Groundwater Chemistry of the Latrobe Valley Influenced by Coal Ash Disposal - 1 : Dissimilatory Sulphate Reduction and Acid Buffering

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ABSTRACT : In excess of one million cubic metres of coal ash are generated annually by power stations in the Latrobe Valley region of Victoria, Australia. The ash has generally been disposed of by hydraulical slurrying with water to disposal ponds. The seepage from the ash pond to local groundwater has been studied for a number of years as part of environmental and dam engineering practice. The monitoring data obtained over the last 15 years has shown reactive groundwater chemistry. The ash seepage (leachate) ranges from strongly to mildly alkaline and typical groundwater is midly acidic. At Loy Yang, the groundwater is still maintaining mildly acidic conditions despite continued seepage from the ash pond. This is thought to be due to acid buffering of the groundwater by the process of dissimilatory sulphate reduction. The geochemical mechanism for this process is presented and discussed for the Loy Yang Power ash disposal system in the Latrobe Valley.

KEYWORDS : dissimilatory sulphate reduction, coal ash leachate, ash disposal, tailings

1.0   INTRODUCTION

The Latrobe Valley region of Victoria, Australia, contains vast brown coal reserves and currently has three main open cut mines supplying coal to power stations for electricity generation, including the Loy Yang Power complex. Coal ash produced by the Loy Yang power stations is currently disposed of by hydraulic slurrying to a disposal pond. Upon commissioning of the pond in 1982, significant ash pond seepage was found to be occurring under the dam embankment. A relief well system was installed in 1983 to lower groundwater pressures. Later in 1986 seepage was found to be occurring in the southern batters of Loy Yang B Station (see Figure 1). The existing network of groundwater monitoring bores was further developed to monitor groundwater chemistry and as part of environmental management and EPA licence requirements additional bores were added to the network (Mulder & Pedler, 1990; Daniels *et al.*, 1993). EPA has permitted existing ponds to continue to operate providing their seepage does not effect the beneficial uses of the aquifers at the project boundaries.

Relatively few case studies have been published regarding the influence of coal ash disposal on groundwater. The published work looks at simplified geochemical analysis, non-reactive solute transport, and/or compare leachate and modelled groundwater quality to various water quality criteria (eg Andrews & Anderson, 1978; Cherkauer, 1980; Le Seur Spencer & Drake, 1987). A review of monitoring data at Loy Yang indicates a dynamic groundwater chemistry limiting the migration of sulphate within the shallow aquifer system. This is thought to be due to reduction of sulphate to hydrogen sulphide and oxidation of organic matter. Typically sulphate reduction leads to an increase in alkalinity and pH; however, at Loy Yang it appears to act as an acidic buffer against the strongly alkaline ash leachate. A review of the geochemical processes and migration of ash leachate within the shallow Haunted Hill Formation aquifer at the Loy Yang site is presented.

2.0   SITE DESCRIPTION

The Loy Yang Power Station complex consists of 2 power stations - 2,000 MW (Loy Yang Power) and 1,000 MW (Edison Mission) with an adjacent open cut mine. A site map is shown in Figure 1. The

open cut mine, power complex, ash disposal pond (with the seepage collection system or "Relief Well Pit (RWP)"), overburden dump, Settling Pond (SP), Saline Water Pumping Station and Fire Services Reservoir (FSR) are the prominent features of the site.

Figure 1 - Loy Yang Site Location Plan (Approximate Only)
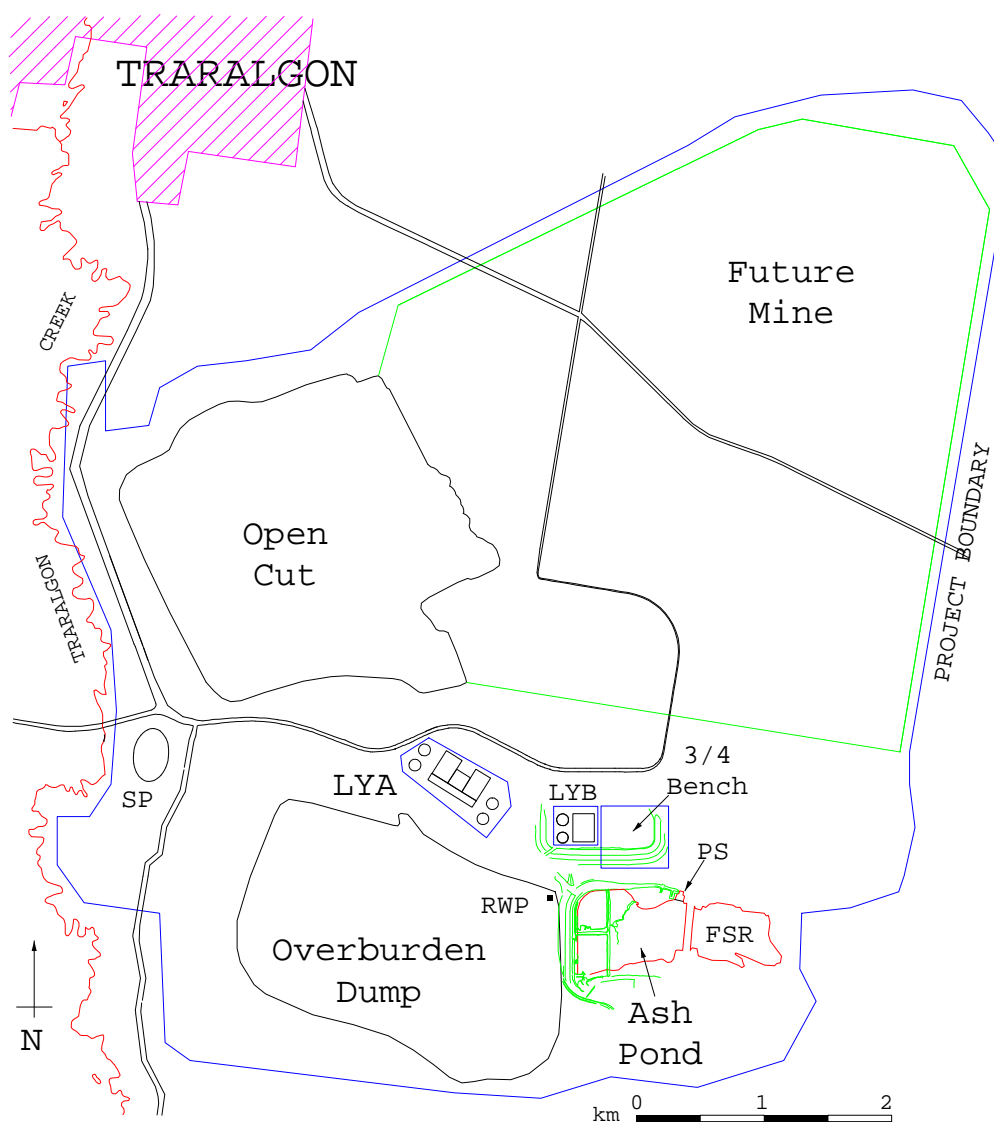
LYA - Loy Yang Power (2,000 MW); LYB - Edison Mission (1,000 MW); PS - Saline Water Pumping Station.

2.1 *Geology & Hydrogeology*

The Latrobe Valley is part of a major structural feature known as the Latrobe Valley Depression (LVD) (Gloe & Holdgate, 1991). 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), 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, or the Strzelecki Group.

The hydrogeology correlates with the major geological formations, principally the Morwell and Traralgon Formation aquifers, 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. The aquifers are generally quite transmissive due to gravels and the coarse nature of the sands. Depressurisation of these aquifers has been occurring at the Hazelwood and Loy Yang mines to maintain geomechanical stability of the open cuts.

The Haunted Hill Formation sediments have been deposited in a strongly fluvial environment and 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.

The HHF forms an unconfined aquifer system above the Late Pliocene unconformity. 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). The Ash Pond and Fire Service Reservoir has formed a seepage mound in the HHF and no significant unsaturated zone is likely to exist beneath the pond. Seepage flows are generally north to the B-Station 3/4 bench and west to the overburden dump.

3.0   SOLUTE TRANSPORT & HYDROCHEMISTRY

3.1   *Selected Monitoring Point Chemistries*

The groundwater monitoring network at the Loy Yang Ash Pond consists of numerous bores concentrated around the western and northern edges of the pond, with a background bore behind the FSR and two downgradient bores west of the pond. The following monitoring points have been chosen to highlight the hydrochemistry and solute transport mechanisms that are thought to be taking place :

Bore 3138U   Background groundwater chemistry before the influence of ash seepage;
Ash Pond   Ambient chemistry of the ash pond, (average from August 1992 to present);
Relief Well Pit   Seepage collection pit at the toe of the ash pond embankment;
Bore 2124U   Intermediate monitoring bore (300 m west from the ash pond embankment);
Bore 3135U   Downgradient monitoring bore (1,100 m west from the ash pond embankment).

Table 1 - Haunted Hill Groundwater Chemistry (mg/l), Western Side of Ash Pond, April 1997

Site	pH	Eh	TDS	Na	K	Ca	Mg	Fe	SO_4	Cl	HCO_3	Alk_F	CO_2	TOC
3138U	6.5	45	550	120	3.1	19	7.2	27	23	210	-	-	-	-
AP	9.7	-	7,290	1,873	71	352	33	0.17	3,950	590	23	-	-	-
RWP	5.0	-	4,100	980	27	54	78	24	2,900	790	4	-	-	-
2124U	4.7	170	1,300	320	0.9	7.6	73	24	510	340	<1	30	158[F]	8
3135U	6.3	55	940	190	1.2	13	43	22	<1	370	360	270	190[L]	63

Notes :
- F - Field value; L - Laboratory value; Eh in mV.
- Hydrogen sulphide samples were also taken, although most results were below detection limits (0.1 mg/l) except for 2124U at 0.3 mg/l and B-Station monitoring bore 3282L at 0.1 mg/l;
- Field measurements of $CO_{2 (aq)}$ were taken by titration with 0.1 M NaOH and phenolphthalein indicator and showed that significant degassing was occurring between the field and laboratory.

3.2   *Ash Pond & Ash Leachate*

The slurry and ash pond water is strongly alkaline and saline, with an average pH of 9.7 and TDS of 7,290 mg/l. The ash water is a sodium-sulphate-chloride type water, with minor amounts calcium, carbonate, potassium and magnesium. The molar ratio of sodium to sulphate is about 2, with sodium and sulphate comprising 80% of the molar mass, and chloride 11%. Ionic strength is moderate at about 0.16. The major ion chemistry and pH are considered to be controlled by impurities such as Al and Ca in the coal. The ash leachate seeping from the base of the pond is expected to have similar chemistry but the exact concentrations depend on a number of factors, including the long term leaching behaviour of the ash and the height and consolidation of the final ash deposit.

3.3 *Haunted Hill Formation Aquifer*

Groundwater of the HHF in the Loy Yang area is of generally low salinity, with background TDS values around 500 mg/l. Localised moderate salinity can be found near the B-Station bench of 2,000 mg/l (TDS). The chemistry is typically a sodium-chloride type water and mildly acidic with pH ranging from 7.0 to 4.0. The molar ratio of sodium to chloride is typically close to unity, with sodium and chloride comprising over 91% of the molar mass. Ionic strength values are low, approximately 0.004. This paper will concentrate on the hydrochemical patterns west of the ash pond, so that the localised effects of higher TDS on the proportions of different ions can be ignored.

3.4 *Solute Transport & Reactive Hydrogeochemistry*

The groundwater monitoring data from the Relief Well Pit and two bores downgradient of the ash disposal pond are shown in Figure 2. This figure indicates chloride has migrated in a conservative manner emerging at the downstream monitoring points as would be predicted by a simplified one-dimensional model using conservative solute transport properties. However, the same model for sulphate predicts concentrations at the distant monitoring bore higher than 1,000 mg/l. For instance, Bore 3135U has higher TDS and chloride levels yet still very low sulphate, below 1 mg/l in April 1997. Hence some mechanism appears to be impeding the long term migration of sulphate within HHF groundwaters.

Figure 2 - Sulphate and chloride migration patterns
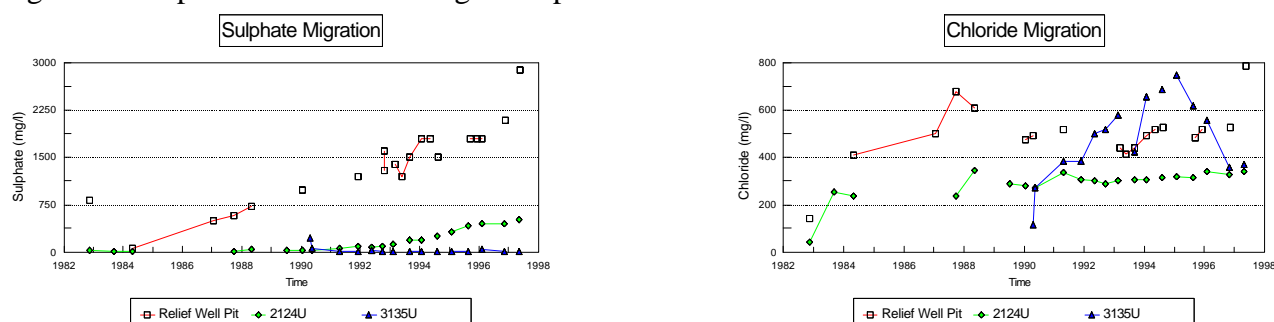
It has long been recognised that sulphate levels in various Latrobe Valley groundwaters are low due to conversion to hydrogen sulphide, since the odour can clearly be detected in groundwater bores (Brumley *et al.*, 1981) and particularly in the Relief Well Pit and bores around the ash pond (Daniels, 1994). Bolger (1984) also recognised that the presence of ferric iron (Fe^{3+}) and pyritic minerals was anomalous since the HHF was deposited in a high energy, oxidising sedimentary environment.

The chemistry at the Relief Well Pit, at the toe of the ash pond embankment, is consistently acidic despite over 15 years of strongly alkaline ash leachate seepage. Many monitoring bores around the ash pond also show a long term trend of slowly decreasing pH. Mixing calculations show (with PHREEQC; Parkhurst, 1995) that with ash leachate, the groundwater should eventually become alkaline within several years, even with groundwater to leachate ratios of 4:1. Therefore, the ratios required to maintain acidic groundwater would be much higher if only mixing is considered. However, this would indicate that seepage flows from the ash pond would be unrealistically smaller than predictions from earlier modelling studies (Pedler & Raisbeck, 1988; Daniels *et al.*, 1993 & 1994).

However, until the current research was initiated to assess the long term migration of the ash leachate plume in the HHF, conservative behaviour of all parameters, including sulphate, was assumed in solute transport modelling (eg - R = 1.1; Mulder & Pedler, 1990) and this important process not taken into account due to the lack of detail. It should be noted that by 1990, sulphate had yet to start increasing in concentration in the intermediate Bore 2124U and the above assumption could be seen as reasonable for modelling purposes.

The above discussion and the differing slopes of the above two graphs suggest that :
- chloride is migrating as a conservative species, with no retardation evident;
- sulphate is not migrating to downgradient wells, indicating that reduction of sulphate to hydrogen sulphide is occurring.

4.0 DISSIMILATORY SULPHATE REDUCTION AND ACID BUFFERING

4.1 *Overview*

Dissimilatory sulphate reduction, where reduced sulphur is mostly excreted as hydrogen sulphide, is typically accompanied by the oxidation of labile short chain organic matter (eg - acetate or formate). Under conditions of high organic matter, sulphate reduction can be approximated by a zero order kinetic process and proceeds at a constant rate. When organic matter is limited, the rate of sulphate reduction is controlled by the availability and reactivity of organic matter (Berner, 1981). With CH_2O representing organic matter, the overall reaction can be represented by (Matthess, 1982) :

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_{2\ (g)} \qquad \Delta G^0 = \text{-104.7 kJ (at pH = 7)} \quad (1)$$

This equation indicates three important conclusions - firstly, sulphate reduction is accompanied by an increase in pH or alkalinity; secondly, the hydrogen sulphide, due to its high reactivity, will react with aquifer sediments to form various sulphide minerals, particularly iron sulphides and pyrites; and thirdly that twice the molar quantity of organic matter is required per mole of sulphate.

4.2 *Dissimilatory Sulphate Reduction at Loy Yang*

In the Loy Yang area, it appears that sulphate reduction is occurring with an acid buffering process and not an increase in alkalinity as predicted by (1). Although Bolger (1984) highlighted the presence of organic matter within the HHF, the exact form and source of the organic matter within the HHF is not yet available, although levels of Total Organic Carbon (TOC) from the most recent monitoring (April/May 1997) indicate relatively low concentrations ranging from 4 - 63 mg/l. The slow increase of sulphate levels in downgradient monitoring bores suggest that the type and availability of organic matter within the groundwater and sediments is now controlling the overall rate of sulphate reduction. Previously in the Latrobe Valley, sources of sulphate would have controlled the overall production of hydrogen sulphide due to the relative abundance of organic matter to sulphate.

There is an excess of free carbon dioxide available in the groundwater, which would contribute to acidity via the formation of carbonic acid. The exact source of this carbon dioxide is unclear, but may be due to the action of other micro-organisms within aquifer sediments and further oxidation of diffuse organic acids from residual organic matter of the HHF and coal layers below.

The excess carbon dioxide is thought to contribute to acid buffering via :

$$CO_{2\ (g)} + H_2O \rightarrow H_2CO_3 \qquad (2) \qquad\qquad H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (3)$$

During groundwater sampling at Loy Yang it is common to see degassing of the sample. Measurements of pH and pCO_2 in the field and laboratory show a small subsequent increase in pH and decrease in pCO_2. This is also consistent with measurements from groundwater samples from the deeper aquifers within Loy Yang mine (Bradley, pers. comm).

5.0   DISCUSSION AND SCOPE FOR FURTHER WORK

It has been shown that dissimilatory sulphate reduction is a viable biogeochemical process for the Loy Yang site. This process slows the migration of sulphate from the ash pond within the Haunted Hill Formation aquifer, and minimises environmental impact. The presence of hydrogen sulphide within groundwaters across the Latrobe Valley would suggest that this process is common across the region. Clearly there is still much work to be done on quantifying this process, eg - determining the behaviour of the bacteria in the HHF, overall reaction rates, the source of organic matter and the excess carbon dioxide, and the final sink for sulphide. The long term beneficial uses of groundwater would not be expected to change since groundwater quality is still within the natural variability of the HHF.

6.0   ACKNOWLEDGEMENTS

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Groundwater Chemistry of the Latrobe Valley Influenced by Coal Ash Disposal - 2 : Preliminary Kinetic Modelling

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ABSTRACT : In a companion paper in the current proceedings (Mudd *et al.*, 1998), it was shown that seepage occurs from the Loy Yang ash disposal ponds, where one of the principal solutes of concern in the seepage is sulphate. Monitoring data and preliminary geochemical analysis suggests that acid buffering and dissimilatory sulphate reduction leads to attenuation of sulphate migration through the groundwater. The process of sulphate reduction accompanied by organic matter oxidation is considered to be controlled by a first order kinetic reaction. A preliminary kinetic model of this process is developed and applied to the migration of sulphate from ash leachate through the Haunted Hill Formation shallow groundwater system at the Loy Yang Power complex in the Latrobe Valley, Victoria. Within the assumptions used, reasonable agreement has been obtained between modelled results and monitoring data collected to date. Based upon this model, estimated rates of attenuation of sulphate are 0.63 mg/l.day.

KEYWORDS : dissimilatory sulphate reduction, ash leachate, attenuation rates, kinetic modelling

1.0   INTRODUCTION

The seepage of solutes from waste disposal and heavy industry is an important environmental concern. Examples include seepage from municipal landfills, mine tailings dams, hazardous waste and chemical storage facilities and the like. The dominant focus on studies of these sites has been on the physical movement of the solutes and their chemical behaviour in groundwater. Previous work included density driven flow for heavy contaminants such as dense hydrocarbons and brines, and radioactive decay sequences for radionuclides or the sorption properties of the aquifer sediments for heavy metals. Little attention, however, has been given to attenuation processes which are outside the realm of traditional mass-action or equilibrium based approaches.

There are many examples of non-equilibrium type processes in groundwater - the electrochemical evolution of leachate below a municipal solid waste landfill, acid mine drainage and the oxidation of pyritic minerals, the long term movement of organic contaminants (pesticides, organochlorines, etc.), and the multitude of microbially mediated processes. Dissimilatory sulphate reduction is an important microbially controlled process in hydrogeology, but has received very little attention to date.

Dissimilatory sulphate reduction has been shown to occur in a wide variety of geologic environments, and, perhaps, the most notable research is concentrated in marine sedimentology (since seawater is high in sulphate) and petroleum geology. It is typically moderated by a specialised group of bacteria known as sulphate-reducing bacteria (SRB) which require particular environmental conditions to thrive. Over the last two decades SRB have found increasing applications in the field of biotechnology, especially the degradation of many organic contaminants (Ensley & Suflita, 1995).

It has been identified that dissimilatory sulphate reduction occurs in the Haunted Hill Formation aquifer at the Loy Yang Power complex in the Latrobe Valley region of Victoria, Australia (Mudd *et al.*, 1998). Once ash leachate enters the groundwater, a very clear attenuation mechanism operates that limits the migration of sulphate by reduction to hydrogen sulphide. The overall reaction can be simplified as (Matthess, 1982) :

$$2CH_2O + SO_4^{2-} + H^+ \rightarrow HS^- + 2H_2O + 2CO_{2\ (g)} \qquad \Delta G^0 = \text{-}104.7 \text{ kJ (at pH = 7)} \quad (1)$$

The process of dissimilatory sulphate reduction is kinetically controlled, and is typically modelled as a first order reaction with respect to organic matter, or zeroth order with respect to sulphate (Berner, 1981; Jørgensen, 1978). A steady state diagenetic model has been developed by these authors, and others, for application to marine floor sediments. The dominant controls on sulphate concentration are assumed to be diffusion, reduction and the rate of sedimentation.

Monitoring data obtained recently at the Loy Yang site and over the last 15 years have given a basic understanding of the attenuation of sulphate, but there remains a lack of detailed field and experimental data on the source of organic matter and the overall controls on the rates involved. Mathematical models can therefore be a useful tool to help estimate rates and investigate controls on the overall process of sulphate reduction. In order to apply the above models, it is necessary to re-define the governing equation to take account of the fact that the water itself is flowing, and that the process of advection, dispersion and the source of organic matter also become important in the overall migration of sulphate. Hence a one-dimensional solute transport model that incorporates the kinetic reduction of sulphate is developed and applied to the Loy Yang site. The model was first calibrated against the migration pattern of chloride, and the calibrated flow and transport parameters were then applied to the migration and attenuation of sulphate.

2.0   THEORETICAL MODEL OF DISSIMILATORY SULPHATE REDUCTION

2.1   *Background and Brief Literature Review*

Dissimilatory sulphate reduction, where the reduced sulphur is mostly excreted as hydrogen sulphide, is an important environmental process in the global sulphur cycle and is now well recognised in sedimentary and petroleum geology and specialised fields of microbiology and biotechnology. Indeed it is recognised as one of the critical processes on which life on earth depends (Postgate, 1984).

The process of dissimilatory sulphate reduction and organic matter oxidation, although thermodynamically favourable, is very slow at typical near surface groundwater conditions of low temperature. Sulphate-reducing bacteria catalyse this process and significantly increase the overall rate at which sulphate reduction occurs. The main environmental requirements of SRB are the presence of reducing conditions, sulphate and suitable energy sources (Jørgensen, 1983). SRB are obligate anaerobes and require anoxic environments to survive. They are thought to be a critical part in overall microbial degradation cycles within the wider environment.

Sulphate reduction is modelled using first order kinetics of organic matter degradation, since it is the reactivity of organic matter which controls the overall process (Berner, 1964) :

$$\frac{dG}{dt} = \text{-}\alpha G \qquad (2) \qquad \text{and} \qquad \frac{dC}{dt} = \text{-}\beta \qquad (3)$$

where G represents metabolisable organic matter (mg/kg), α is the organic matter reactivity constant (kg/l.day), C the sulphate concentration (mg/l) and β the sulphate reactivity constant (mg/l.day). It is assumed that the reactivity of organic matter, α, is constant over time, and that equation (2) applies when there is an infinite source of organic matter relative to sulphate (Jørgensen, 1978). This assumption, however, is not strictly valid for field conditions.

It has been found by numerous authors that the reactivity of organic matter decreases with age since the more reactive organics are used first by bacteria (eg - Jørgensen, 1983; Middelburg, 1989, Berner, 1981). This has led to the development of multiple component models, such as the Multi-G model, power function models and continuum models to account for the change in organic matter reactivity (eg. - Jørgensen, 1978; Westrich & Berner, 1984; Middelburg, 1989; Boudreau & Ruddick, 1991). For modelling purposes, only two or three components are required for time frames of tens of years, but for time scales approaching 10^4 to 10^7 years, up to eight components are required

(Middelburg, 1989). Due to the lack of field data concerning organic matter in the HHF at the Loy Yang site, the basic approach of Berner (1964) will be used to estimate the rates of sulphate reduction with a one-dimensional solute transport equation.

2.2 *One-Dimensional Solute Transport Incorporating Kinetic Sulphate Reduction*

The overall one-dimensional solute transport equation incorporating chemical reactions is (Zheng & Bennett, 1995) :

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} + \Sigma R \tag{4}$$

where C is the (sulphate) concentration in groundwater, t is time, D_x is the hydrodynamic dispersion coefficient, v_x is the linear groundwater velocity, and ΣR is the sum of reactions affecting the concentration of the solute. This equation is for uniform flow in a non-deforming saturated medium. Based on equation (1), the rate of organic matter degradation is twice the rate of sulphate degradation, an approach used by Westrich & Berner (1981) and Appelo & Postma (1993). By substituting equations (2) and (3) into (4), it is possible to derive the overall solute transport equation for sulphate which incorporates the kinetic reduction of sulphate as :

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2} - v_x \frac{\partial C}{\partial x} - \frac{1}{2}\alpha G \tag{5}$$

Therefore, in flowing groundwater with a high input of sulphate, there will be a progressive depletion of organic matter along the flowpath. To the best of the authors' knowledge, equation (5) has not been applied to sulphate reduction in groundwater.

2.3 *Numerical Solution*

A block-centred explicit, upward finite difference scheme (Zheng & Bennett, 1995) was used to solve (5) subject to the following boundary and initial conditions :

$$x = 0, C(0,t) = f(t); \quad t = 0, C(x,0) = C_0, G(x,0) = G_0 \quad \text{and} \quad x = X_{max}, \frac{\partial C}{\partial x} = 0 \tag{6}$$

where f(t) is the input concentration function, C_0 and G_0 the background sulphate and organic matter concentrations, and X_{max} the maximum flow length. The scheme is subject to the following stability criteria :

$$\Delta t \leq \frac{\Delta x^2}{2D_x + v\Delta x} \tag{7}$$

The organic matter content is determined by the following relationship :

$$G_{i+1} = G_i - \frac{\partial G}{\partial t}\partial t \quad = G_i (1 - \alpha\partial t) \tag{8}$$

3.0   MODELLING RESULTS

3.1   *Flow and Transport Parameters*

In order to model the migration of sulphate, the basic flow and transport parameters needed are linear groundwater velocity, hydrodynamic dispersion, initial organic content, and the kinetic rate constant. The source concentrations or boundary conditions are also required. However, the first step is to model the migration of chloride which is known to migrate as a conservative ion, and hence the reaction term in equation (4) will be equal to zero. This allows calibration of the model before the effects of sulphate reduction are taken into account.

3.2   *Source Leachate Concentrations*

It is known that the concentration of different solutes within leachate will vary according to many factors. These include the variability of waste over time, disposal density, pretreatment (eg - slurrying of the ash to the disposal pond), placement sequence, depth or height of disposal, time, and the moisture loading of the waste (Farquhar, 1989). Taking into account all of these factors precisely is a challenging task, considering the scale of waste disposal facilities and the heterogeneity found in such systems.

In the current paper, two different approaches were used for approximating the source leachate concentrations emanating from the ash pond base. The first and simplest method used was a constant source concentration based upon the average concentration within the ash pond (chloride - 590 mg/l, sulphate - 3950 mg/l). The second method used was the variable concentration of chloride over time within the ash pond. A third method has been proposed by Farquhar (1989) to calculate a leachate function based upon leachability studies and the flow rate through a waste profile. However, the method is intended for unsaturated dry waste profiles and would need to be extended to the saturated and high water content conditions within the ash pond, and hence it was not applied in this paper.

Figure 1 - Chloride and sulphate source concentrations within the ash pond.
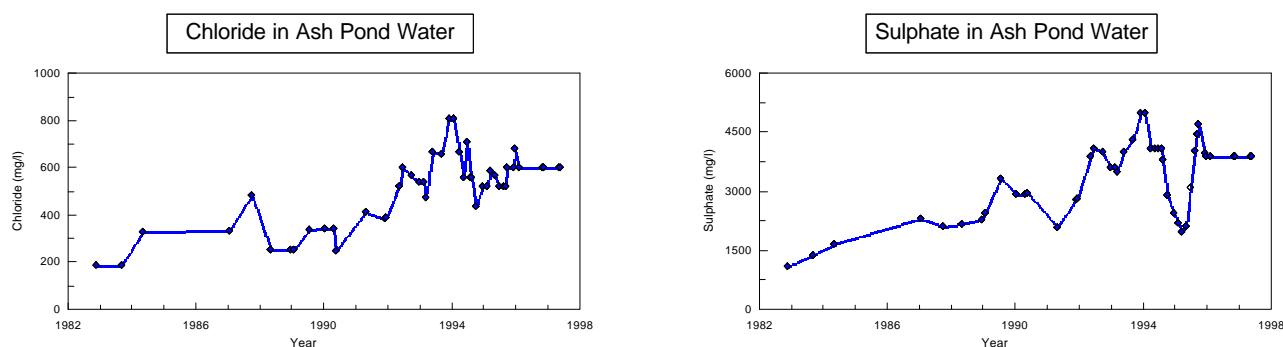
3.3   *Calibration to Chloride Data*

The following parameters were determined by visual calibration to the observed chloride migration pattern - linear groundwater velocity 0.05 (m/day); hydrodynamic dispersion 60 (m^2/day); and background chloride 140 (mg/l). 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.

Figure 2 - Chloride calibration - (a) constant source; (b) ambient ash pond concentration.
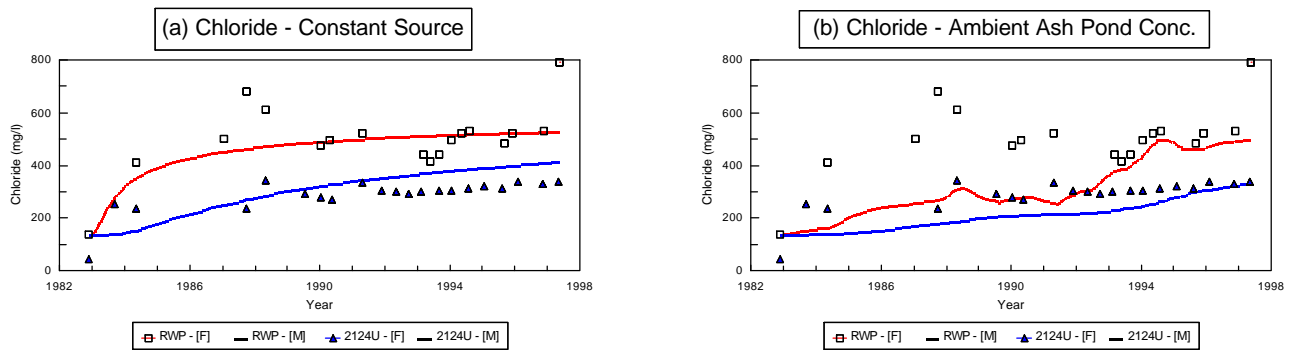

The above graphs give a reasonable approximation to monitoring data obtained to date (refer to Mudd *et al.* (1998) for detail on the monitoring bores). The constant source gives a good fit to the relief well pit, while the ambient ash pond concentration gives a close correlation with the peaks and troughs in the monitoring data and the steady state concentrations are more closely predicted for both bores. Both source types will be used for sulphate modelling.

3.4   *Kinetic Sulphate Reduction Modelling*

Using the flow and transport parameters from the chloride calibration, the following results were obtained for kinetic sulphate reduction. The initial organic matter content (G_0) was 1,250 mg/kg (0.125% by aquifer sediment mass) and the rate constant, α, was 0.001 kg/l.day (1,000 mg/l.day). The Haunted Hill Formation aquifer is a sandy-silty-clayey system, and would be expected to have organic content in the above range. Sensitivity analyses show that a higher/lower organic content attenuates the migration of sulphate too strongly/weakly and the concentration of sulphate in bore 2124U is below detection or too high respectively.

Figure 3 - Sulphate results : (a) constant source & (b) ambient ash pond concentration.
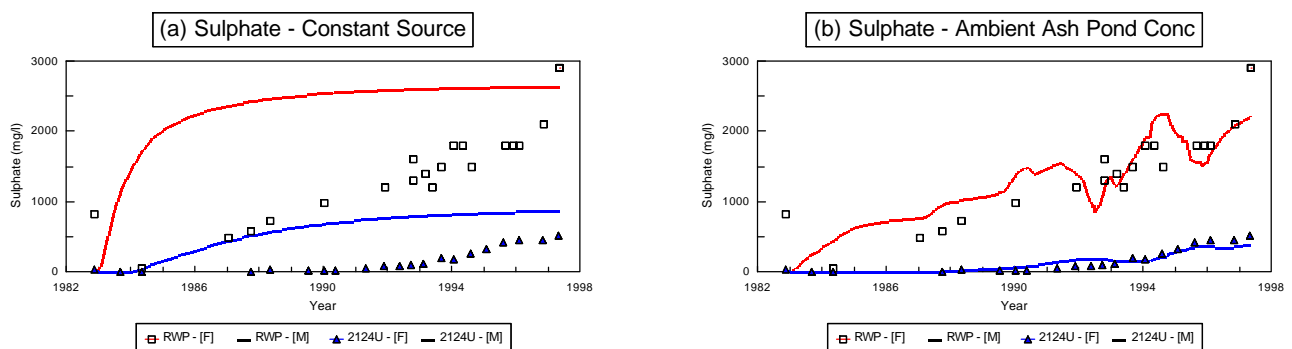
4.0   DISCUSSION

A one-dimensional kinetic model for the solute transport of sulphate has been developed and applied to monitoring data obtained over the last 15 years from the Loy Yang ash disposal site. The model was first calibrated to chloride using either a constant source concentration or the variable concentration found within the ash pond over time. Both source boundaries gave reasonable correlation with monitoring data and so the same approach was used for sulphate. However, the constant source for sulphate significantly overestimates the monitoring data, whereas the variable source closely fits the data.

It is recognised that the assumptions used in developing the above model do need further field and laboratory investigation to validate many of these assumptions as realistic. This includes the quantity and form of organic matter within the aquifer sediments and groundwater, the bacteria driving this process and their characteristics, the value of the rate coefficients, and the nature of the source concentrations emanating from the base of the ash pond.

The most crucial assumption, however, that needs to be verified is that the rate of organic matter oxidation is twice that of sulphate reduction. Although this would be effectively accounted for in the above results through the selection of an appropriate value of α, this value may not be realistic for in-situ processes and would need to be determined experimentally.

Given the above assumptions, reasonable agreement has been found between model results and monitoring data for both chloride and sulphate. It emphasizes the importance of adopting the right controlling processes for a solute being transported through groundwater. Based on equation (5), the maximum estimated rate of sulphate reduction is therefore 0.63 mg/l.day ($\frac{1}{2}\alpha G_0$).

5.0   ACKNOWLEDGEMENTS

6.0   REFERENCES

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