.70	10.740
5.846	1511.14	10.839
24.026	1511.14	6.710
24.031	1512.07	8.021
24.057	1518.38	9.953
24.808	1705.66	10.395
24.821	1708.91	10.245
25.004	1754.53	10.365
25.016	1757.46	10.350
25.093	1776.62	10.357
25.112	1781.30	10.402
25.126	1781.30	
25.132	1784.05	18.303
25.137	1785.29	10.702
25.843	1952.17	9.848
25.863	1956.29	8.522
25.974	1983.50	10.267
26.147	2026.31	10.320
26.163	2030.18	9.676
26.772	2234.50	13.997
26.785	2238.87	13.795
26.803	2245.11	13.869
26.808	2247.23	21.216
26.898	2298.53	23.680
26.981	2345.96	23.717
27	2356.70	23.852
27.244	2495.74	23.702
27.275	2512.97	23.485
27.745	2705.06	17.022
27.761	2713.54	22.145
27.772	2719.41	23.463
27.841	2758.60	23.515
27.927	2807.28	23.553
27.953	2821.76	23.478

Table A7.6 - Small Column Outflow Data

Day	Outflow Total (mm)	Outflow Rate (mm/hr)
0.000	0.00	0.000
0.281	0.00	6.645
0.738	72.87	11.326
0.783	85.14	10.920
0.988	138.65	11.271
0.990	139.40	10.895
1.790	348.58	10.316
1.796	349.96	11.106
2.101	431.40	11.075
2.108	433.06	11.054
2.738	600.16	10.737
2.743	601.59	11.054
3.058	685.05	10.829
3.061	685.95	11.015
3.769	873.21	10.621
3.777	875.16	11.047
4.276	1007.35	12.007
4.278	1007.95	10.996
4.951	1185.71	12.123
4.957	1187.33	10.996
5.833	1418.42	10.160
5.839	1419.95	0.275
6.782	1426.17	0.000
6.784	1426.17	0.007
7.013	1426.20	0.000
7.792	1426.20	0.000
9.029	1426.20	0.000
10.792	1426.20	0.000
24.057	1426.20	9.985
24.808	1606.10	10.976
24.82	1609.39	10.704
25.098	1680.75	9.661
25.104	1682.20	10.487
25.843	1868.18	10.341
25.852	1870.42	10.623
26.15	1946.37	12.681
26.152	1947.01	13.700
26.785	2155.02	13.655
26.791	2157.06	21.907
26.982	2257.47	25.313
26.985	2259.58	23.685
27.244	2406.43	23.603
27.252	2411.15	17.466
27.756	2622.50	21.943
27.76	2624.33	23.529
27.956	2734.91	22.267
27.96	2737.14	0.009
28.799	2737.32	0.007
30.888	2737.67	0.000
32.93	2737.67	0.000

Appendix A8 - Source Code for the Ash Leaching Solute Transport Model

Appendix A8 - Source Code for the Ash Leaching Solute Transport Model

A8.1 Overview

Chapter 8 developed a solute transport model which incorporated ash leaching in saturated porous media. The model used a finite difference technique for numerical solution, presented in Appendix A1. The program was developed in FORTRAN 77 (Lahey, 1994) on an IBM-Microsoft DOS based personal computer, for programming simplicity. The code for the model was modified manually for each variation of the relevant input parameters.

A8.2 Source Code Used for Ash Leaching

```
      PROGRAM COLUMN
C Developed by    :  Gavin Mudd
C Started on      :  December 10, 1996
C
C Version 1.0     :  Completed January 28, 1997
C - Simple Leaching Model of Chris Black's Column Leaching Studies
C------------------------------------------------->
C Define Variables and Arrays for the main leaching routine
C
      REAL VEL,LV,TEND,ALPHA,CAREA,CMAX,HCOL,CPOR,CPV,g0,cndiv,
     +     tout,CERR,PORVOL,stotb,MERR,SERR,londis,effdiff,hyddis,
     +     linvel,peclet,cinit,beta
      DOUBLE PRECISION Cnew,Cold,S,M,TIME,LR,DZ,DTZZ,TZAN,cour,sinit,dt
      INTEGER NDIV,STEP,tint
      DIMENSION Cnew(2000),cold(2000),M(2000),LR(2000),S(2000),
     +          tout(75),tint(75)
      CHARACTER*12 OUTFILE,BFILE,toutfile
C------------------------------------------------->
C Array Variables
C C - Leachate Concentration (mg/l)  ---> S - Contaminant Mass in Ash (mg)
C M - Ash Concentration (mg/kg)      ---> LR - Leaching Rate (mg/l/s)
C------------------------------------------------->
C Define Variables and Arrays for importing data (Black, 1990)
C
      REAL BC,BTIME,BS,BM,BMASS,BVOL,BLV
      INTEGER BINT
      DIMENSION BC(18),BS(18),BM(18),BLV(18),BINT(18),BTIME(18)
C
C Read in column leaching data of Black (1990)
C
      BFILE='blackdat.txt'
      OPEN(4,BFILE,STATUS='OLD')
      READ(4,*)
      DO J=1,16
         READ(4,*)BTIME(J),BLV(J),BC(J),BS(J),BM(J)
      END DO
```

```
C
C Allow a one pore volume phase shift for column saturation
C Add 9.9 days and 1 pore volume to each row of data
C     DO J=1,16
C        BTIME(J)=BTIME(J)+9.8974
C        BCPV(J)=BCPV(J)+1.0
C        BLV(J)=BLV(J)+217.26
C     END DO
      BMASS=0.300
      BVOL=3.1663E-04
C------------------------------------------------->
C Definition of Constants
C
C VEL - Darcy velocity (m/day)   ---> LINVEL - Seepage Vel. (m/day)
C CPOR - Column Ash Porosity     ---> PORVOL - Column Pore Volumn (m^3)
C CPV - Number of Column Pore Volumes
C BMASS - Mass of Ash in Column (kg) ---> TEND - Simulation length (days)
C BVOL - Total Volume of Column (m^3) ---> HCOL - Height of Column (m)
C NDIV - Number of Divisions or Nodes
C CAREA - Column Cross-Sectional Area (m^2)
C CMAX - Maximum Leachate Concentration (mg/l)
C ALPHA - Leaching Rate Constant (day^-1)
C SINIT - Initial Mass per Node (mg)  --->  DZ - Delta Z (m)
C G0 - Influent concentration (mg/l)  --->  DT - Delta T (days)
C------------------------------------------------->
C Set and calculate various constants
C
      VEL=0.011
      CAREA=0.001963495
      HCOL=BVOL/CAREA
      PORVOL=2.1726E-04
      CPOR=PORVOL/BVOL
      linvel=vel/cpor
      londis=0.05*hcol
      effdiff=4.32E-05
      hyddis=londis*linvel+effdiff
C     write(*,*)'Number of divisions (spatial resolution) : '
C     read(*,*)ndiv
      ndiv=161
      DZ=HCOL/NDIV
      dtstab=(dz**2)/(2*hyddis+linvel*dz)
      dtcour=dz/linvel
      dtpec=(dz**2)/hyddis
      write(*,*)'Courant based DT is   < ',dtcour
      write(*,*)'Peclet based DT is    < ',dtpec
      write(*,*)'Stable DT range is    < ',dtstab
      write(*,*)
      dt=0.99999999*dtstab
      peclet=linvel*dz/hyddis
      cour=linvel*dt/dz
      g0=0.0
      TEND=BTIME(16)
      CMAX=BC(2)
      SINIT=BM(1)*BMASS/NDIV
      DTZZ=hyddis*DT/(DZ*DZ)
      TZAN=DT*DZ*CAREA*CPOR*1000
      DO J=1,16
         BINT(J)=INT(BTIME(J)/DT)
      END DO
      write(*,*)'Courant Number    : ',cour
      write(*,*)'Peclet Number     : ',peclet
      write(*,*)
      write(*,*)'Time Step (days)  : ',dt
      write(*,*)
      WRITE(*,*)'ALPHA (leaching rate constant)  : '
      READ(*,*)ALPHA
C     beta=1.0
C     WRITE(*,*)'BETA (leaching rate power)      : '
C     READ(*,*)BETA
```

```
C------------------------------------------------->
C Read in "tout.txt" file of output times
      toutfile='tout.txt'
      open(5,toutfile,status='old')
      do j=1,56
         read(5,*)tout(j)
         tint(j)=int(tout(j)/dt)
      end do
C------------------------------------------------->
C Open output file and write basic input parameters
C
      OUTFILE='colleach.txt'
      OPEN(2,OUTFILE,STATUS='UNKNOWN')
      WRITE(2,*)'         Fly Ash Column Leaching Numerical Model'
      WRITE(2,11)
11    FORMAT(57('-'))
      WRITE(2,*)'      Column Leaching Data of C. Black (1990) - SO4'
      WRITE(2,11)
      WRITE(2,14)linvel
14    FORMAT('Average Linear Velocity (m/day)           = ',2x,F10.4)
      WRITE(2,15)CMAX
15    FORMAT('Maximum Concentration (mg/l)              = ',2x,F7.1)
      WRITE(2,16)BM(1)
16    FORMAT('Initial Ash Conc. (mg/kg)                 = ',1x,F8.1)
      WRITE(2,17)STOTB
17    FORMAT('Initial Leachable Mass (mg)               = ',2x,F7.1)
      WRITE(2,24)PORVOL*1000000
24    FORMAT('Column Pore Volume (ml)                   = ',3x,F7.2)
      WRITE(2,25)HCOL*1000
25    FORMAT('Height of Ash in the Column (mm)          = ',4x,F6.2)
      write(2,26)hyddis
26    format('Hydrodynamic Dispersion Coeff. (m^2/day)  = ',6x,F9.7)
      WRITE(2,*)
      WRITE(2,27)NDIV,DZ*1000
27    FORMAT('Spatial Resolution (n = ',I3,') (DZ) (mm)    = ',5x,F6.3)
      WRITE(2,28)DT
28    FORMAT('Time Step Used (DT) (days)                = ',6x,F8.6)
      WRITE(2,29)ALPHA
29    FORMAT('Leaching Rate Constant (ALPHA) (/day)     = ',6x,F9.7)
      WRITE(2,*)
      write(2,30)peclet,cour
30    format('Peclet No. = ',F7.4,4x,'&    Courant No. = ',F9.6)
      write(2,*)
      WRITE(2,33)
33    FORMAT('  Time  Leachate   Error    Leachable   Error',
     +          '     Ash     Error   Leaching')
      WRITE(2,36)
36    FORMAT('          Conc.            Mass of Ash   ',
     +          '         Conc.             Rate')
      WRITE(2,37)
37    FORMAT('  days    mg/l       %          mg        %',
     +          '       mg/kg     %     mg/l/day')
      WRITE(2,*)
C---------------------------------------------------->
C Initialize the Conc., Leaching, Mass and Ash Arrays
C
      TIME=0.0
      LV=0.0
      STEP=0
      DO J=1,NDIV
         cold(j)=cmax
         LR(J)=ALPHA*(CMAX-Cold(J))
         s(J)=sinit-cmax*0.1/ndiv
         M(J)=BM(1)
      END DO
      STOTB=BM(1)*BMASS
      mb=STOTB/BMASS
      cndiv=cold(ndiv)
      WRITE(2,47)TIME,Cndiv,CERR,stotb,SERR,mb,MERR,LR(NDIV)
```

```
47    FORMAT(F6.2,1x,F8.1,2x,F7.2,5x,F8.2,1x,F6.2,4x,F8.1,1x,
     +       F6.2,3x,F6.2)
C---------------------------------------------------->
C Begin Leaching Calculations - Main Finite Difference Routine
C
50    TIME=TIME+DT
      STEP=STEP+1
      LV=vel*TIME*CAREA*1000000
      LR(1)=ALPHA*((S(1)/SINIT)**beta)*(CMAX-Cold(1))
      Cnew(1)=Cold(1)-cour*(Cold(1)-g0)
     +        + DTZZ*(Cold(2)-2*Cold(1)+g0)+DT*LR(1)
      S(1)=S(1)-TZAN*LR(1)
      M(1)=S(1)/(BMASS/NDIV)
      DO J=2,NDIV-1
         LR(J)=ALPHA*((S(J)/SINIT)**beta)*(CMAX-Cold(J))
         Cnew(J)=Cold(J)-cour*(Cold(J)-Cold(J-1))
     +           + DTZZ*(Cold(J+1)-2*Cold(J)+Cold(J-1))+DT*LR(J)
         S(J)=S(J)-TZAN*LR(J)
         M(J)=S(J)/(BMASS/NDIV)
      END DO
      LR(NDIV)=ALPHA*((S(ndiv)/SINIT)**beta)*(CMAX-Cold(ndiv))
      Cnew(ndiv)=Cold(ndiv)-cour*(Cold(ndiv)-Cold(ndiv-1))
     +          - DTZZ*(Cold(ndiv)-Cold(ndiv-1))+DT*LR(ndiv)
      S(NDIV)=S(NDIV)-TZAN*LR(NDIV)
      M(NDIV)=S(NDIV)/(BMASS/NDIV)
      do j=1,ndiv
         cold(j)=cnew(j)
      end do
      cndiv=cnew(ndiv)
C
C Calculate the % error to original data
C and output if time is the same
C
      do j=1,56
         IF(STEP.EQ.tint(J))THEN
           cerr=0.0
           serr=0.0
           merr=0.0
           WRITE(2,47)TIME,cndiv,CERR,STOTB,SERR,MB,MERR,LR(NDIV)
         END IF
      end do
      do j=2,16
         if(step.eq.bint(j))then
           if(j.eq.2)then
             STOTB=STOTB-cmax*0.1
             else
             stotb=stotb-cndiv*0.25
           end if
           MB=STOTB/BMASS
           CERR=100*((cndiv-BC(J))/BC(J))
           SERR=100*((STOTB-BS(J))/BS(J))
           MERR=100*((MB-BM(J))/BM(J))
           WRITE(2,47)TIME,cndiv,CERR,STOTB,SERR,MB,MERR,LR(NDIV)
         end if
      end do
      IF(TIME.LT.TEND) GOTO 50
      CPV=LV/(PORVOL*1000000)
      WRITE(2,*)
      WRITE(2,101)LV
101   FORMAT('Total Leachate Collected (ml)        = ',1x,F6.1)
      WRITE(2,102)CPV
102   FORMAT('Total Number of Column Pore Volumes  = ',2x,F5.2)
      STOP
      END
```