

## Studies on the Attenuation of Sulphate in Latrobe Valley Groundwaters

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**ABSTRACT :** Research to date has shown that there is strong attenuation of high sulphate seepage from the ash ponds of Latrobe Valley power stations. This is thought to be via reduction of sulphate and oxidation of residual organic matter within aquifer sediments. Although qualitative evidence suggests the dominant geochemical mechanisms involved, no comprehensive field data is yet available to quantify this process. Recent field work has been aimed at extending the groundwater chemistry database and identifying the bacteria involved in this process. This work is presented and geochemical analyses using PHREEQC are also presented. The implications for environmental management of groundwater quality beneath the ash ponds at Latrobe Valley power station complexes is discussed.

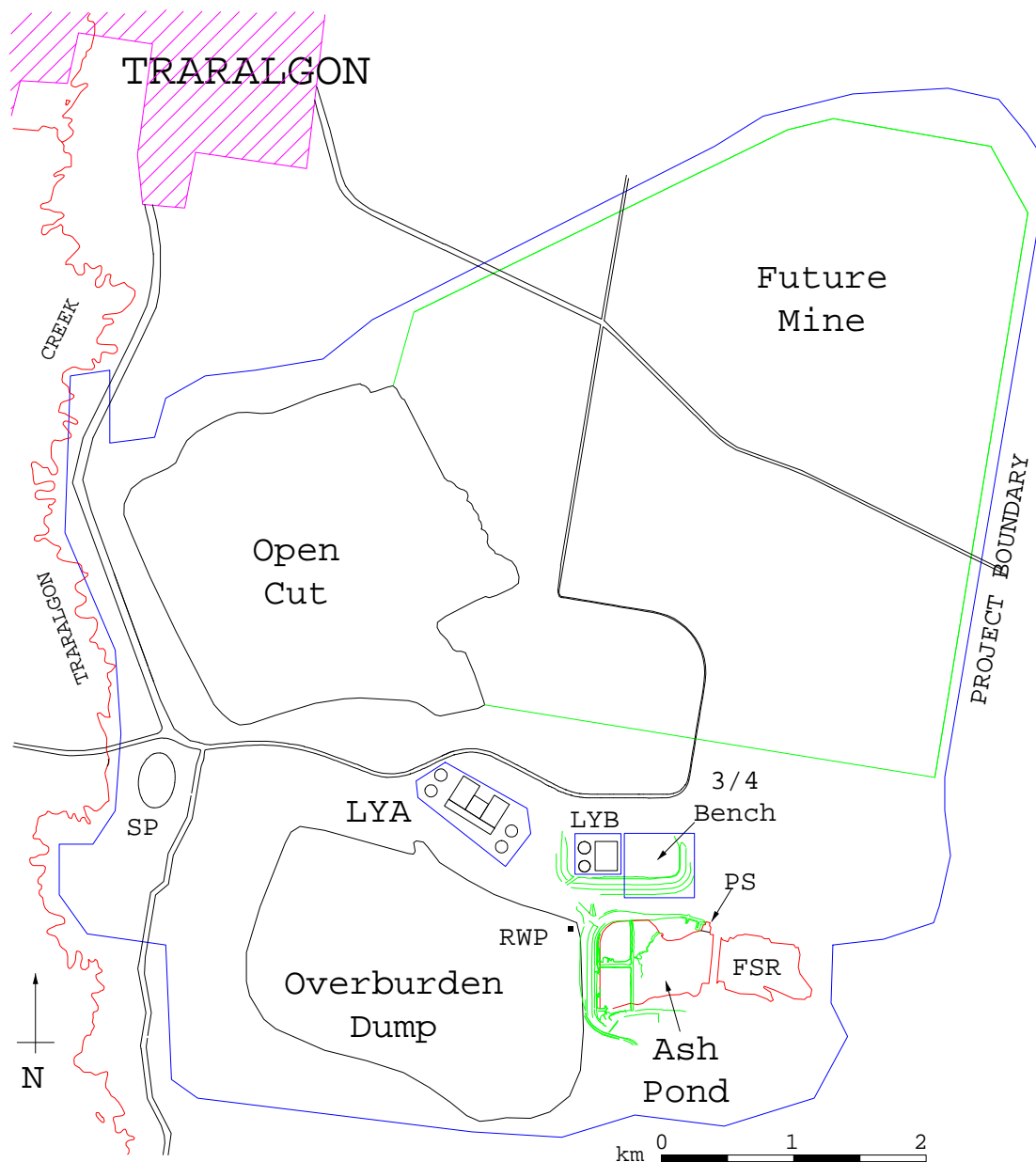
**KEYWORDS :** sulphate reduction, sulphate-reducing bacteria, natural attenuation, coal ash

### 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. Coal ash produced by the Loy Yang power stations is currently disposed of by hydraulic slurring to a disposal pond. Upon commissioning of the pond in 1982, significant ash pond seepage was found to be occurring to the west under the dam embankment. A relief well system was installed in 1983 to lower groundwater pressures. In 1986 seepage was found to be occurring to the north in the southern batters of Loy Yang B Station (see Figure 1). The existing network of 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). The Victorian Environment Protection Authority (EPA) has licensed existing ponds to continue to operate providing their seepage does not effect the beneficial uses of the aquifers at the project boundaries, as specified in the EPA's recent Groundwater Policy (EPA, 1997). The main solutes of concern in the coal ash seepage are sodium, sulphate and chloride.

### SITE DESCRIPTION

The Loy Yang Power Station complex consists of 2 power stations (2,000 MW owned by Loy Yang Power Pty Ltd (LYP) and 1,000 MW owned by Edison Mission Energy Pty Ltd (EME)), associated infrastructure (LYP) and an adjacent open cut mine (LYP). A site map is shown in Figure 1. The open cut mine, power station complexes, Ash Pond (AP; including the seepage collection system or "Relief Well Pit (RWP)"), Overburden Dump, Saline Water Pumping Station (PS) and Fire Services Reservoir (FSR) are the important features of the site.



**Figure 1 - Location of the Latrobe Valley and a Plan of the Loy Yang Complex (approximate only)**  
 (LYA - Loy Yang A owned by LYP; LYB - Loy Yang B owned by EME)

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 HHF 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 (Daniels *et al.*, 1993).

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 AP and FSR 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, along pre-existing groundwater flowpaths in the vicinity.

## ENVIRONMENTAL MONITORING & GROUNDWATER CHEMISTRY

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 (refer to Figure 1) :

Bore 3138U	Background groundwater chemistry before the influence of ash seepage;
Ash Pond	Ambient chemistry of the ash pond;
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 1998**

Site	pH	Eh	TDS	Na	K	Ca	Mg	Fe	SO <sub>4</sub>	HS <sup>-</sup>	Cl	HCO <sub>3</sub>	CO <sub>2</sub> (aq)	TOC
3138U <sup>1</sup>	6.5	45	550	120	3.1	19	7.2	27	23	-	210	-	-	-
AP <sup>2</sup>	9.0	-	7,800	1,800	74	360	46	0.27	4,300	-	590	32 <sup>3</sup>	-	-
RWP	4.9	125	4,600	1,200	32	64	75	23	2,800	0.5	550	12	238	3
2124U	4.3	136	1,700	330	0.5	8	110	18	810	1.0	340	<2	343 <sup>F</sup>	3
3135U	4.6	38	880	200	1.6	15	50	130	<5	<0.1	380	310	1,936 <sup>F</sup>	47

Notes :

<sup>1</sup> - No sample available in April 1998 - the data is from April 1997.

<sup>2</sup> - Sample from Feb. 2, 1998.

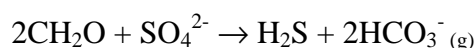
<sup>3</sup> - CO<sub>3</sub> is 24 mg/l (all other samples had CO<sub>3</sub> <2 mg/l).

- All analyses performed by WSL Consultants Pty Ltd under contract to Loy Yang Power Pty Ltd.
- F - Field value; L - Laboratory value; pH & Eh (in mV) measured in the field.
- Field measurements of CO<sub>2</sub> (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 (APHA, 1992).

In general, it can be seen that salinity decreases away from the ash pond, due mainly to the disappearance of sulphate within the groundwater. Comparing the monitoring trends for chloride and sulphate suggest that chloride is migrating through the HHF aquifer conservatively without attenuation (although the chloride concentration in ash pond seepage is only marginally above background variability), while sulphate is being strongly attenuated. The measured redox state of the samples in the field may be slightly influenced by the use of bailers for sampling. The redox potential calculated by PHREEQC using the sulphide/sulphate redox couple indicate reducing conditions within the aquifer (refer to later section). A negative redox state is also indicated by the dominant nitrogen species being ammonia, with only minor amounts of nitrate. More detail is presented in Mudd *et al.* (1998a & 1998b).

## REACTIVE SULPHATE CHEMISTRY & ATTENUATION

Previous work has highlighted that the strong sulphate attenuation is due to the reduction of sulphate to sulphide (Mudd *et al.*, 1998a). The sulphide is thought to react with minerals or iron in aquifer sediments and precipitate as relatively insoluble metal sulphides (Mudd *et al.*, 1998a). The process is kinetic or rate-controlled and mediated by sulphate-reducing bacteria (SRB) through the oxidation of labile organic matter (Chapelle, 1993). Although not widely appreciated, the literature is starting to show the importance and usefulness of SRB becoming increasingly recognised in many different industries, ranging from the cleanup of hydrocarbon contaminated sites to remedial processes for radioactively contaminated sites. The process of sulphate reduction can be represented as (Chapelle, 1993) :



A preliminary kinetic model of the process was developed and applied to the observed seepage monitoring data for chloride (treated as a conservative species) and sulphate, and gave good results when a variable source concentration within the ash pond was used (Mudd *et al.*, 1998b). The model was considered preliminary due to conservative assumptions made.

The pH of the groundwater is critical in the behaviour of sulphide and carbonate species during sulphate reduction. For a pH greater than 7 (alkaline), the sulphide will form  $\text{HS}^-$  rather than  $\text{H}_2\text{S}$ , while for a pH lower than 7 (acidic) the bicarbonate will dissociate to  $\text{CO}_2$  rather than  $\text{HCO}_3^-$  (Drever, 1997). The groundwater within the HHF aquifer is mildly acidic, with a pH ranging between 4.3 to 6.5, with the lower values near the most active seepage zone west of the ash pond. Thus the presence of  $\text{CO}_2$  is expected, although concentrations of  $\text{CO}_2$  in bore 3135U are much higher than accountable due to sulphate reduction alone. The source of this extra  $\text{CO}_2$  remains unclear. The high  $\text{CO}_2$  levels are thought to contribute to acid buffering of the groundwater and maintain the mildly acidic conditions observed to date, despite the general trend of sulphate reduction increasing alkalinity and pH (Mudd *et al.*, 1998a).

There is currently no data available to quantify or identify the important organic materials involved in the process. At the time of writing, new groundwater monitoring bores were being drilled and constructed and aquifer sediment samples were being obtained for chemical testing and analysis. The samples will be analysed for Total Organic Carbon (TOC) and fulvic and humic acids. Chapelle (1993) provides an excellent review on this topic.

## GEOCHEMICAL ANALYSIS

The groundwater chemistry presented above has been analysed using the PHREEQC geochemical computer program by Parkhurst (1995). The saturation indices for the different groundwaters with respect to important minerals are presented below in Table 2. All analyses were equilibrated with their respective free carbon dioxide concentration (calculated using thermodynamic constants in the PHREEQC database). Where sulphide concentrations were below detection levels (0.1 mg/l), a value of 0.01 mg/l was assumed.

The AP water is over-saturated with respect to carbonate species, although significantly under-saturated for carbon dioxide after equilibration to atmospheric  $\text{CO}_2$ . This is consistent with previous investigations of ash pond mineralogy in the Latrobe Valley. Black (1990) identified calcite as a major mineral within the ash pond at the Hazelwood complex, and was thought to be formed by exposure of ash pond water and sediments to atmospheric carbon dioxide. The AP water is near saturation with respect to gypsum and anhydrite.

**Table 2 - Geochemical Analysis of HHF Groundwater Bores : Saturation Indices**

Mineral	Formula	3138U	AP	RWP	2124U	3135U
Aragonite	CaCO <sub>3</sub>	-	0.52	-4.68	-6.16	-2.90
Calcite	CaCO <sub>3</sub>	-	0.67	-4.53	-6.01	-2.75
Carbon Dioxide	CO <sub>2</sub>	-	-4.64	-0.57	-0.40	0.00
Siderite	FeCO <sub>3</sub>	-	-4.29	-2.68	-3.38	0.35
Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	-	0.67	-8.77	-10.67	-4.80
Anhydrite	CaSO <sub>4</sub>	-2.99	-0.31	-1.10	-2.21	-4.64
Gypsum	CaSO <sub>4</sub> 2H <sub>2</sub> O	-2.71	-0.06	-0.85	-1.96	-4.39
Hydrogen Sulphide	H <sub>2</sub> S	-	-7.63	-3.92	-3.63	-5.65
Redox (calc.)	(mV)	-	-294	-28	11	-15

The influence of dissolved carbon dioxide on HHF groundwater chemistry is also marked, with the saturation indices after equilibration to CO<sub>2</sub> becoming more positive, especially for bore 3135U (which had the highest CO<sub>2</sub> level). The high iron level of bore 3135U gives rise to over-saturation with respect to siderite.

### PRELIMINARY BACTERIAL IDENTIFICATION

In order to determine the presence of sulphate-reducing bacteria within the HHF at Loy Yang, a small series of groundwater samples from bores in the HHF aquifer were obtained on July 24, 1997. The samples were obtained using bailers and stored in sterilised bottles within a cold environment. Although it is acknowledged that sampling groundwater may underestimate the bacterial population due to bacteria preferentially colonising aquifer sediments (Chapelle, 1993), the principal objective was to test for the presence of viable sulphate-reducing bacteria and not undertake systematic bacterial population studies. Thus samples of groundwater were considered to be sufficient for this purpose.

The groundwater samples were delivered to EML Consulting Services Pty Ltd for further analysis and testing using APHA (1992) methods for SRB. The samples were membrane filtered through sterile 0.45 mm pore size membranes and incubated on specialised SRB-prepared agar plates for up to 21 days, although no change was observed after about 6 days (EML, 1997). After incubation there was considerable growth evident but no indicative blackening to indicate pyrite formation and hence sulphate reduction (EML, 1997). Bacterial smears were obtained from three samples, heat-fixed, stained by Grams method and examined under the microscope. Although not conclusive, this indicated that the bacteria isolated may be *Clostridia* species or possibly *Desulfotomaculum* species (EML, 1997). No samples exhibited the morphology typical of *Desulfovibrio* species (EML, 1997).

### CONCLUSIONS

The groundwater chemistry of the Loy Yang site is varied and dependent on many complex biogeochemical processes. It is clear that attenuation of sulphate in the seepage is occurring through reduction to sulphide, mediated by bacteria present within the Haunted Hill aquifer. The bacteria involved, possibly *Desulfotomaculum* or *Clostridia* species, control the rates of sulphate reduction and organic matter oxidation. The exact form and nature of the organic matter are as yet unclear, although future field work is planned to elucidate this aspect of the process. The production of carbon dioxide in this process exerts a strong influence on the chemistry of the groundwater, maintaining mildly acidic conditions through the formation of carbonic acid despite the influx of strongly alkaline ash seepage. However, further research is required to qualify and quantify the bacteria and biogeochemical processes involved.

There are two important implications for the management of ash seepage at Loy Yang. The first is that natural attenuation by sulphate-reducing bacteria may continue to provide sufficient buffering capacity to satisfy the requirements of EPA (1997), assuming that widespread distribution of favourable biogeochemical conditions is appropriate. The second is that the rate of the attenuation processes may be artificially enhanced through the addition of short chain organic acids (if required) to ensure that the objectives of environmental management continue to be met to the satisfaction of Loy Yang, the community and the EPA.

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