# Incidence of Barium Pollution in Mine Water Discharge in an Underground Coal Mine

R. N. Singh and I. Porter

Department of Civil, Mining and Environmental Engineering,
University of Wollongong, Northfields Avenue,
Wollongong, NSW 2522,
Australia

## ABSTRACT

This paper is concerned with a case history of waste water quality management in an underground coal mine in the Illawarra region. The main chemical constituents of mine water associated with underground coal mining are described and a typical colliery water discharge licence condition for the Illawarra region is given. A case-study is presented showing the chemical analysis of a mine water discharge having an extremely high concentration of suspended solids and consistently high barium concentrations, averaging some 15 mg/l barium, over a relatively short sampling period. A laboratory based chemical precipitation study indicated that the barium content in mine water could be reduced by 91% by using ferric sulphate and lime. On the basis of the information obtained from the environmental audit process an alternative method of water treatment and reuse incorporating 51% reduction in the water consumption and a 32% reduction in off-site discharge has been suggested.

## INTRODUCTION

Coal mining activities invariably cause lowering of ground water level of the overlying unconfined aquifer or depression of the piezometric surface of the confined aquifer in the vicinity of the coal seam being mined. This change in piezometric pressure or ground water table induces ground water inflow to the mine workings which, in turn, causes a range of operational and environmental problems during underground mining. However the water pollution problems may still persist even after decommissioning of the mining operations. Regular monitoring of ground water inflow and chemical analyses of mine water may indicate the source of water or the possible dilution of the mine water from different sources. This paper describes the source of mine water pollution in underground coal mines.

## TYPES OF POLLUTANTS IN UNDERGROUND COAL MINING OPERATIONS

The water pollutants encountered in underground coal mines may be broadly classified into four general classes as follows:

Physical Pollutants
Chemical - Inorganic pollutants
              - Organic pollutants
Bacteriological Pollutants
Radiological Pollutants

It may be noted that Bacteriological and Radiological pollutants are not important in coal mining.

## Physical Pollutants

One of the major physical parameters characterising minewater pollution is pH which is the measure of molar concentration of hydrogen ions in solution. The solubility of metal in water is pH dependent at low values and a high value of pH results in precipitation of metal oxides from the solution. High sulphur in coal in the presence of water, oxygen and bacteria forms sulphuric acid and lowers the pH of the mine water. A pH below 6.5 may be corrosive to plumbing fixtures and reticulation systems. Suspended solids or non-filterable residues are defined as the concentration of solid matter in suspension giving rise to one of the most visible pollutants in the receiving water. Dark coloured suspended particles associated with coal mining effluent may be perceived by the public as a nuisance. Turbidity is the measure of fine suspended matter in mine water which scatters the light and gives a cloudy appearance to mine water. Turbidity readings are not required by Law for mine effluent but may be useful for water pollution studies. Total dissolved solids (TDS) content in the water sample is numerically expressed as electrical conductivity (EC) displayed by the ability of aqueous solution to carry an electric current. High levels of mineralisation is the typical characteristic of many coal mining discharges. The electrical conductivity of mine water varies from 1000 to 10,000 µS/cm. Turbidity readings are not required by law for mine effluent but may be useful for water pollution studies.

## Chemical pollutants

The major constituents of chemical pollution in mine water are alkalinity, acidity, chlorides, sulphates, nutrients expressed as nitrogen and phosphates, and non-toxic and toxic metals. Alkalinity is a measure of the water's ability to neutralise acids and its principle components are bicarbonates ($HCO_3^-$) carbonates ($CO_3^{--}$), and hydroxide ions. The metals such as sodium, potassium, calcium, manganese, iron and magnesium are essentially non-toxic and are found in variable concentrations in mine water.

Calcium and magnesium ions essentially impart hardness to mine water whereas iron and manganese ions contribute to decolourisation of water and formation of scales in the pipe lines and pumps. Metals such as zinc, aluminium, and barium may be found in small quantities in the mine water in coal mines. However, in the metal processing industry, the water effluent may contain arsenic, cadmium, chromium, lead, copper, mercury and vanadium. In the case of uranium mining, other radionuclii and radon may be present. The characterisation, assessment and control of mine water quality in active as well as closed mines is an important part of any environmental control program.

Acidity in mine water is derived from the dissolution of carbon dioxide or sulphuric acid. The main effect of acid will be the reduction of pH of the mine water resulting in unwanted metal dissolution into the mine water discharge thus contaminating the receiving water.

Nitrogen in water can originate from organic sources, ammonia, or from other oxidised forms such as nitrates. Nitrogen content in coal is usually small and in mine water it may not present any problems. Phosphorous occurs in mine water as phosphates, an essential nutrient for plant growth. When discharged in excessive concentrations in the receiving water such as streams and lakes, phosphate will eventually lead to eutrophication due to excessive plant growth called " algae blooms". It is recommended that the phosphate content of receiving water should not exceed 50 µg/l for maintenance of a congenial aquatic environment.

Chloride is naturally present in mine water in small quantities depending upon the geological formation with which the water has been in contact. A study of water analysis results from underground coal mines in the North East of England has revealed a common inter-relationship between the ionic concentrations of the salts dissolved in water. A log/log plot of the ionic concentrations of sodium, potassium, magnesium, calcium, barium and manganese against the concentration of chlorides, ammonium or bicarbonates show a linear relationship. Figure 1 shows the linear relationship between chloride ions and calcium ions obtained from a confined aquifer (Edmunds 1975).

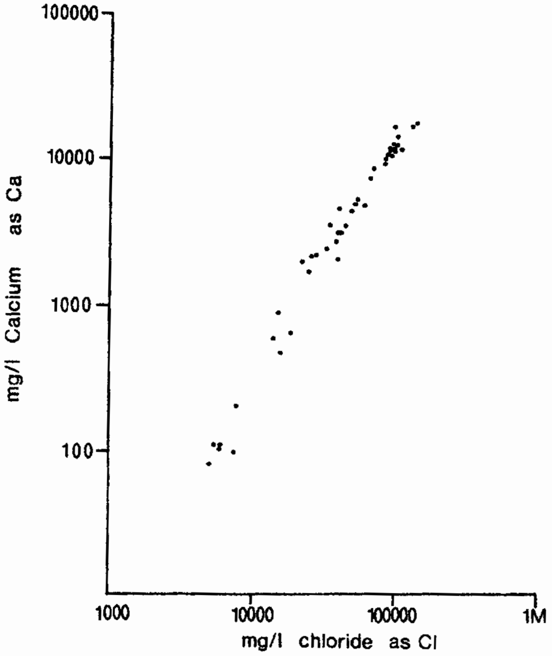

Figure 1 Relationship between calcium and chloride ions in the Harvey and Maudlin Seams, Northumbershire, England ( Edmunds 1975)

## ESTABLISHMENT OF WATER QUALITY CHARACTERISTICS OF THE COAL MEASURES.

From the 1970's to the 1980s, testing was undertaken in the U.K. of a large number of water samples having a wide range of water qualities from underground coal mines in the U.K. (Glover 1973, Glover 1983a,b ). Based on this study, it is now possible to use water quality to identify mine water from a wide range of sources. The basic principles involved in the identification of the source of mine water are the ratio of ionic concentration {eg Na/$\Sigma$ total cation} or Mg/$\Sigma$(Mg$^+$+Ca$^+$)} and the spatial distribution of the sources of the dissolved salts. Based on the above principles, the source of the water samples originating from confined coal measure aquifers, unconfined aquifers, abandoned old underground workings and surface water can be identified (see Singh 1994).

### Confined aquifers

Figure 2 shows the linear variation of the chloride ion distribution in confined aquifer with depth in the British Coal Measures. A gradual increase in chloride ion concentration is noted in the same aquifer and also stepwise increase in chloride ion concentration on the down - throw side of the boundary fault ( Bredehoeft et al 1963, Skipsey 1974, and Edmunds 1975). The chloride content of the various aquifers also increases with depth in the higher orders of magnitude of concentration.

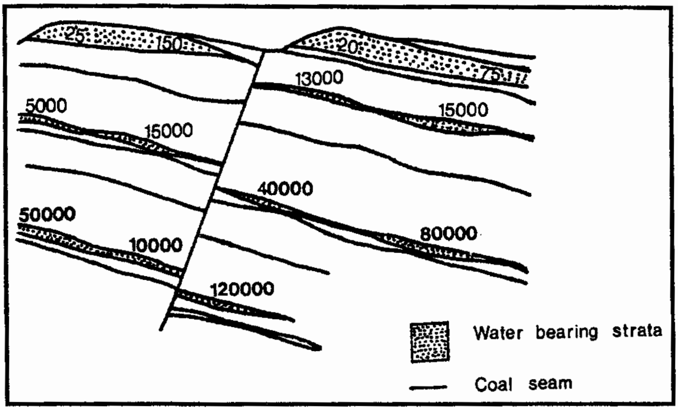

Figure 2 Spatial distribution of chloride ions with depth in a confined aquifer (after Glover 1983, Braedhoeft et al 1963)

The evidence suggests that the dissolved salts are in geochemical equilibrium with the strata with which they are in contact. The aquifer salt is able to migrate freely between the confined aquifers over geological time if under hydraulic pressure. Increasing concentration of salt with depth may be attributed to the movement of brine along the bedding planes with further movement of salt bearing water across the bedding plane under artesian pressure (Skipsey 1974).

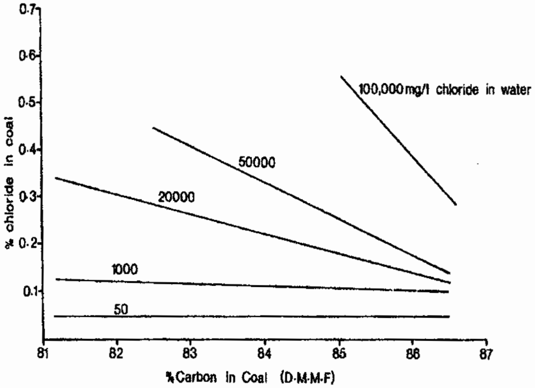

Figure 3 Inter-relation between chloride ions in coal, chloride in the aquifer and fixed carbon content of coal (Skipsey 1974)

Figure 3 shows the inter-relationship with chloride ion concentration in a coal seam in the vicinity of a confined aquifer with the concentration of fixed carbon in the adjoining coal seam underlying the aquifer. The water from the confined coal measure aquifers has distinct characteristics as follows:

- Alkalinity of the ground water initially increases and then decreases with depth.

- Salinity of ground water increases with depth in the same aquifer and with the depth of various aquifers.
- Chlorides, sodium, magnesium and calcium concentrations in water increase with depth.
- Manganese, barium and strontium were found in the deeper coal measure aquifers and their content is found to increase with depth.
- Absence of traces of sulphate ions is a characteristic of confined aquifers.

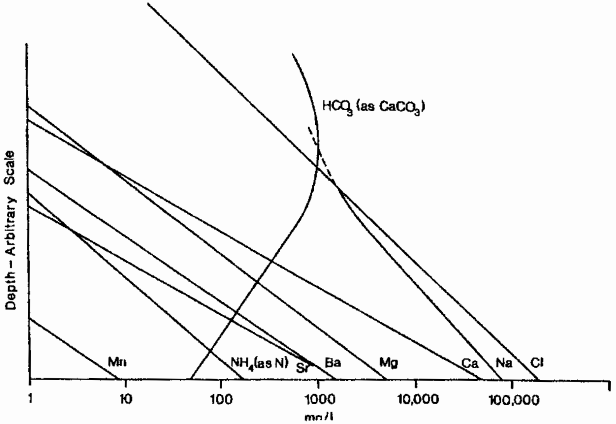

Figure 4 Increase in metal content of aquifer water with depth in the British Coal Measures ( after Glover 1983a)

### Chemical characteristics of unconfined aquifers

The chemical characteristics of water in an unconfined aquifer will differ greatly with the aquifer type, ie whether it is outcropping or situated in a concealed coalfield. The ground water in outcropping aquifers which are 50m to 100m deep have low chloride concentrations of <100mg/l, hardness between 100 to 500 mg/l and sulphate concentration between 50 to 300 mg/l. The chemical characteristics of deeper concealed and unconfined aquifers are intermediate between those of a typical coal measure aquifer and those in the overlying strata.

### Chemical characteristics of abandoned mine workings

The chemical characteristics of water in an abandoned coal mine are basically akin to those of the aquifer water but in addition it contains oxidation products of pyrites and other minerals. Thus, abandoned mine water contains considerable quantities of iron or other sulphates and low concentrations of dissolved $H_2S$. Moreover, the pH value is stabilised between 5.3 and 6.8. Dissolved sulphates remain in the water indefinitely and the oxidation potential of the water declines to a lower value.

## Barium in mine water

A literature review indicated that barium compounds occur as trace elements in many igneous, sandy and calcareous sedimentary rocks (Bowen, 1979; Swaine, 1990). Most coal contains barium in the form of barytes ($BaSO_4$) and witherite ($BaCO_3$). The barium compounds found in coal typically occur in mineral veins as reported by Forstner and Whittman (1979) in a colliery in Durham, U.K. Table 1 is a compilation of barium levels in selected rocks, naturally occurring water and some Australian coals. Barium contents in many soils range from 100 - 1000 mg/ kg, however in some geological formations such as fossil fuels much higher levels in excess of 1000 mg/kg have been reported (Bowen , 1979).

Table 1 Barium contents of various geological materials (Adopted from Swaine, 1990; Bowen, 1979; Forstner and Whittman, 1979; and Thomas 1995)

| Minerals | Barium (mg/ kg) |
|---|---|
| **Rocks** | |
| Granite Rock | 420 |
| Shales | 850 |
| Marine clays | 2300 |
| Sandstone | 320 |
| Limestone | 90 |
| Carbonates | 10 |
| Basalt | 250 |
| **Coal** | |
| Latrobe valley , Victoria | 60-800 |
| St Vincent Basin, South Australia | 220-440 |
| Leigh Creek, South Australia | 100-2000 |
| Collie, Western Australia | 43-519 |
| Hunter Valley New South Wales | 20-1500 |
| Western area , NSW | 20-300 |
| Southern Coalfields, NSW | 40-100 |
| Site of Investigation | 270-6300 |
| Sea water | 0.013 |
| Fresh water | 0.01 |

## Physiological effects of Barium

The physiological effects of barium on the human body has been studied by various medical workers amongst them is Brenniman and Levy (1985). Australian Drinking Water Guidelines (1994) suggests a limit of 0.7 mg/l barium in drinking water. In the majority of Australian water supplies the barium concentration ranges between 0.0005 mg/l to 0.3 mg/l. In high concentrations, barium causes constriction of blood vessels, contraction of alimentary canal, convulsion and paralysis. A number of long term studies on the effects of barium on heart disease have shown that no adverse effects were found with barium concentrations in water up to 7 mg/l. In a study using a small number of volunteers, no adverse effects were observed after 12 week's exposure to drinking water with up to 10 mg/l barium (Brenniman and Levy, 1985).

## MINE WATER QUALITY AUDIT - A CASE HISTORY OF A COAL MINE

The main objective of this study was to carry out a Mine Water Quality Audit in a coal mine situated in the environmentally sensitive Illawarra Region, New South Wales, Australia. There are

11 coal mines currently in operation in the Southern Coal Fields producing approximately 13.35 million tonnes of saleable coal per year. The coal field is a major producer of hard coking coal, which is utilised in the coke ovens in the Port Kembla and Whyalla Steelworks and exported to Japan and Europe. Most coal mines in the region are located in the catchment area of the water authority and discharge their effluent to creeks and water courses under licensing conditions imposed by the Environmental Protection Authority (EPA) of New South Wales. In order to meet the increasingly stringent water quality guide lines of the EPA and the high environmental standards expected by the local community, the mining industry has established a regular program of monitoring and testing of mine water effluent. In addition, occasional mine water audits are carried out for characterising the sources of waste water in the colliery and assessing the efficacy of current wastewater treatment processes. Mass balances of water input and discharge from various mining operations and industrial processes are carried out to identify areas of unexplained losses and sources of waste water. The treatment technologies are evaluated, in plant control, and waste water reduction and reuse methods are assessed.

## GENERAL QUALITY OF MINE WATER DISCHARGE IN THE ILLAWARRA COAL MINES

It is known that the mine effluent quality varies significantly from mine to mine in the Illawarra region (Singh 1994, Sivakumar et al, 1992, Singh, et al, 1995). The discharge license conditions also vary from mine to mine depending on the source and the receiving waters. The colliery water discharge licence conditions typically require that the selected water quality parameters should be monitored at a minimum of monthly intervals to meet the following conditions:

| | |
|---|---|
| Five day Biochemical Oxygen Demand | < 20 mg/L |
| Chemical Oxygen Demand | Not specified but a target is set at (50 mg/L) |
| Non-filterable Residue | < 30 mg/L |
| Grease and Oil | < 10 mg/L |
| pH | Between 6.5 to 8.5 |

This paper describes a research study concerned with mine water quality management in a mine located in the tablelands about 60 km from the coast within the Illawarra region.

### Site Description

The Colliery concerned is situated about 60 km north west of Wollongong where underground mining operations started in 1970. The average coal production from this mine is about 2 million tonnes of coal per annum. The surface facilities at the mine occupy three separate areas as follows:

(i) The main site for the access shaft ( No 3 Shaft), the administration buildings, pit head bath, workshop, washery and coal stockpiles and coal loading and handling facilities are situated within a rail loop just west of the main Sydney-Melbourne main railway line.

(ii) The reject tips are located east of the rail loop and occupy a large coal refuse disposal area. Because of their size and exposure to weather, the waste stockpiles are prone to water and wind erosion. In the waste tip area, the soil overburden is removed and replaced with the coal refuse from the washery. The waste is then compacted, progressively rehabilitated and revegetated.

(iii) The No. 2 shaft site is located about 3 km north east of the railway loop.

The water discharged from the mining complex comes from seven major sources; these being:

(a) Mine water from three pumps,
(b) Water from surface amenities and storm water runoff near the office block,
(c) Surface run-off and storm water runoff from coal stock piles, conveyor belt spray and waste dump area,
(d) Air compressor,
(e) Plant wash down bay,
(f) Gas drainage plant, and
(g) Water from washery plant and tailings dam.

The site concerned has three EPA (NSW) licensed discharge points. License No. 1 is located on the property boundary down stream from the final settlement dam 4, Licence No. 2 is located down stream of the final treatment dam at No. 2 shaft site and Licence No. 4 is located at the reject disposal area and area adjacent to the reject loading bin. In addition to these three licensed discharge points, a non-licensed discharge point is located near the coal stockpile and silt drying area towards the southern side of the railway loop (Singh et al, 1996).

## WASTEWATER QUALITY AUDIT

There are 12 water sampling and monitoring points where the water quality is monitored in three monthly intervals. The parameters measured are pH, electrical conductivity, non-filterable residue, concentration of total dissolved solids and barium. Water quality monitoring at 6-monthly intervals is also carried out at two selected sites (point 3 and 4 in Table 2) where, in addition to the above parameters, BOD concentration and Faecal Coliform counts are also monitored. Table 2 shows chemical characteristics of the water from the mine under consideration.

Table 2 Water quality analyses results of the mine site (Thomas, 1995)

| **Sampling Point** | **pH** | **EC µS/cm** | **NFR (mg/l)** | **TDS (mg/l)** | **BOD (mg/l)** |
|---|---|---|---|---|---|
| 1. Town water supply | 7.26 | 156 | < 1.0 | - | - |
| 2. Mine water | 6.84 | 2210 | 48 | 748 | - |
| 3. Sewage treatment plant maturation Dam 1 | 7.25 | 500 | 25 | 340 | >28 |
| 4. Discharge from maturation Dam 1 to maturation Dam 2 | 9.24 | 416 | 50 | 284 | 20 |
| 5. Discharge from conveyor belt spray & central coal Stockpile silt trap | 8.22 | 303 | 1500 | 206 | - |
| 6. Discharge from air compressor | 6.76 | 797 | 2 | 104 | - |
| 7. Washdown effluent | - | - | - | - | - |
| 8. Effluent from Dam 1 | 7.66 | 1428 | 84 | 972 | - |
| 9. Effluent from Dam 2 | 8.05 | 1427 | 64 | 311 | - |
| 10. Effluent from Dam 3 | 8.27 | 1452 | 9 | 397 | - |
| 11. Washery effluent | 8.69 | 1424 | 66 | 968 | - |
| 12. Dam 4 discharge (License 1) | 8.33 | 1441 | 14 | 980 | - |

A two yearly testing programme is carried out by the mine operators at six selected stations where complete water analysis including the determination of 32 physical and chemical parameters took place. The sampling locations are designated as follows :

| | |
|---|---|
| Mine water | A |
| License discharge point 1 | B |
| Creek upstream of license discharge point 1 | C |
| Creek downstream of license discharge point 1 | D |
| River upstream of discharge point | E |
| River downstream of discharge point | F |

Complete water analysis was necessary to assess the performance of the wastewater treatment and general water quality management at the site. These parameters are also required to ensure compliance with discharge requirements under the Clean Waters Act (1970).

A typical result for 1994 is given in Table 3 where the chemical constituents of the water are given in milli-equivalents per litre and cation ratio for different water sources. The cation concentrations of water samples are calculated in milli-equivalents by dividing the concentration in milligram/litre by the equivalent weight of the ion under consideration.

Table 3 Wastewater classification at the mine site

| Parameters | Mine water m eq/l A | Licensed discharge m eq/l B | Creek upstream meq/l C | Creek downstream m eq/l D | River upstream meq/l E | River downstream meq/l F |
|---|---|---|---|---|---|---|
| Aluminium | 0.004 | 0.015 | 0.137 | 0.101 | 0.036 | 0.051 |
| Calcium | 0.659 | 1.148 | 0.085 | 1.262 | 0.130 | 0.379 |
| Copper | < 0.001 | < 0.001 | < 0.001 | <0.001 | < 0.001 | < 0.001 |
| Magnesium | 1.517 | 0.88 | o.214 | 0.971 | 0.296 | 0.485 |
| Sodium | 3.349 | 11.397 | 0.783 | 6.873 | 0.739 | 3.393 |
| Iron | 0.390 | 0.057 | 0.036 | 0.025 | 0.050 | 0.043 |
| Manganese | 0.050 | 0.009 | < 0.001 | 0.004 | 0.003 | 0.003 |
| Nickel | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 | < 0.001 |
| Potassium | 0.072 | 0.317 | 0.087 | 0.315 | 0.054 | 0.118 |
| Zinc | 0.002 | 0.003 | 0.002 | 0.002 | 0.002 | 0.002 |
| Total Cation | 6.043 | 13.827 | 1.345 | 9.554 | 1.310 | 4.474 |
| Chloride | 4.823 | 2.426 | 0.790 | 0.903 | 2.200 | 1.213 |
| Sulphate | 0.333 | 0.25 | 0.104 | 0.562 | 0.042 | 0.167 |
| Total Anion | 8.156 | 2.676 | 0.894 | 1.456 | 2.242 | 1.380 |
| Cl/ $SO_4$ | 14.483 | 9.704 | 7.596 | 1.607 | 52.38 | 7.263 |
| Mg / (Mg+ Ca) | 0.697 | 0.434 | 0.716 | 0.435 | 0.695 | 0.510 |
| Sodium/ ΣCation | 0.525 | 0.825 | 0.582 | 0.719 | 0.564 | 0.758 |

meq/l = milli equivalents per litre

The results of these 6 discharge point analyses as shown in Table 3 indicate that B, D and F belong to one group of water while samples A, C and E to another group displaying similar chemical characteristics. This indicates that the characteristics of water in the creek and the river are influenced by the license No. 1 discharge resulting in dilution. Although the quantity of mine water forms a major part of the license No. 1 discharge, it shows no resemblance because the

(i) Process water has a disproportionate effect on the cation component of the license No. 1 discharge.

(ii) Cation component of the wastewater undergoes changes during the retention period in the settlement dams over a period of 7 days.

(iii) Cation component of the mine water is variable.

## Characteristics of wastewater at the Mine

Interpretation of the wastewater sampling results in Table 2, and examination of mine water discharge indicates that the mine water has a near neutral pH averaging 6.87 over the sampling period and relatively high conductivity and total dissolved solids(TDS). The conductivity and the TDS levels enable the water to be classified in Class 3, characterising the water as highly saline, which cannot be used for irrigation on soils that are not freely draining. The suspended solids content (NFR) of the mine water was variable ranging between 39 to 390 mg/ l and the suspended solids were usually reddish brown in colour at low concentration and blackish at high concentrations.

The treated discharge from the sewage plant showed near neutral pH averaging 7.5 and low suspended solids content ranging from 25 to 45 mg/l. The discharge had low to medium conductivity and medium total dissolved solids, thus placing it as Class 2, Medium Saline Water. This water is suitable for irrigating soils if moderate draining by the soil can be tolerated. The BOD5 of the domestic wastewater, ranging from 28 to 54 mg/l, was slightly higher than levels expected for sewage that has undergone secondary treatment.

The discharge from the first maturation pond exhibited a very high mean pH value of 9.4 over the sampling period and low to high suspended solids ranging from 27 to 132 mg/l. The increase in NFR compared to the discharge from the sewage treatment plant can be attributed to the heavy growth of algae in the maturation pond No.1. Conductivity and TDS levels enabled classification of this discharge as the Sewage Treatment Plant effluent. The BOD5 of the effluent is variable ranging between 18 to 85 mg/l.

The pH of the wastewater discharged from the conveyor belt and central stockpile was near neutral, ranging from 7.5 to 8.2. The suspended solid content of the wastewater discharge before entering the silt traps was very high, ranging between 55 to 1500 mg/l consisting of very fine coal particles. The water also had a visible oil slick on the surface and low TDS content, placing it in the Low Salinity category, suitable for irrigation under a range of soils. The salinity of this discharge indicated that the coal fines are not a major contributing factor to the salinity of the wastewater in the colliery.

The wastewater from the machinery wash down bay displayed high pH ranging from 9 to 12. Suspended solids content was also extremely high (850 mg/l) for a discharge exiting from a washdown silt trap. High conductivity and TDS levels characterise this effluent in the class 3 high saline water, which can be used for irrigating only the freely draining soils.

Gas plant discharge was of near neutral pH averaging 6.7 for the sampling period and had very low suspended solid (6 mg/l). Conductivity and TDS contents were moderate to high, placing the wastewater in Class 3, high saline water .

Washery discharge was characterised by a high pH water (average 8.6), containing very high suspended solids (54-196 mg/l) comprising very fine coal particles. Conductivity and TDS levels were high, placing the wastewater in Class 3. The discharge exhibited visible frothing indicating the presence of surfactants (Thomas 1995).

The license No. 1 discharge was measured as having a relatively high pH for the sampling period, averaging 8.2, which is within the stipulated colliery's discharge limit of 8.5. Suspended solid levels were low, ranging from 2 to 23 mg/l . Conductivity and the TDS levels place the discharge in Class 3 (high salinity water) which is suitable for irrigation of soils with good draining properties.

## BARIUM INVESTIGATIONS

Wastewater discharged from the mine site under investigation displayed high barium contents which could raise the barium levels of receiving river water. The host river for the mine water discharge is rated as Class P (Protected Water) which limits the barium content in the effluent to 1 mg/l. This limit is regularly exceeded by discharges from dam 4 (License No. 1) and dam 6 in the stockpile area. In the period from January 1994 to February 1995, the barium concentration in Dam 4 and Dam 6 discharges averaged at 2.54 mg/l and discharge averaged at 2.81 mg/l. Options for acceptance of various barium discharge levels in the receiving water are currently under review by the EPA. Table 4 presents a typical result of barium analysis in the mine wastewater circuit in the colliery with a view to isolating the source of the barium in the mine water discharge.

Table 4 Barium analysis results for the mine wastewater (Thomas, 1995)

| **Sample points** | **pH** | **EC (µs/cm)** | **NFR (mg/l)** | **Barium (mg/l)** |
|---|---|---|---|---|
| 1. Town water | 7.10 | 109 | <1 | 0.14 |
| 2. License 1 | 8.20 | 1472 | 3 | 3.92 |
| 3. Mine water | 6.67 | 974 | 19 | 12.24 |
| 4. Maturity pond discharge | 9.94 | 458 | 41 | 0.09 |
| 5. Gas plant discharge | 6.38 | 690 | 2 | 1.90 |
| 6. Washery discharge | 8.54 | 1424 | 436 | 6.00 |
| 7. Coal stockpile runoff | 8.32 | 1678 | 166 | 2.9 |
| 8. Central stockpile drainage | 7.55 | 356 | 2282 | 11.60 |
| 9. Plant wash down | 8.55 | 506 | 91 | 7.91 |

### Source of barium in the colliery discharge

The amount of barium contamination in the wastewater in the colliery shown in Table 4 is variable which may be derived from a combination of sources. Table 4 also indicates that the largest contributor of barium to the colliery's wastewater is mine water, followed by washery water, plant wash down bay and central stockpile drainage. Pinning down the actual generating point is difficult. If isolation of the point source was possible then a strategy of segregation and treatment options could be examined.

It is suggested that the source of barium contamination in mine wastewater may be one of the following:

(i) Natural rocks surrounding the aquifers

(ii) Leachate from coal containing high level of barium
(iii) Oil based drilling fluids containing barytes as a filler
(iv) Lubricants.

An analysis of coal from the 3 different locations within the central stockpile on two different dates using Atomic Absorption Spectroscopy has indicated that the coal from this site contains barium at between 270-630 mg/kg of coal (Thomas, 1995). Tests carried out by the mine operator on the lubricants used at the site have indicated that the barium levels in the oil and lubricants used are not high enough to form a major source of contamination, as that oil spillage is small compared with various other sources. However, moderate to high barium content of the coal and the high barium content in the leachate from the central stockpiles indicate that coal itself may be a major contributor to barium in the colliery's wastewater. It may be observed that ground water travelling in coal aquifers would have the capacity to dissolve barium by ion exchange between ground water and coal stratum over a geological time span.

**Barium removal process**

Barium can be removed from the wastewater by using one the following processes:

(i) The chemical precipitation process;
(ii) Physical adsorption process; and
(iii) Ion exchange process

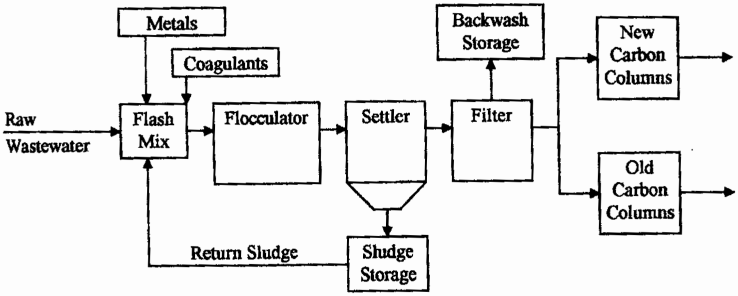

Figure 5 Barium removal process using chemical precipitation (Maruyama 1985 quoted in Thomas 1995)

Thomas (1995) carried out laboratory experiments using precipitation methods and discussed the relative efficiency of the above three processes for barium removal from wastewater. It was concluded that the most feasible method of reducing barium to below 1 mg/l level in the wastewater from the mine concerned was the chemical precipitation method shown in Figure 5. Chemical precipitation processes create a sludge which mine operators feel comfortable disposing of as a solid waste compared to dealing with liquid waste. Other treatment processes, namely ion exchange and reverse osmosis methods have limitations that would require tighter process control during their operation.

## CONCLUSIONS

Mine wastewater characterisation and auditing techniques provide a powerful tool to assess periodically the efficacy of the mine wastewater treatment system to assist operators to respond effectively to changes of mining and processing conditions. This technique has been successfully applied to a mine site in the Illawarra region where wastewater of dissimilar chemical characteristics could be segregated for separate processing.

The wastewater auditing technique has enabled identification of the presence of barium in the mine wastewater. Based on the wastewater monitoring and the chemical analyses of the coal, it has been concluded that barium in the wastewater originates from the coal. Laboratory assessment of various barium removal options has indicated that the chemical precipitation method is a suitable option for the mine concerned. The wastewater quality monitoring method has also indicated that the site needs to upgrade its NFR treatment system to deal with heavy storm events. A new flow sheet of a proposed mine wastewater treatment strategy was developed by Thomas (1995) which allows considerable reuse of water for dust suppression, thus reducing the water consumption by about 50%.

## ACKNOWLEDGMENTS

The research work reported in this paper forms a part of BE (Honours) theses of G.L. Thomas, K Wingrove and S Thompson supervised by the authors. The original contribution of the honours students to this paper and access to the notes by A. Prof. M. Sivakumar and Dr H.B. Dharamappa is gratefully acknowledged. Thanks are also due to the management of mining companies concerned for allowing access to their mining operations and for making their facilities available. Particular thanks are due to Mr D. Olsen and Mr K.Woodley for providing access to the mine site and their help throughout the investigations and to Mr P Turner, University of Wollongong for his help with computer graphics. However, the opinions expressed in this paper are responsibilities of the authors alone and not necessarily that of the management. Valuable help given by Dr J. Shonhardt is also gratefully acknowledged.

## REFERENCES

BOWEN, H. J. M. (1979), “Environmental Chemistry of the Elements”, Academic Press, New York.

BRENIMAN, G. R. and LEVY, P. S. (1985), “Epidemiological Study of Barium in Illinois Drinking Water Supplies”., Advances in Modern Environmental Toxicology, Princeton Publishing, Vol. 9, pp 231-249.

BREDHOEFT , J.D. , BLYTH , C. R., WHITE W. A. and MAXEY C. B. (1963), “ Possible mechanism of concentration of Brines in Subsurface Formations”, Bulletin of American Association of Petroleum Geologists, Vol. 47, Feb. 1963, pp 257-269.

DHARAMAPPA H. B., SIVAKUMAR M, AND SINGH R N, (1995), "Wastewater Minimisation and Reuse in Mining Industry in Illawarra Region", Conference on Water Resources at Risk, American Institute of Hydrology and International Mine Water Association, 14-18, May 1995, Denier, Colorado, Paper No., IOWA p 11 -22

DHARAMAPPA, H. B., K WINDGROVE, M, SIVAKUMAR and R. N. SINGH, (1997) ,"Wastewater and Stormwater Minimization in an Underground Mine", First Asia-Pacific Roundtable Conference on Clean Production, 12-14 November 1997, Bangkok, Thailand, Theme: Cleaner Technology, Case History , Paper No. 8, pp1-20

EDMUNDS, W.M (1975), “ Geochemistry of Brines in North East of England”, Transsaction of the Inst. of Min. and Metallurgy, May 1975, B39-B52.

FORSTNER, U AND WITTMAN, G. T. W. (1979), Metal Pollution in the Aquatic Environment, Springer- Verlag.

GlOVER, H. G. and CHAMBERLAIN , E.A. C. ( 1976), " Water Quality Systems in Coal Measures Formations in Great Britain", Symposium on Environmental Problems Resulting from Coal Mining Activities Katowice, Poland, Economic Commission for European Coal Committee, 18-20 October 1976, pp 1-20

GlOVER, H.G., (1983a),"The Hydrogeochemistry of British Coal Measures", Geological Society of London, Hydrogeological Group Meeting, 7 June 1983, Paper No.3, pp 1-12

GlOVER, H. G. (1983b), "Mine Water Pollution - An overview of the problem and Control Strategies in the U.K"., Mat. Science Tech., Vol. 15, Pretoria, pp 59-70

LONGSDON, G. S., SORG, T. G., and SYMONS, J. M. (1994), "Removal of Heavy Metals by Conventional Treatments", Proceedings of the 16th Water Quality Conference, University of Illinois, Urbana, 13-14 February, 1994.

MYERS, A. G., SNOEYINK, V. L. AND SNYDER, D. W. (1985), "Removing Barium and Radium through Calcium Cation Exchange", Journal of American Water Works Association, Vol. 77, No. 5, May, pp 60-66.

SKIPSEY, E. (1974), " Distribution of Alkali Chlorides in British Coal Seams", Fuel , Vol. 53, October 1974, pp 258-267

SINGH, R. N. (1994), "Mine Water, Origin, Inflow Prediction and Control", University of Wollongong, Chapter 14, pp 14.5-14.17.

SINGH, R. N., SIVAKUMAR, M AND ATKINS A. S., (1995), " Application of IT to Site Water Management for Pollution Control", World Mining Environment Congress, 11- 14 December 1995, New Delhi, ISBN 905410 715 4, Balkema, Rotterdam, pp 69- 84

SINGH R.N., DHARMAPPA, H.B. AND SIVAKUMAR, M., (1996), Wastewater Quality Management in Coal Mines in the Illawarra Region, International Conference on Mining and the Environment, Bandung, March 6-7, 1996, Paper 9, pp 1-16

SINGH R.N., SIVAKUMAR, M., AND ATKINS, A.S., (1995), 'Application of Executive Information System (EIS) to Mine Site Water Pollution Control', Mine Water and The Environment, Annual Issue, 1995, pp 96-106

SIVAKUMAR, M , SINGH, R. N. AND MORTON S. G. S., (1992),"Mine Water Effluent Quality in the Illawarra Region, National Conference on Environmental Engineering Gold Coast, The I. E. Aust, 17 - 19 June 1992, pp 6

SIVAKUMAR, M., MORTON, S. G. S., AND R.N. SINGH (1993), " Water Problems in Coal Mining in Illawarra Region', Paper presented at the First African Symposium on Mine Drainage and Enviroronmental Protection, International Mine Water Association, Kankola Division, Chiliabowmbwe, Zambia, 13-17 September 1993, Paper 45, pp 1-13.

SIVAKUMAR, M., SINGH, R. N. AND MORTON, S. G. S. (1992), "Coal Mine Drainage Quality in Illawarra Region", Mine Water and the Environment, Vol. 11, No 2, June 1992, pp 1-16.

SIVAKUMAR, M., SINGH, R. N. AND MORTON, S.G.S. (1994), " Water Quality Management in Underground Coal Mining in Illawarra Region', Mine Water and the Enviroronment, Journal of the International Mine Water Association, Paper 2, Vol 13, March 1994, pp 1-13.

SIVAKUMAR, M., SINGH, R. N. AND MORTON, S. G. S. (1994), " Case History Analysis of Mine Water Pollution", Fifth International Mine Water Congress, Nottingham (U.K), September 1994, Vol 2, pp 823 -824

SWAINE, D. J. (1990), "Trace Elements in Coal", Butterworth.

THOMSON, S L (1995) , "Mine water management case study; Appin Colliery", BE (Honours) Thesis, University of Wollongong, pp 93.

THOMAS, G. L. (1995), "Treatment and Reuse of Mine Water in the Illawarra Region", BE (Honours) Thesis, University of Wollongong, pp 138.

WINGROVE, K. (1996), "Wastewater management in Illawarra coal mines", BE Thesis, University of Wollongong, Wollongong, Australia