Chapter 8

Mine effluents and acid mine drainage

Different types of process effluents and waste waters are produced as a result of mining. These may arise due to the extraction process, by the subsequent preparation of the mineral that is mined, from the disposal of spoil or from stockpiles. The rock mass from which the groundwater involved is derived, the mineralogical character of the material mined and the spoil, and the preparation processes employed all affect the type of effluent produced. Drainage problems also result from past mining operations.

8.1. Effluents associated with coal mines

Generally, the major pollutants associated with coal mining are suspended solids, dissolved salts (especially chlorides), acidity and iron compounds (Bell and Kerr, 1993). When suspended solids enter a small stream they may cause the water to become turbid and may deposit a fine layer of sediment over the bed of the stream, both of which adversely affect aquatic life. However, the character of drainage from coal mines varies from area to area and from coal seam to coal seam. Hence, mine drainage waters are liable to vary in both quality, and also in quantity, sometimes unpredictably, as the mine workings develop. Nonetheless, drainage water, for example, from coal mines in Britain can be classified as hard, alkaline, moderately saline, highly saline, alkaline and ferruginous, and acidic and ferruginous (Best and Aikman, 1983; Table 8.1). Colliery discharges have little oxygen demand, the biochemical oxygen demand (BOD) normally being very low. Elevated levels of suspended matter are associated with most coal mining effluents, with occasionally high values being recorded. Although not all mine waters are highly mineralized, a high level of mineralization is typical of many coal mining discharges and is reflected in the high values of electrical conductivity. Highly mineralized mine waters usually contain high concentrations of sodium and potassium salts, and mine waters that do not contain sulphate may contain high levels of strontium and barium. Similarly, not all mine waters are ferruginous, and in fact some are of the highest quality and can be used for potable supply. Nonetheless, mine

Table 8.1 Composition of coal mine drainage waters (From Bell and Kerr, 1993)

Column number	*1*	*2*	*3*	*4*	*5*	*6*
Approximate percentage of waters in each class	55%	25%	10%	7%	7%	2%
Quality	Hard alkaline		Moderately saline	Alkaline and ferruginous	Acidic and ferruginous	Highly saline
pH value	7.8	6.8	8.2	6.9	2.9	7.5
Alkalinity, mg l^{-1} $CaCO_3$	260	850	240	340	Nil	190
Calcium, mg l^{-1}	75	28	90	190	125	2560
Magnesium, mg l^{-1}	90	17	40	130	90	720
Dissolved iron, mg l^{-1}	0.1	0.5	0.1	25	122	0.6
Suspended iron, mg l^{-1}	0.1	2	0.1	21	0.1	0.2
Manganese, mg l^{-1}	0.1	0.1	0.1	6	7	0.9
Chloride, mg l^{-1}	180	200	3400	42	50	30 800
Sulphate, mg l^{-1}	170	210	250	1720	1250	350

waters are commonly high in iron and sulphates. The low pH values of many mine waters are commonly associated with highly ferruginous discharges. In some associated streams the pH value is less than 4.0, the iron concentration is greater than several hundred milligrams per litre and the sulphates exceed one thousand milligrams per litre. Iron in mine water draining from coal mines may be in the more stable ferrous form underground but it may oxidize in the presence of oxygen to ferric iron whereby it may form an orange precipitate termed ochre. Ochre often is seen as deposits at points of discharge and coating stream beds.

The high level of dissolved salts that often is present in mine waters represents the most intractable water pollution problem connected with coal mining. This is because dissolved salts are not readily susceptible to treatment or removal. In some situations this option is not available. The range of dissolved salts encountered in mine water is variable, with electrical conductivity values up to 335 000 μS cm^{-1} and chloride levels of 60 000 mg l^{-1} being recorded (Woodward and Selby, 1981). Some average values for various coal mining effluents associated with the Nottinghamshire Coalfield, England, are given in Table 8.2.

The principal groups of salts in mine discharge waters are chlorides and sulphates. The former occur in the groundwater lying in the confined aquifers between coal seams in most coalfields in Britain, South Wales being a notable exception. These salts are released into the workings by mining operations. In general, the salinity increases with depth below the surface and with distance from the outcrop or incrop. The concentration of ions in mine waters conform to established ratios that are remarkably consistent

Table 8.2 Average quality characteristics of coal mining effluents in the Nottinghamshire Coalfield, England (From Bell and Kerr, 1993)

Type of effluent	*BOD (ATU) (mg l^{-1})*	*Suspended solid (mg l^{-1})*	*Chloride (mg l^{-1})*	*Electrical conductivy (μS cm^{-1})*	*Minimum pH*	*Other potential contaminants*
Mine waters	2.1	57	4900	14 000	3.5	Iron barium nickel, aluminium sodium sulphate
Drainage from coal stocking sites	2.6	128	600	2200	2.2	Iron, zinc
Spoil tip drainage	3.1	317	1600	4100	2.7	Iron, zinc
Coal preparation plant discharges	2.1	39	1500	4200	3.2	Oil from flotation chemicals
Slurry lagoon discharges	2.4	493	2000	6100	3.8	

throughout British coalfields. The more saline waters contain significant concentrations of barium, strontium, ammonium and manganese ions. Dissolved sulphates occur only in trace concentrations in waters of confined aquifers.

Mine drainage waters at the point of discharge almost invariably contain sulphates that are either present in the groundwater lying in the more shallow unconfined aquifers, or are generated in the workings by the action of atmospheric oxygen on pyrite. The physical changes such as delamination, bedding plane separation, fault reactivation and fissuring of rock masses caused by mining permit air to penetrate a much larger surface area than the immediate boundaries of the working faces and associated roadways. These changes also alter the hydrogeological conditions within a coalfield and allow wider movement of groundwater through the rock masses than existed prior to mining. These factors mean that groundwater comes in contact with a large surface area of rock, and is exposed to atmospheric oxidation. Hence, the groundwater becomes contaminated. Pyrite may occur in relatively high concentrations, particularly in the upper part of a coal seam or in associated black shales. As noted previously, the primary oxidation products of pyrite are ferrous and ferric sulphates, and sulphuric acid. Sulphates and sulphuric acid react with clay and carbonate minerals to form secondary products including manganese and aluminium sulphates. Further reactions with these minerals and incoming waters give rise to tertiary products such as calcium and magnesium sulphates. Generally, the stratal waters are sufficiently alkaline to ensure that only the tertiary products appear in the discharge at the surface (columns 1, 2, 3 and 6 of Table 8.1). Exceptionally both primary and secondary products may appear in waters from intermediate depths (column 4 of Table 8.1). The primary oxidation products tend to predominate in very shallow workings liable to leaching by meteoric water (column 5 of Table 8.1).

Precipitation of metal hydroxides occurs as acid mine water is neutralized by water into which it flows. Acidic ferruginous mine water also may contain high concentrations of aluminium that precipitates as hydroxide as the pH value rises on entering a receiving body of water, giving a milky appearance to the water. Concentrations of heavy metals may be high in some acid waters and may exert a toxic effect.

The prevention of pollution of groundwater by coal mining effluent is of particular importance. Movement of pollutants through strata is often very slow and is difficult to detect. Hence, effective remedial action is often either impractical or prohibitively expensive. Because of this there are few successful recoveries of polluted aquifers. In coalfields of the east Midlands and south Staffordshire, England, colliery spoil was often tipped on top of the Sherwood Sandstone, which is the second most important aquifer in Britain. Although modern tipping techniques may render spoil impervious, surface water run-off can leach out soluble salts, especially chloride. This may result in the loss of up to 1 tonne of chloride per hectare of exposed spoil heap per annum under average rainfall conditions (spoil heaps may extent to many hundreds of hectares in area). The run-off from these spoil heaps may discharge directly into drainage ditches or to land around the periphery of the heap and infiltrate into the aquifer. Figure 8.1 shows the isopleths for chloride ion concentration in the groundwater of the Sherwood Sandstone in the concealed part of the Nottinghamshire Coalfield in the 1980s. It also indicates the locations of the working collieries at that time and so demonstrates the relationship between elevated chloride ion level in the groundwater and mining activity. Such pollution of an aquifer can be alleviated by lining the beds of influent streams that flow across the aquifer or by providing pipelines to convey mine discharge to less sensitive water courses that do not flow across the aquifer.

Old adits often are unmapped and unknown, and even currently discharging ones are not always immediately evident. An examination of the catchment data is often the only way that such discharges come to light. Discharges from old adits and mine mouths are usually gravity flows. The number of gravitational discharges from abandoned mines in the Fife coalfield, Scotland, are shown in Figure 8.2 and the associated discharges are listed in Table 8.3.

8.2. Acid mine drainage

The term acid mine drainage (AMD) or acid rock drainage (ARD) is used to describe drainage resulting from natural oxidation of sulphide minerals

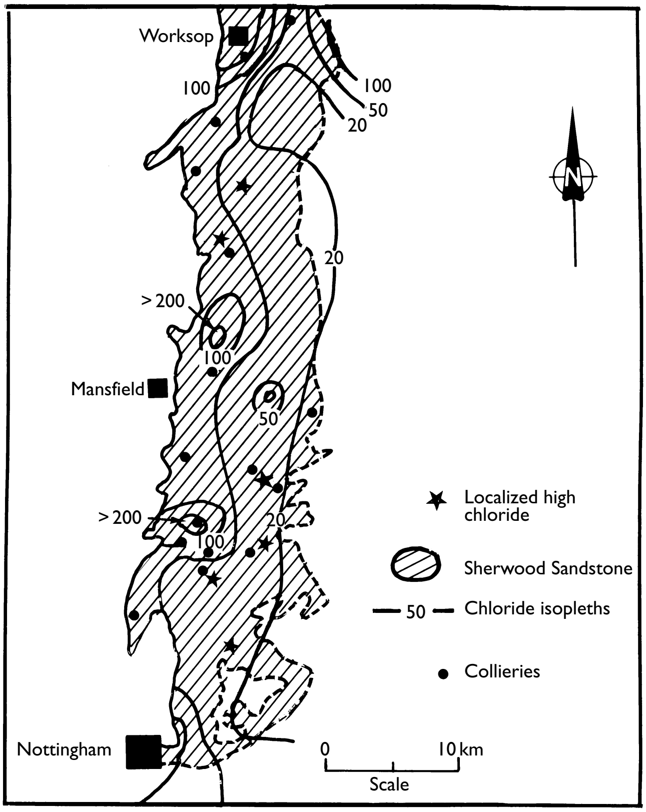

Figure 8.1 Chloride contours (in mg l^{-1}) for groundwater in the Sherwood Sandstone aquifer of the concealed Nottinghamshire Coalfield, England, in the late 1970s/early 1980s. (From Bell and Kerr, 1993.)

that occur in mine rock or waste that are exposed to air and water. This is a consequence of the oxidation of sulphur in the material to a higher state of oxidation and, if aqueous iron is present and unstable, the precipitation of ferric iron with hydroxide occurs. It can be associated with underground workings, with opencast workings, with spoil heaps, with tailings ponds or with mineral stockpiles (Brodie *et al.*, 1989). For instance, Sracek *et al.* (2004) have provided a recent account of the characteristics of acid mine drainage associated with a waste rock pile at Mine Doyon, Quebec.

Acid mine drainage is responsible for problems of water pollution in major coal and metal mining areas around the world. However, it will not occur if the sulphide minerals are non-reactive or if the rock contains

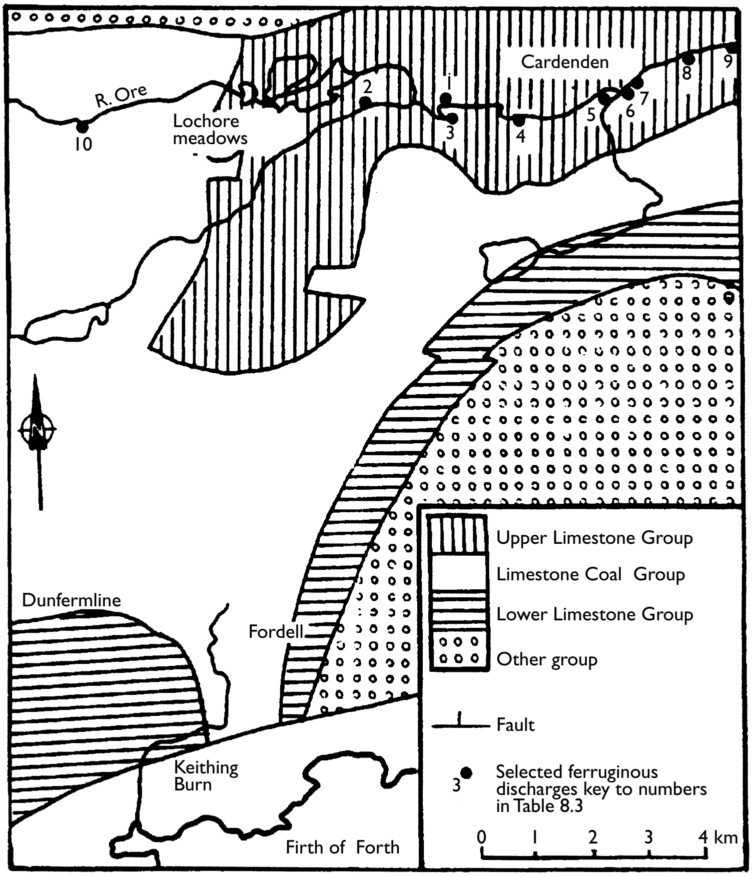

Figure 8.2 Location map of places referred to in Table 8.3 along the River Ore, Fifeshire Coalfield, Scotland, scale in kilometres. (From Bell and Kerr, 1993.)

sufficient alkaline material to neutralize the acidity. In the latter instance, the pH value of the water may be near neutral but it may carry elevated salt loads, especially of calcium sulphate. The character and rate of release of acid mine drainage is influenced by various chemical and biological reactions that occur at the source of acid generation (see later). Moreover, the development of acid mine drainage is time dependent and at some mines may evolve over a period of years. If acid mine drainage is not controlled it can pose a threat to the environment since acid generation can lead to elevated levels of heavy metals and sulphate in the water that obviously have a

Table 8.3 Examples of iron loading along River Ore (From Bell and Kerr, 1993)

Location	*Average flow* $(l\,s^{-1})$	*Average iron* $(mg\,l^{-1})$	*Average loading* $(kg\,day^{-1})$	*Receiving stream*	*Origin*
1 Inchgall	0	—	—	Ore	Coal outcrop
2 Glencraig	1	—	—	Fitty Burn	Fissure?
3 W Colquhally	22	8	15	Fitty Burn	Drainage adit
4 Minto Pit	38	4	13	Ore	Drainage adit
5 Cardenden Gas Works	8	2	1	Den Burn	Coal outcrop
6 Cardenden Sewage Works upstream	4	11	4	Ore	Seepage
7 New Garden No 1	10	13	11	Ore	Pit shaft?
8 New Garden No 2	5	11	5	Ore	Borehole
9 Cluny	16	49	68	Ore	Pit shaft/ borehole
10 Blairenbathie	36	5	15	Ore	Pit shaft

Table 8.4 Examples of acid mine drainage groundwater

pH	*EC*	NO_3	*Ca*	*Mg*	*Na*	*K*	SO_4	*Cl*	*TDS*
6.30	444	11.8	401	289	418	18.5	2937	26.7	4114
5.9	421	4.9	539	373	202	23.8	3275	73.5	4404
3.0	3130	29.4	493	3376	228	12.7	47 720	86.9	51 946
2.9	2370	64.8	627	621	102	6.9	14 580	33.4	16 039
2.8	1680	19.6	509	561	70	0.7	27 070	53.5	28 284
3.2	857	7.4	614	309	103	12.5	2857	173.8	4078
1.9	471	0.1	174	84	247	7	3250	310	4844
2.4	430	0.1	114	48	326	9	1610	431	2968
2.9	377	0.1		61	278	6	1256	324	2490
2.3	404	0.1	113	49	267	4	2124	353	3364

Note
Except for pH and EC $(mS\,m^{-1})$ all units are expressed in $mg\,l^{-1}$.

detrimental effect on its quality (Table 8.4). This can have a serious impact on the aquatic environment, killing fish and amphibians, as well as vegetation (Fig. 8.3).

Generally, acid mine drainage from underground mines occurs as point discharges (Geldenhuis and Bell, 1997). A major source of acid mine drainage may result from the closure of a mine (Bell *et al.*, 2002). When a mine is abandoned and dewatering by pumping ceases, the water level rebounds and groundwater reoccupies the strata (Younger, 1995). However, the workings often act as drainage systems so that the water does not rise to its former level. Consequently, a residual dewatered zone remains

Figure 8.3 Dying vegetation as a result of acid mine drainage contaminating the ground.

that is subject to continuing oxidation. Groundwater may drain to the surface from old drainage adits, river bank mine mouths, faults, springs and shafts that intercept strata in which water is under artesian pressure. Nonetheless, it may take a number of years before this happens. Burke and Younger (2000), and Dumpleton *et al.* (2001) described modelling methods used to assess such problems in two coalfield areas in England. Mine water quality is determined by the hydrogeological system and the geochemistry of the upper mine levels. Hence, in terms of a working mine it is important that groundwater levels are monitored to estimate rebound potential. In addition, records should be kept of the hydrochemistry of the water throughout the workings, drives and adits so that the potential for acid generation on closure can be assessed.

The large areas of fractured rock exposed in opencast mines or open-pits can give rise to large volumes of acid mine drainage. Even when abandoned, slope deterioration and failure can lead to fresh rock being exposed, allowing the process of acid generation to continue. Where the workings extend beneath the surrounding topography, the pit drainage system leads to the water table being lowered. Increased oxidation can occur in the dewatered zone.

Spoil heaps represent waste generated by the mining operation or waste produced by any associated smelting or beneficiation. As such they vary from waste produced by subsurface mining on the one hand to waste produced by any associated processing on the other. Consequently, the sulphide content of the waste can vary significantly. Acid generation tends to occur in the surface layers of spoil heaps where air and water have access to sulphide minerals.

Tailings deposits that have a high content of sulphide represent another potential source of acid generation (see Chapter 7). However, the low permeability of many tailings deposits together with the fact that they commonly are flooded means that the rate of acid generation and release is limited. Consequently, the generation of acid mine drainage can continue to take place long after a tailings deposit has been abandoned.

Mineral stockpiles may represent a concentrated source of acid mine drainage. Major acid flushes commonly occur during periods of heavy rainfall after long periods of dry weather. Heap-leach operations at metalliferous mines include, for example, cyanide leach for gold recovery and acid leach for base metal recovery. Spent leach heaps can represent sources of acid mine drainage, especially those associated with low pH leachates.

8.3. Acid generation

Certain conditions including the right combination of mineralogy, water and oxygen are necessary for the development of acid mine drainage. Such conditions do not always exist. Consequently, acid mine drainage is not found at all mines with sulphide bearing minerals. The ability of a particular mine rock or waste to generate net acidity depends on the relative content of acid generating minerals and acid consuming or neutralizing minerals. Acid waters produced by sulphide oxidation of mine rock or waste may be neutralized by contact with acid consuming minerals. As a result the water draining from the parent material may have a neutral pH value or negligible acidity despite ongoing sulphide oxidation. If the acid consuming minerals are dissolved, washed out or surrounded by other minerals, then acid generation continues. Where neutralizing carbonate minerals are present, metal hydroxide sludges, such as iron hydroxides and oxyhydroxides are formed. Sulphate concentrations generally are not affected by neutralization unless mineral saturation with respect to gypsum is attained. Hence, sulphate sometimes may be used as an overall indicator of the extent of acid generation after neutralization by acid consuming minerals.

Oxidation of sulphide minerals may give rise to the formation of secondary minerals after some amount of pH neutralization if the pH is maintained near neutral during oxidization (Table 8.5). However, other minerals may form instead of or in addition to those listed in Table 8.5. This will depend upon the extent of oxidation, water chemistry and the presence of other minerals such as aluminosilicates. The secondary minerals that are developed may surround the sulphide minerals and in this way reduce the reaction rate.

The primary chemical factors that determine the rate of acid generation include pH value; temperature; oxygen content of the gas phase if saturation is less than 100%; concentration of oxygen in the water phase; degree of saturation with water; chemical activity of Fe^{3+}; surface area of exposed metal sulphide; and chemical activation energy required to initiate acid generation. In addition, the biotic micro-organism, *Thiobacillus ferrooxidans* may accelerate reaction by its enhancement of the rate of ferrous iron oxidation. It also may accelerate reaction through its enchancement of the rate of reduced sulphur oxidation. *Thiobacillus ferrooxidans* is most active in waters with a pH value around 3.2. If conditions are not favourable, the bacterial influence on acid generation will be minimal.

As remarked, acid mine drainage occurs as a result of the oxidation of sulphide minerals, notably pyrite, contained in either mine rock or waste when this is exposed to air and water. In the case of pyrite, the initial reaction for direct oxidation, either abiotically or by bacterial action, according to Lundgren and Silver (1980) is:

$$2FeS_2 + 2H_2O + 7O_2 \rightarrow 2FeSO_4 + 2H_2SO_4 \tag{8.1}$$

Subsequent biotic and abiotic reactions that lead to the final oxidation of pyrite by ferric ions (indirect oxidation mechanism), can be represented as follows:

$$4FeSO_4 + O_2 + 2H_2SO_4 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O \tag{8.2}$$

$$Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4 \tag{8.3}$$

$$4Fe^{2+} + O_2 + 4H \rightarrow 4Fe^{3+} + 2H_2O \tag{8.4}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4 + 16H \tag{8.5}$$

Reaction (8.1) shows the initiation of pyrite oxidation, either abiotically (auto-oxidation) or biotically. As noted earlier, the biotic micro-organism primarily responsible for acid water pollution from mine waste is *Thiobacillus ferrooxidans*. *Thiobacillus ferrooxidans* converts the ferrous

Table 8.5 Summary of common sulphide minerals and their oxidation products (After Brodie *et al*., 1989; reproduced by kind permission of Robertson Geoconsultants Inc)

Mineral	*Composition*	*Aqueous end products of complete oxidation*[a]	*Possible secondary minerals formed at neutral pH after complete oxidation and neutralization*[b]
Pyrite	FeS_2	Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; gypsum
Marcasite	FeS_2	Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; gypsum
Pyrrhotite	Fe_3S	Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; gypsum
Smythite, Greigite	Fe_3S_4	Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; gypsum
Mackinawite	FeS	Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; gypsum
Chalcopyrite	$CuFeS_2$	Cu_2, Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; copper hydroxides and carbonates; gypsum
Chalcocite	Cu_2S	Cu^2, SO_4^2, H	Copper hydroxides and carbonates; gypsum
Bornite	Cu_5FeS_4	Cu^2, Fe_3, SO_4^2, H	Ferric hydroxides and sulphates; copper hydroxides and carbonates; gypsum
Arsenopyrite	FeAsS	Fe_3, AsO_4^2, SO_4^2, H	Ferric hydroxides and sulphates; ferric and calcium arsenates; gypsum
Realgar	As_2S_2	AsO_4^2, SO_4^2, H	Ferric and calcium arsenates; gypsum
Orpiment	As_2S_3	AsO_4^2, SO_4^2, H	Ferric and calcium arsenates; gypsum
Tetrahedrite and Tennenite	$Cu_{12}(Sb,As)_4S_{13}$	Cu^2, SbO^3, AsO_4^2, SO_4^2, H	Copper hydroxides and carbonates; calcium and ferric arsenates; antimony materials, gypsum
Molybdenite	MoS_2	MoO_4^2, SO_4^2, H	Ferric hydroxides; sulphates; molybdates; molybdenum oxides; gypsum
Sphalerite	ZnS	Zn^2, SO_4^2, H	Zinc hydroxides and carbonates; gypsum
Galena	PbS	Pb^2, SO_4^2, H	Lead hydroxides, carbonates, and sulphates; gypsum
Cinnabar	HgS	Hg^2, SO_4^2, H	Mercuric hydroxide; gypsum
Cobaltite	CoAsS	Co^2, AsO_4^2, H	Cobalt hydroxides and carbonates; ferric and calcium arsenates; gypsum
Niccolite	NiAs	Ni_2, AsO_4^2, SO_4^2, H	Nickel hydroxides and carbonates; ferric, nickel and calcium arsenates; gypsum
Pentlandite	$(Fe,Ni)_9S_8$	$Fe_3Ni_2SO_4^2H$	Ferric and nickel hydroxides; gypsum

Notes

a Intermediate species such as ferrous iron (Fe^{2+}) and $S_2O_3^{2+}$ may be important.

b Depending on overall water chemistry other minerals may form with or instead of the minerals listed above.

iron of pyrite to its ferric form. The formation of sulphuric acid in the initial oxidation reaction and concomitant decrease in the pH make conditions more favourable for the biotic oxidation of the pyrite by *Thiobacillus ferrooxidans*. The biotic oxidation of pyrite is four times faster than the abiotic reaction at pH 3.0 (Pugh *et al*., 1984). The presence of *Thiobacillus ferrooxidans* also may accelerate the oxidation of sulphides of antimony, arsenic, cadmium, cobalt, copper, gallium, lead, molybdenium, nickel and zinc.

Hence, the development of acid mine drainage is a complex combination of inorganic and sometimes organic processes and reactions. In order to generate severe acid mine drainage ($pH < 3$) sulphide minerals must create an optimum micro-environment for rapid oxidation and must continue to oxidize long enough to exhaust the neutralization potential of the rock.

8.4. Prediction and control of acid mine drainage

Accurate prediction of acid mine drainage is required in order to determine how to bring it under control. The objective of acid mine drainage control is to satisfy environmental requirements using the most cost effective techniques. The options available for the control of polluted drainage are greater at proposed rather than existing operations as control measures at working mines are limited by site specific and waste disposal conditions. For instance, the control of acid mine drainage that develops as a consequence of mine dewatering is helped by the approach taken towards the site water balance. In other words, the water resource management strategy developed during mine planning will enable mine water discharge to be controlled and treated, prior to release, or to be re-used. The length of time that the control measures require to be effective is a factor that needs to be determined prior to the design of a system to control acid mine drainage.

Prediction of the potential for acid generation involves the collection of available data and carrying out static tests and kinetic tests. A static test determines the balance between potentially acid generating and acid neutralizing minerals in representative samples. One of the frequently used static tests is acid-base accounting. Acid-base accounting allows determination of the proportions of acid generating and neutralizing minerals present. As mentioned earlier, the mineral components considered as acid generating are the sulphides, the most common of which are pyrite and pyrrhotite. Carbonates and hydroxides are regarded as neutralizing minerals. Feldspars may be considered potentially acid consuming minerals but are less effective than calcite. Obviously, a sample will produce net acidity in a period of time if the acid potential (AP) exceeds the neutralizing potential (NP), that is, if the net neutralization potential (NP – AP) is negative. Initially, the pH of a sample paste is measured to assess the natural pH value of the material, as well as to determine if acid generation has occurred prior to analysis.

Generally, if the pH of the paste is less than 5, then there probably has been acid generation in the sample. Next the total sulphur content of the sample is measured and the maximum potential acidity as sulphuric acid is calculated from the sulphur content. Finally, the neutralization potential is found by using a base titration procedure of a pre-acidified sample. However, static tests cannot be used to predict the quality of drainage waters and when acid generation will occur. If potential problems are indicated, the more complex kinetic tests should be used to obtain a better insight of the rate of acid generation. Kinetic tests involve weathering of samples under laboratory or on-site conditions in order to confirm the potential to generate net acidity, determine the rates of acid formation, sulphide oxidation, neutralization, metal dissolution and to test control techniques. The static and kinetic tests provide data that may be used in various models to predict the effect of acid generation and control processes beyond the time frame of kinetic tests. An evaluation of static tests as used to predict the potential for acid drainage generation has been provided by Adam *et al.* (1997).

There are three key strategies in acid mine drainage management, namely, control of the acid generation process, control of acid migration, and collection and treatment of acid mine drainage (Connelly *et al.*, 1995). Control of acid mine drainage may require different approaches, depending on the severity of potential acid generation, the longevity of the source of exposure and the sensitivity of the receiving waters. Mine water treatment systems installed during mine operation may be adequate to cope with both operational and long-term post-closure treatment with little maintenance. On the other hand, in many mineral operations, especially those associated with abandoned workings, the long-term method of treatment may be different from that used while a mine was operational. Hence, there may have to be two stages involved with the design of a system for treatment of acid mine drainage, one for during mine operation and another for after closure (Cambridge, 1995).

Obviously, the best solution is to control acid generation, if possible. Source control of acid mine drainage involves measures to prevent or inhibit oxidation, acid generation or containment leaching. If acid generation is prevented, then there is no risk of the resultant contaminants entering the environment. Such control methods involve the removal or isolation of sulphide material, or the exclusion of water or air. The latter is much more practical and can be achieved by the placement of a cover over acid generating material such as waste or air-sealing adits in mines. Bussiere *et al.* (2004) maintained that covers with capillary barrier effects (CCBE) were considered to be one of the most effective methods of controlling acid mine drainage from mine wastes. They considered the use of CCBE on low sulphide tailings to control drainage from tailings. A series of leaching column tests were undertaken from which Bussiere *et al.* concluded that

CCBEs with a moisture retaining layer can limit the production of acid mine drainage from acid generating tailings beneath, maintaining the leachate pH near neutrality. In addition, Bussiere *et al.* found that these covers also reduced the heavy metal content of acid mine drainage, for example, the amounts of zinc, copper and iron were reduced to less than 1%. Bussiere *et al.* (2003) indicated that the hydraulic behaviour of layered CCBEs is influenced by the inclination of the slope. As the upper part of a slope usually contains less groundwater than the lower part, it is less efficient than the lower part as far as limiting gas migration (i.e. oxygen) is concerned. Gandy and Younger (2003) referred to the use of a clay cover to reduce the availability of oxygen to sulphide minerals in a spoil heap that had been generating acid mine drainage. A monitoring programme was established after placement of the cover and this showed that both the acid generating potential of the spoil and the concentration of contaminants, notably iron and sulphate, in the discharge water decreased. Monitoring programmes of groundwater are important, especially when a mine has been closed (Younger and Robins, 2002).

Migration control is considered when acid generation is occurring and cannot be inhibited. Since water is the transport medium, control relies on the prevention of water entry to the source of acid mine drainage. Water entry may be controlled by diversion of surface water flowing towards the source by drainage ditches; prevention of groundwater flow into the source by interception and isolation of groundwater (this is very difficult to maintain over the long-term); and prevention of infiltration of precipitation into the source by the placement of cover materials but again their long-term integrity is difficult to ensure.

Release control is based on measures to collect and treat acid mine drainage. In some cases, especially at working mines, this is the only practical option available. Collection requires the collection of both ground and surface water polluted by acid mine drainage, and involves the installation of drainage ditches, and collection trenches and wells.

In general, methods of treatment of acid mine drainage fall into two main groups, namely, active and passive treatment systems. Cambridge (1995) pointed out that conventional active treatment of mine water requires the installation of a treatment plant, continuous operation in a closely controlled process and maintenance. Hence, the capital and operational costs of active treatment are high. According to Younger (2000), the classic approach to active treatment of acidic and/or ferruginous mine drainage involves three steps. First, oxidization, usually by a simple cascade, that helps convert soluble ferrous iron to the less soluble ferric state, as well as permitting the pH value to rise by venting carbon dioxide, where present, until equilibration with the atmosphere has been achieved. Second, dosing with alkalis, generally hydrated lime [$Ca(OH)_2$] or less often with caustic soda (NaOH), raises the pH value, thereby lowering the solubility of most problematic metals, and providing hydroxyl ions for rapid precipitation of metal hydroxides. Third, accelerated sedimentation normally is brought about by using a clarifier or lamellar plate thickener, frequently aided by the addition of flocculants and/or coagulants. Acid mine water treated with active systems tends to produce a solid residue that has to be disposed of in tailings lagoons. This sludge contains metal hydroxides. However, according to Cambridge, the long-term disposal of such sludge in tailings lagoons is not appropriate. Alternatively, sludges could be placed in hazardous waste landfills but such sites are limited.

Treatment processes have concentrated on neutralization to raise the pH and precipitate metals. Lime or limestone are commonly used to treat acid mine waters, this raises their pH value, although offering only a partial solution to the problem (Zinck and Aube, 2000). Adding lime or limestone also causes iron and other metals to precipitate out of solution. The decant water from the settling process is usually of a high enough quality for it to be discharged directly into surface water courses. However, there are drawbacks associated with liming, first, it may be expensive to maintain due to scaling. Second, the pH needed to remove metals such as manganese may cause the remobilization of other metal hydroxides such as that of aluminium. Third, there may be problems with the long-term disposal of sludge, which is produced in large volume. Other alkalis such as sodium hydroxide may be used, but are more expensive although they do not produce such dense sludges as does lime. The sludges recovered from alkali neutralization, followed by sedimentation and consolidation, are of relatively low density (2–5% dry solids), but drain fairly well. Bodurtha and Brassard (2000) suggested that powdered slag from the steel making industry potentionally could be useful in neutralizing acid mine drainage due to its high content of basic minerals. From their investigation, they noted that only 60% by volume of the slag dissolved but that the process still had the same neutralizing capacity of calcite. Furthermore, Bodurtha and Brassard suggested that the transfer from saturation to pH driven dissolution would be brought about by armouring of the grain surface by the precipitation of iron oxides.

The oxidation of pyrite can be eliminated by flooding a mine with water. However, it obviously is not possible to flood an active mine. It also is not possible to flood abandoned mine workings that are above the water table and that are drained by gravity. Tailings that are acid generating can be covered with water. More sophisticated active treatment methods involve osmosis (waste removal through membranes), electrodialysis (selective ion removal through membranes), ion exchange (ion removal using resin), electrolysis (metal recovery with electrodes) and solvent extraction (removal of specific ions with solvents). A state-of-the-art review of active systems has been provided by Coulton *et al.* (2003).

Passive systems try to minimize input of energy, materials and manpower, and so reduce operational costs. In other words, they should utilize naturally available energy sources such as topographic gradient, microbial metabolic energy, photosynthesis and chemical energy, and need infrequent maintenance to operate successfully (Hedin *et al.*, 1994). Such treatment involves engineering a combination of low maintenance biochemical systems (e.g. anoxic limestone drains, subsurface reactive barriers to treat acidic and metalliferous groundwater, aerobic reed beds and anaerobic wetlands, and rock filters for aerobic treatment of ferruginous waters). A wetland treatment system, in particular, can be integrated aesthetically into the surrounding environment (Fig. 8.4). If not properly managed, however, the generation of ochreous sludge may overwhelm a wetland. This is brought about by the reed beds not being able to transform the dissolved iron to iron sulphides but instead enhancing the oxidization process to precipitate iron as hydroxyferrous sulphates. Passive systems do not produce large volumes of sludge, the metals being precipitated as oxides or sulphides in the substrate materials.

Nuttall and Younger (2000) mentioned that certain difficulties had been met with in Britain when passive systems had been used to treat hard net alkaline mine waters with elevated dissolved zinc. These waters are not amenable to sulphidization in compost based systems like anoxic limestone drains as zinc sulphide does not precipitate readily at neutral pH. They suggested that closed system limestone dissolution, with concomitant precipitation of zinc carbonate minerals offers a means of passive treatment of such waters. This is brought about by using sealed beds of limestone gravel in which zinc is removed as smithsonite ($ZnCO_3$). Such a closed system requires venting after a few hours retention time to restore the partial pressure of carbon dioxide to relatively aggressive values.

Nuttall (2003) described a pump and treat system that was constructed at Whittle Colliery, Northumberland, England, where the system receives groundwater pumped from a purpose sunk drillhole that extends into the drift for the mine. In this way, mine water levels are kept below predicted decant points, which would otherwise give rise to discharges at the surface, and mine water can be treated in a designated setting. The passive system consists of an aeration chamber, two settling lagoons and three aerobic reed beds. Nuttall remarked that the system proved very successful in removing iron. A somewhat similar system using a drillhole to pump groundwater from the Six Bells Colliery in South Wales has been described by Jarvis *et al.* (2003). There two settlement lagoons and a wetland were used to treat the mine water. As most of the iron present in the mine water is in the ferrous state, a hydrogen peroxide dosing system also was installed. This was to ensure effective oxidation of the iron and limit hydrogen sulphide odours around the discharge. The effect of dosing with hydrogen peroxide was to reduce the mean concentration of iron in the effluent to $5\ \mathrm{mg\,l^{-1}}$, which will reduce further as the wetland matures. Although acid mine drainage from the former Wheal Jane tin mine in Cornwall, England, is remediated using conventional lime treatment, a pilot scheme has been established that uses

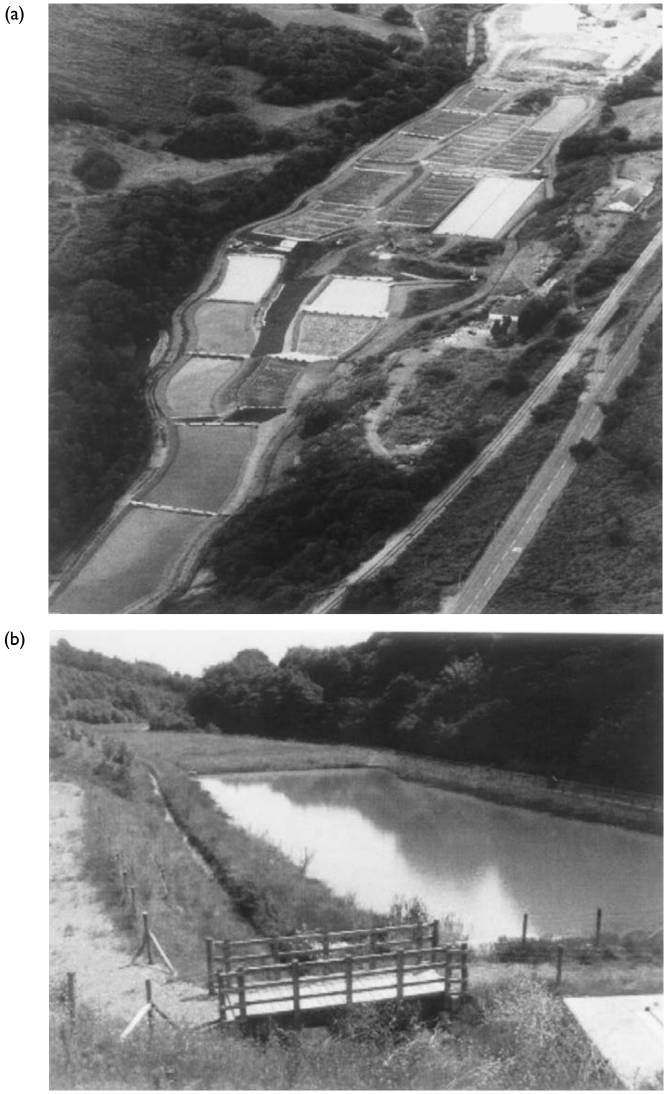

Figure 8.4 Taff Merthyr mine water treatment scheme, South Wales. (a) When Taff Merthyr, Deep Navigation and Trelewis collieries closed in 1990, mine water rebound resulted in discharge from two shafts at Taff Merthyr Colliery causing pollution of a 3 km stretch of the Bargoed Taff, a tributary of the River Taff. The treatment scheme is an aeration and settlement system to facilitate oxidation and settlement of iron. A series of aerobic surface flow reed beds follow the aeration and settlement treatment. There are 16 wetland cells with a fall of 1 m between cells to re-aerate the water by means of cascades. The sludge in the settlement tanks needs to be emptied every five years, the parallel arrangement of the system allowing one tank to continue in operation while the other is emptied. (b) Reed beds following aeration and settlement. (Reproduced by kind permission of the Coal Authority.)

a passive system. According to Hallberg and Johnson (2003), the latter consists of 5 aerobic wetlands, 1 compost reactor (anaerobic cell) and 10 algal ponds or rock filters. The aerobic cells facilitate the removal of iron by oxidation of ferrous iron and hydrolysis of ferric iron, as well as bringing about the co-precipitation of arsenic with ferric iron. Chalcophilic metals (e.g. zinc and cadmium) are removed as sulphides in the compost bioreactor, which also generates alkalinity. The rock filters encourage the removal of manganese by oxygenic photosynthesis increasing the pH of the mine water and thereby promoting oxidation and precipitation of manganese, and by mineralization of dissolved organic carbon compounds in water draining from the compost bioreactor. Furthermore, there is the option to pre-dose the acid mine drainage flowing into the passive system with lime to a predetermined pH or to treat by using an anoxic limestone drain.

A number of novel treatments of acid mine water were reviewed by Davison (1990). These included the use of lime products, fertilizers and bulk organic matter. Calcium carbonate is the most readily available lime product but calcium hydroxide, sodium carbonate and sodium hydroxide are more soluble. Davison noted that when the neutralizing capacities of calcium and sodium based lime products were compared their efficiency was found to depend on the initial pH value and the calcium content of the water being neutralized. Davison went on to discuss the possibility of generating base by the addition of fertilizer in terms of considering base generating reactions associated with the decomposition of organic carbon. He pointed out that theoretically the addition of phosphate fertilizer means that each mole of phosphate added generates 94 moles of base so that practically 10–30 moles should be achievable. The production of base is governed by what proportion of organic material that is formed undergoes aerobic or anaerobic decomposition. Even if organic material is not a particularly efficient neutralizing agent it often is freely available, which could make its use a viable option. For example, Davison suggested that sewage sludge could be used to treat acid waters. Subsequently, Younger and Rose (2000) also mentioned the use of sewage sludge as a means of treating acidic mine waters. Sulphates are removed from the mine water by bacterial sulphate reduction.

Choi and West (1995) referred to the use of phosphate [francolite, $Ca_{10-x-y}Na_xMg_x(PO4)_{6-2}(CO_3)_zF_{0.4z}F_2$] pebbles as a possible method of treating acid mine drainage at Friar Tuck abandoned mine in south-west Indiana. Laboratory tests showed that, depending on flow rate, phosphate pebbles removed up to 1200 mg l^{-1} of ferric iron, 8600 mg l^{-1} of sulphate and 800 mg l^{-1} of aluminium in three weeks. Their removal is inversely proportional to the flow rate and the flow rates concerned varied from 1.17×10^{-4} to 1.05×10^{-3} litres per minute per kilogram of phosphate pebble. In addition, the pH value of the acid mine drainage increased from around 2.1 and 2.2 to 3.2. This was due to the carbonate present in the francolite. The Ca ion reacts with the sulphate in the mine water, with gypsum being precipitated. Choi and West maintained that if a phosphate pebble system is to work successfully, then the ratio of Fe^{3+}/Fe_{total} should be high. Hence, aeration ponds are required to oxidize ferrous to ferric iron. They also indicated that the particle size is important, recommending that the pebble size should be 50 mm and that it should be clean. A smaller size will stop reacting with the mine water as it will become plugged with gypsum precipitate.

Natural zeolites have been used to remove heavy metals from acid mine drainage. The filtering abilities of zeolites offer a versatile and environmental friendly option to capture most contaminants found in water systems. Natural zeolites can perform these functions due to their high ion exchange capacity, adsorption–desorption energies and ability to be modified. For instance, when dry the zeolites adsorb relatively high volumes of liquid (e.g. 100 g of zeolite absorbs 70 g of liquid). Zeolites have an open regular crystalline framework that generates an electric field that interacts, attracts and binds various cations and, after modification, anions. They can remove ammonium (NH_4^+) and metal cations such as Pb, Cu, Cd, Zn, Co, Cr, Mn and Fe from acid mine drainage, with the recovery of ammonium and some metals (Pb, Cu) being as high as 97%. Lindsay *et al.* (2002) described the use of zeolites as a remediation option for acid mine drainage from mines on the west coast of South Island, New Zealand. The primary aim at these sites was to reduce the Fe content entering the streams from mine drainage and raise the pH to natural background levels of between 4 and 5.

Another relatively new and promising method of dealing with acid mine drainage, according to Fytas and Bousquet (2002), is to coat the sulphide minerals with silicates. Pyrite is treated with a solution containing H_2O_2, sodium silicate and a buffering agent. The H_2O_2 oxidizes a small amount of the pyrite thereby producing ions of ferric iron. These ions subsequently react with the silicate ions to form ferric hydroxide-silica, which is precipitated on the surface of the pyrite to give a protective coating that prevents oxidation.

Due to the impact on the environment of acid mine drainage regular monitoring is required. The major objectives of a monitoring programme developed for acid mine drainage are, first, to detect the onset of acid generation before acid mine drainage develops to the stage where environmental impact occurs. If required, control measures should be put in place as quickly as possible. Second, it is necessary to monitor the effectiveness of the prevention-control-treatment techniques and to detect whether the techniques are unsuccessful at the earliest possible time.

Banks *et al.* (2002) noted that it is not unusual to find water draining from pyrite rich mines or wastes that are circum-neutral or even alkaline. These waters may have modest loadings of heavy metals. This may be explained as a consequence of the mine water not coming into contact with sulphide minerals, possibly because of the low content of sulphide minerals or them being coated with non-acidic material; of large pyrite grain size limiting the oxidation rate; of oxygen not coming into direct contact with sulphide minerals or influent water being highly reducing; or of subsequent neutralization of acidic minerals by other minerals or highly alkaline waters. In fact, after an investigation of discharges from coal mines in Britain, Rees *et al.* (2002) recognized a number of different types of discharge in terms of their chemistry, which was influenced by the hydrogeological conditions. They noted that drainage from flooded workings and pumped discharges were net alkaline whilst drainage from flooded and free-draining workings are either moderately net alkaline or net acidic. Drainage from spoil heaps usually had a pH value below 5 and net alkalinity values as low as $-2500\ \mathrm{mg\,l^{-1}}$ $CaCO_3$. Rees *et al.* further commented that iron was the major contaminant of concern but that many mine waters contained less than $30\ \mathrm{mg\,l^{-1}}$ and that iron to sulphate ratios were less than unity. Dey *et al.* (2003) contended that the best practice for the passive treatment of net alkaline ferruginous mine waters in Britain usually involves pre-treatment, through cascade aeration and settlement, followed by treatment in wetlands. The aim is to remove 30–50% of the iron in the settlement lagoons prior to the mine water entering the wetlands, hence allowing more effective sludge management and so prolonging the life of the wetland. Dey *et al.* also mentioned that an alternative for the pre-treatment stage could be to use autocatalytic oxidation and ochre accretion within an ochre bed without any supporting media. They suggested that such a system possibly could remove 90% of the dissolved iron from ferruginous mine water.

8.5. Case history 1

A tin mine in the North-West Province, South Africa, was forced to cease production because of the decline in the price of the metal (Bullock and Bell, 1995). However, before a mine in South Africa can close officially, a certificate of closure must be granted to the mine by the Department of Mineral and Energy Affairs. Section 2.11 of the Minerals Act (August, 1991) also states that mines that are to close, must implement an environmental management programme. The programme should include remedial measures to ensure that no pollution will occur when the mine is closed. Accordingly, a ground and surface water investigation was undertaken at the mine as part of the required environmental management programme. The objectives of the investigation were, first, to assess whether pollution of ground and surface water had occurred as a result of mining, second, to identify any sources of pollution and, third, to offer solutions to any problem of pollution found to exist.

The tin deposits are hosted by rocks of the Rooiberg Fragment, which is found within the western lobe of the Bushveld Complex. The local geology consists of the Leeuwpoort Formation, above which occurs the Smelterskop

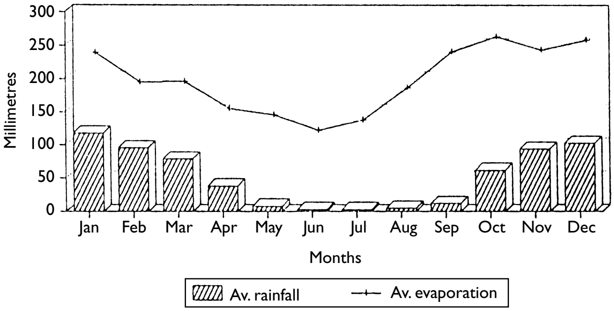

Figure 8.5 Average rainfall and evaporation in the region.

Quartzite Formation. The Leeuwpoort Formation consists of the Boschoffsberg Quartzite Member overlain by the Blaauwbank Shale Member. The tin occurs in Boschoffsberg Quartzite Member. The soils in the area are mostly residual, predominantly comprising sandy loams with lesser quantities of silty loams and silty clay loams.

The area is one of water shortage. The mean annual precipitation in the area is 620 mm with the average monthly rainfall varying from about 3–118 mm. The rainy season lasts from October to May, with most rain falling in January. Mean temperatures in the area reach a maximum in December–January and a minimum in June–July. For example, the maximum mean temperature in January is around 29°C–31°C, the minimum falling to 17°C. In July the maximum mean temperature is around 22°C, the minimum being between 3°C and 6°C. The amount of evapotranspiration affects the amount of surface run-off and groundwater recharge. It exceeds the precipitation every month of the year (Fig. 8.5). The potential water loss reaches a maximum during August, September and October. The water courses and watersheds in the area are shown on Figure 8.6. As the area is situated in a semi-arid region run-off is limited to very short periods of heavy rainfall. In order to catch surface run-off, two reservoirs were constructed in the mine lease area and are known as the Top and Bottom Dams.

8.5.1. Geohydrology and hydrochemistry

Almost all the groundwater in the region occurs in secondary aquifers associated with the Boschoffsberg Quartzite Member. These secondary aquifers consist of weathered and fractured rock, and lie directly beneath the soil surface. The occurrence of groundwater is controlled particularly by structural geology in that drillholes with moderate yields are associated with dykes, which have fractured the Boschoffsberg rocks. In fact, a series

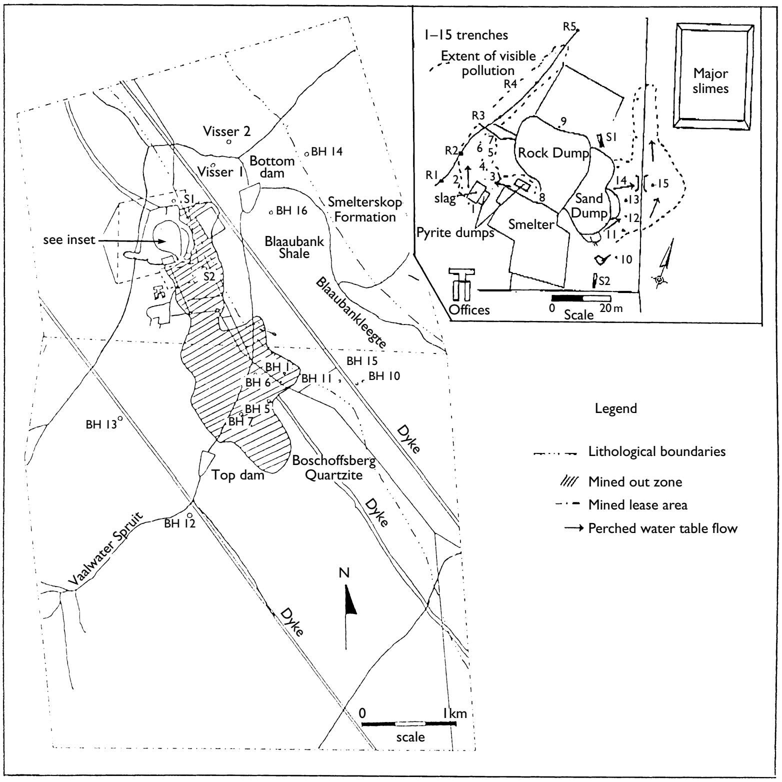

Figure 8.6 The mine lease area showing location of major dumps, boreholes, sampling points and trenches.

of cross-cutting dykes compartmentalizes the groundwater. Therefore, groundwater moves along fractures until it intersects a dyke where is it impounded. Lateral movement of groundwater then takes place along the dykes, flowing from south-east to north-west. The quantity of groundwater stored in the secondary aquifers is limited, while the permeability of such aquifers is generally low. Groundwater represents the primary supply of potable water for both domestic purposes and stock watering. Any possibility of pollution affecting these limited groundwater resources represents a significant threat to the community.

A perched water table exists around the major dumps at the mine and is impounded by a layer of ferricrete in the soil horizon. Water movement in the perched water table was determined by digging a series of exploratory trenches around the mine and observing from which direction water seeped into the trenches (Fig. 8.6). Movement of this water is topographically controlled and eventually finds its way into the Boschoffsberg Quartzite aquifer system. Although the quality of the water in the perched water table is poor, attenuation processes improve the quality as it percolates into the aquifer system proper. During the rainy season the sand and rock dumps at the mine site act as 'sponges' and water slowly percolates down through the dumps (Fig. 8.6). The sand and rock dumps, however, are underlain by impermeable tailings. Hence, the interface between the tailings (slimes) and dumps acts as a substrate along which water flows and slowly seeps into the surrounding soil horizon.

Extensive underground mine workings (hatched area on Fig. 8.6) further complicated the prediction of groundwater movement in the area. These workings were supplied by natural groundwater recharge. The underground tunnels overrode any structural control on groundwater movement in the vicinity of the mine. As water continues to flow into the mine workings, it will exert some influence on the groundwater regime until the workings are flooded.

In order to ascertain whether pollution of ground and surface water was occurring, samples of water and soil were taken for analysis. Samples also were taken from the dumps around the mine for analysis. Groundwater from all the boreholes on the mine lease area was sampled, as well as from the boreholes of local farmers. Groundwater samples were taken after a borehole had been pumped for a period so as to ensure that the groundwater sampled was actually from the aquifer and not groundwater that had been lying stagnant in the borehole. Further groundwater samples were obtained from the underground workings. As mentioned earlier, a series of trenches were excavated around the mine area and a number of these trenches contained groundwater that also was sampled. Surface water samples were taken from the reservoirs and streams. In the case of the latter, samples could only be taken after thunder showers as water flow in the streams only lasted a couple of hours after a rain storm. The soil samples were obtained from the trenches. They were all taken from a depth of 300 mm from the top of the trench. A number of sediment samples also were taken from the stream to the west of the smelter (Fig. 8.6).

Samples from the major dumps were taken from a depth greater than 500 mm below the surface. This was considered a suitable depth below which oxidation and leaching had not occurred. All the samples were taken from the upper parts of the dumps as both leaching and oxidation were more significant on the sides.

Table 8.6 lists the results obtained from chemical analyses carried out on surface water in the mine lease area. The high sulphate concentration and low pH in some of the surface samples was attributable to acid mine drainage.

Table 8.6 Analysis of surface water (After Bullock and Bell, 1995)

	Stagnant water	*River water*	*Bottom dam*	*Vaalwater*	*Top dam*	*South African limits (Anon., 1993)*	
						1	2
pH	2.4	4.1	7.4	7.1	7.3	6.0–9.0	5.5–9.5
COD	1410	38	—	83	—	*	*
EC (mS m^{-1})	865	57.2	65	82	138	70	300
Total hardness	32 409	219	249	523	663	300	650
Total N	38.4	2.5	<0.2	0.2	<0.2	6	10
Ca	163	64	82	66	93	150	200
Mg	74	12	32	30	22	70	100
Na	4	11	65	51	97	100	400
K	<1	9	8	23	10	200	400
SO_4	11 189	236	174	119	57	250	600
Cl	18	6	42	34	42	200	600
F	<0.1	<0.1	1.5	0.7	8.37	1.0	1.5
Fe	3580	2.4	—	0.2	—	0.1	1

Notes

All units expressed as mg l^{-1}, except pH and where stated.

* Chemical oxygen demand (COD) – general standards should not exceed 75 mg l^{-1} after applying the chloride correction.

1 Maximum limit for no risk.

2 Maximum permissible limit for insignificant risk.

Although the Piper diagram (Fig. 8.7) generally is used to classify groundwaters with different chemical compositions, it also was used to evaluate the surface waters in the mine area. This was to allow comparison of the chemical characteristics of the surface water with those of the groundwater. According to the classification introduced by Piper (1944), in all the water samples the alkaline earths exceeded the alkalies and the strong acids exceeded the weak acids. The fact that the strong acids exceeded the weak acids indicates that some surface water had been affected by acid mine drainage, presumably from the dumps. Non-carbonate hardness exceeded 50% in the stagnant water and the river water samples. In the water samples from the Vaalwater, Bottom Dam and Top Dam, not one of the cation-anion pairs exceeded 50%.

8.5.2. Dumps as sources of pollution

Analysis of surface water indicated that it had been affected by acid mine drainage. First, the material in the waste dumps was examined to determine whether they acted as sources of the pollution. This waste material had

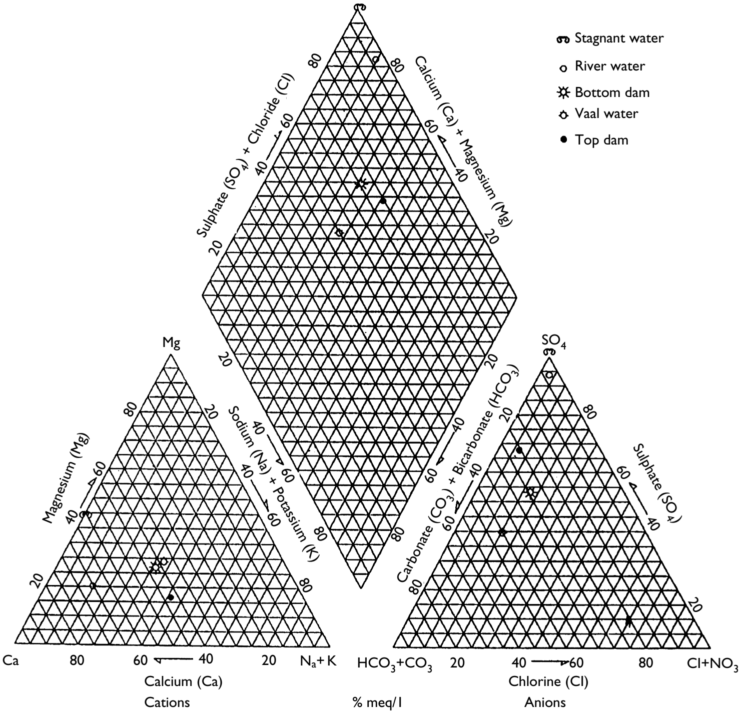

Figure 8.7 Piper diagram of surface water quality.

been disposed of in an area that covers approximately 1.2 km^2. The dumps included pyrite dumps, slimes dumps (tailings impoundments), a slag dump, a sand dump, and a rock dump.

An estimated 8125 tonnes of pyrite material had been deposited in pyrite dumps. An elemental analysis of material from the major pyrite dump showed that sulphur accounted for some 45% and iron for nearly 36% (Table 8.7). The particle size distribution of the material is illustrated in Figure 8.8. Because of the fine particulate nature of the material, the individual particles presented a very large surface area in relation to their volume that made them susceptible to leaching and other chemical reactions. The outer surfaces of the pyrite dumps were coated to a varying extent with a crust of sulphur material that was 20–70 mm in thickness. An aerobic zone could be distinguished from an anaerobic zone in this crust. The yellow and ochre coloured aerobic zone contained a greater than average concentration of iron and sulphur because of capillary action, which brought dilute salt

Table 8.7 Metals in the pyrite dumps

Element	%
S	45.14
Fe	35.57
Cu	2.20
Sn	1.02
Co	0.49
Ni	0.134
Pb	0.2
As	0.14
Sb	0.02

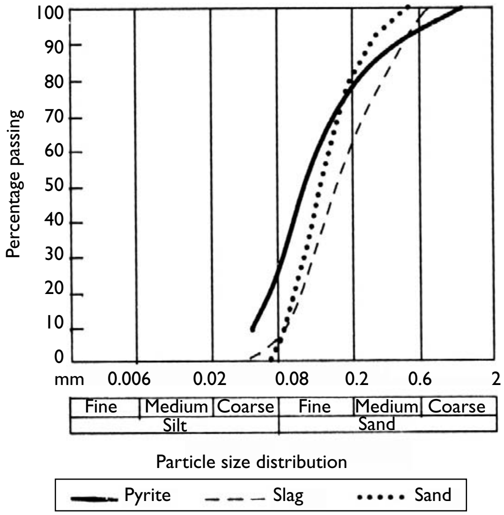

Figure 8.8 Particle size distribution of material in the pyrite, slag and sand dumps.

solutions from the interior of a dump to the surface. Subsequent loss of moisture at the surface due to evaporation resulted in a build-up of metallic salts. The surface temperature of the dumps was in excess of 40°C during the day in the summer months. The moisture content, 200 mm below the surface of the dumps, was approximately 12%. A paste pH value of 3.2 was obtained for the pyrite material. Brodie *et al.* (1989) maintained that a paste pH below 4 means the oxidation of sulphide minerals has occurred.

According to Halbert *et al.* (1983), the generation of sulphate with bacteria, at a pH of 3.0 and a temperature of 21°C is 1.17 moles kg^{-1} tailings per month. Taking into consideration the small particle size of this waste material, that the pH value of the paste is 3.2, that the surface temperature of the pyrite dumps exceeded 40°C in the summer months and 21°C in the winter, and the fact that *Thiobacillus ferrooxidans* cultures were present in the crust on the dumps, production rates of sulphate exceeded 1.17 moles kg^{-1} tailings per month. In fact, Halbert *et al.* maintained that the rate of generation of sulphate increased approximately threefold for every 10°C increase in temperature. Therefore, assuming an average annual surface temperature of 30°C, the sulphate generation rate on the pyrite dumps was estimated around 3.68 moles kg^{-1} tailings per month. This implies that in one month 353.5 mg of sulphate will form from 1 kg of waste. This rate of sulphate generation, however, probably was never reached because the yellow crust on the dumps inhibited the access of oxygen and so reduced the rate of oxidation. Nevertheless, after rain had fallen the yellow coating partly dissolves, although within two days the crust could reform, paying testimony to the initial rapid oxidation rates.

Further proof of the high generation rates of sulphate was obtained from the results of acid-base account tests on the pyrite material. The results gave an acid potential of 1410.625 g $CaCO_3$/kg, a neutralizing potential of −40.6 g $CaCO_3$/kg, and a net neutralizing potential of −1451.7 g $CaCO_3$/kg. According to Brodie *et al.* (1989), samples with a negative net neutralization potential and a ratio of neutralizing potential to acid potential of less than 1:1 have a high potential for acid generation. The acid-base accounting results therefore clearly demonstrated that the pyrite dump material had an extremely high potential to produce acidic waters.

The soil samples were scanned for a number of elements using an inductively coupled plasma mass spectrometer (I.C.P-MS). The results are given in Table 8.8. In addition, an attempt was made to ascertain the depth to which acidic waters had penetrated the substrate below the major pyrite dump. This was done by digging a trench to a depth of 2.5 m with a backactor. Soil samples were taken at different depths within the trench. The results of the analyses are given in Table 8.9 and suggest that acidic waters had penetrated to a depth greater than 2.5 m. There appeared to be a relationship between the pH value and the iron percentage, that is, as the iron content increased the pH decreased.

Metal ions and toxic salts are brought into solution more readily in acid conditions ($pH < 5.5$). Therefore, as acidic surface waters moved through the pyrite dumps they absorbed heavy metals and toxic salts. Once the waters infiltrated into the soil, however, the pH of the water increased as it came in contact with cations adsorbed on to clay minerals. For example, a predominance of cations such as Ca, Mg, Na and K tends to raise the pH when they are released from clay. As the water lost acidity, heavy metals and toxic salts were precipitated in the soil. The relatively high heavy metal concentrations observed in the soil accumulated in this fashion (Table 8.8).

Table 8.8 Semi-quantitative analysis of soil samples (After Bullock and Bell, 1995)

Element	*T1*	*T2*	*T3*	*T4*	*T5*	*T6*	*T7*	*T15*	*Sand*	*Slag*	*R1*	*R2*	*R3*	*R4*	*R5*
pH	4.36	7.78	5.04	4.62	2.9	7.1	3.73	3.04	8.24	8.05	6.54	6.25	2.84	4.37	6.67
EC	152	120	182	360	469	342	314	31 000	47	2000	35	2210	1228	279	47
Ca	871	95	8011	4424	3227	3982	4792	147	428	3836	141	1666	496	3997	374
Mg	378	25	434	1846	473	1577	894	47 296	130	19 419	50	2176	9949	643	122
Al	113	46	0	85	1399	2	860	30 782	0	8	8	17	15 829	167	8
Mn	98	0	91	421	345	46	262	46 202	6	14	4	380	759	89	8
Fe	15	3	2	10	454	9	10	24 731	1	16	1	19	3790	24	2
Co	20	0	3	43	91	1	67	3916	0	1	0	285	823	39	0
Ni	9	0	1	8	11	1	28	484	0	0	0	37	23	11	0
Cu^{2+}	178	1	0	35	450	0	225	14 820	0	5	0	12	3924	34	2
Cu^{3+}	179	1	0	35	440	0	231	15 192	0	5	0	12	3944	35	1
Zn	4	0	0	7	4	0	3	226	0	0	0	3	16	2	0

Notes

All values except pH and electrical conductivity ($mS\,m^{-1}$) are in $mg\,kg^{-1}$.

T1 etc. = trench samples; R1 etc. = stream samples.

Table 8.9 Results of soil analysis from a trench dug below the major pyrite dump

Depth (m)	*pH*	*Fe (%)*	*S (%)*
0.11	5.4	4.41	0.19
0.22	5.2	4.47	1.30
0.36	6.0	3.58	0.35
1.26	4.1	6.65	0.66
2.2	4.6	6.31	0.49

Samples also were taken of the sediment in the stream running alongside the dumps (Fig. 8.6; Table 8.8). Sediment sample R5 was taken from the stream bed just as it exited the mine lease area. Analysis of this sample suggested that pollution in the stream had not yet spread beyond the mine lease area.

The tailings or slimes material in the impoundments consisted of very fine rock powder (<6 μm) that was left behind after crushing, milling and severance. Samples of this material analysed by X-ray fluorescence (XRF) gave the following results:

• Major elements (>1%)	Silica	Tin
	Aluminium	Iron
	Sodium	Calcium
	Potassium	Magnesium
• Minor elements (0.1–1%)	Rubidium	Zirconium
	Titanium	Phosphorus
• Trace elements (<0.1%)	Manganese	Chromium
	Sulphur	Barium
	Copper	Lead
	Cadmium	Strontium

The surface temperature of the old tailings impoundments varied, to some extent depending on the amount of vegetation cover, however, in summer it ranged from 20°C to 30°C. The moisture content of the old tailings also varied somewhat, with older impoundments showing a lower moisture content (3%) than the most recent impoundment (5%). The paste pH of the material was 7.8.

The results of acid-base accounting carried out on tailings material showed an acid potential of 5.0 g $CaCO_3$/kg, a neutralizing potential of 40 g $CaCO_3$/kg and a net neutralizing potential of 35 g $CaCO_3$/kg. Hence, the tailings material had a potentially acid consuming character and would not contribute to the acid mine drainage problem at the tin mine (Fig. 8.9). The fact that vegetation was well established on the flanks and upper surfaces of the tailings impoundments was indicative of their low pollution potential.

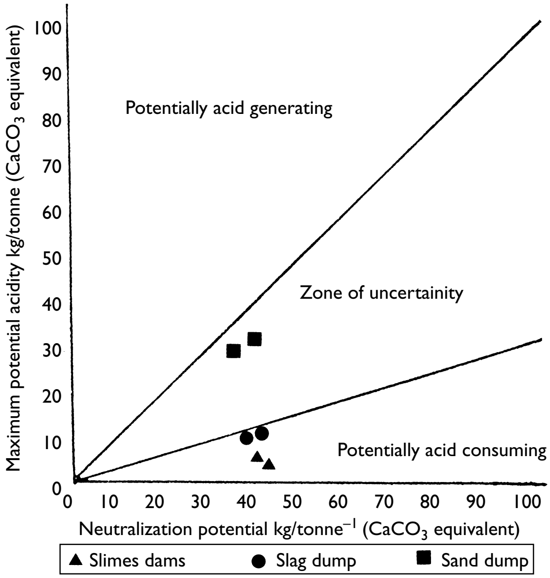

Figure 8.9 Acid-base account for slimes dams, and slag and sand dumps.

Table 8.10 Metals in the slag material

Element	%
Cu	0.12
As	0.009
Ni	0.008
Pb	0.01
Zn	52 ppm
S	0.35
Fe	3.63
Mg	5.01

The slag dump material consisted of crushed slag, char, ferrosilicon, limestone and fluorspar that remained after the secondary melt. An estimated 5000 tonnes of material existed in the dump. An analysis of the metals present in the slag dump is shown in Table 8.10 and a particle size distribution of the material is provided in Figure 8.8. The surface temperature of this dump exceeded 40°C during the summer months. The moisture content of the dump was not determined as active waterborne dumping was still in progress. However, the natural soil surrounding this dump had a moisture content of 15%. Salts also had precipitated on the surface of the soil. The paste pH of the material was 8.1. Grasses had started to inhabit the lower flanks of the dump but the upper surface remained barren.

The slag dump was not isolated from the natural drainage by cut-off berms or paddocks and therefore during heavy summer rains material was washed from the dump onto the surrounding flat land. If this material were to come into contact with acidic waters from the pyrite dumps, then the heavy metals present could be taken into solution. A small pyrite dump, east of slag dump, produced such acidic waters.

Trenches were dug in the soil around the slag dump (Fig. 8.6). Groundwater seeped into some of the trenches immediately but the water level tended to stabilize within 24 hours. Soil and water samples were taken from the trenches and the results are given in Tables 8.8 and 8.11, respectively.

The results of acid-base accounting tests done on the slag material showed an acid potential of 10 g $CaCO_3$/kg, a neutralizing potential of 40 g $CaCO_3$/kg and a net neutralizing potential of 30 g $CaCO_3$/kg. Consequently, the slag material had a potentially acid consuming character (Fig. 8.9). This is not necessarily surprising as sulphides had been extracted prior to dumping the slag.

The sand dump material was derived from the ore passing through a dense media separator. The separation was gravitational and therefore removed most of the sulphides along with the ore so that they were not disposed of with the sand material. An estimated 6000 tonnes of the sand dump material occurred in the area of the mine lease. This material had a dominant sand size fraction and consequently a high permeability (Fig. 8.8). The moisture content of the sand dump material was low, averaging 3%. The paste pH of the material was 8.2. Again the surface of the dump in the summer months was in excess of 40°C. The concentration of the major elements in this dump are given in Table 8.8.

Acid-base accounting tests carried out on the sand material indicated that the acid potential was 30 g $CaCO_3$/kg, the neutralizing potential was 38 g $CaCO_3$/kg and the net neutralizing potential was 8 g $CaCO_3$/kg. Accordingly, the sand material fell into the zone of 'uncertainty' (Fig. 8.9), that is, the material could either be acid consuming or acid generating depending on the local conditions.

The particles in the rock dump varied in size from 20 to 30 mm up to 300 mm. A mine rock classification developed by Brodie *et al.* (1989) was used to determine whether acidic waters seeped from this dump (Table 8.12). This classification uses visual, physical and geochemical characteristics to classify mine rock, in particular to identify relatively homogeneous rock units with respect to the quality of drainage water. The classification is based on six key properties, namely, particle size, sulphide type, sulphide surface exposure, alkali type, alkali surface exposure and slaking characteristics. The relative importance of each of these properties is taken into account by a weighting system. Since the neutralizing capacity of the alkaline material present prevents acid generation, these weighting factors are negative. Admittedly, the method does have shortcomings because it does not take account of a number of factors. Nevertheless, it does provide a relatively rapid means of assessment. The highest AMD or ARD potential value obtainable in the classification is 68 and the lowest ARD potential is −20. The rock dump material had a value of 2 and therefore probably would not produce any acidic seepage.

8.5.3. Chemistry of the groundwater

It can be seen from Table 8.11 that some of the groundwater samples had extremely high concentrations of sulphate. As with the surface water, these high values in the groundwater were associated with the acid mine drainage. Acidic waters, however, need not originate only at the surface. Oxidation of sulphides in old underground workings also can result in the formation of acidic water. The pH of this water, however, showed no evidence of acidity (see S1 and S2 in Table 8.11), as any acidic waters that did form were quickly neutralized by ankerite [Ca (Mg, Fe^{+2}, Mn)$(CO_3)_2$], which was present in relative abundance in the host rock. Therefore, the signs of mine water degradation were higher sulphate concentrations, higher electrical conductivity and total dissolved solids (TDS) values.

Figure 8.10(a) represents a Piper plot of water samples taken from farm and mine boreholes that appeared to be unpolluted. The alkaline earths exceeded the alkalies in these samples and, with the exception of those samples from BH12, Blaauwbank and Sleepwa, the weak acids exceeded the strong acids. In all samples the secondary alkalinity exceeded 50%, so that the chemical properties of the water were dominated by alkaline earths and weak acids. This can be compared with Figure 8.10(b) on which poor quality water samples from trenches and underground workings are plotted. In these samples the alkaline earths exceeded the alkalies, the strong acids exceeded the weak acids and the secondary salinity (non-carbonate hardness) exceeded 50%.

Piper (1944) maintained that in order to show that a certain water is a mixture of two others, one graphic criterion and one graphic-algebraic criterion must be satisfied. As far as the graphic criterion is concerned, in all three fields of the Piper diagram the apparent mixture must occur on straight lines between the points of its two inferred components. In addition, the area concentration of plots in the central field must conform to the principle that the concentration of a mixture is necessarily greater than the least, but less than the greatest, of the several concentrations of its

Table 8.11 Results of groundwater analysis

Sample	*pH*	*EC*	*NO$_3$*	*Ca*	*Mg*	*Na*	*K*	*SO$_4$*	*Cl*	*HCO$_3$*	*CO$_3$*	*TDS*	*Hardness*	*Alkaline*
T2	7.43	187	3.9	17.1	14.3	364	30.6	427	121.0	372.1	3	1167	102	310
T3	6.30	444	11.8	401	289	418	18.5	2937	26.7	24.4	0	4114	2171	20
T4	5.9	421	4.9	539	373	202	23.8	3275	73.5	18.3	0	4404	2866	15
T11	3.01	3130	29.4	493	3376	228	12.7	47 720	86.9	0.0	0	51 946	15 123	0
T12	2.9	2370	64.8	627	621	102	6.9	14 580	33.4	0.0	0	16 039	4121	0
T13	2.8	1680	19.6	509	561	70	0.7	27 070	53.5	0.0	0	28 284	3579	0
T15	3.2	857	7.4	614	309	103	12.5	2857	173.8	0.0	0	4078	2807	0
S1	7.54	497	4.7	475	430.8	367	20.1	3463	25.4	280.6	0	4933	2729	240
S2	7.74	190	1.0	153	123.5	131	5.2	805.5	62.2	353.8	9	1467	601	305
BH1	7.99	129	42.9	79	74.2	54	19.1	405.6	63.6	85.4	0	781	434	70
BH5	8.15	165	61.4	106	85.7	92	8.8	581.2	48.6	112.0	0	1057	520	103
BH6	7.73	182	57.5	129	99.5	85	10.0	683.4	49.4	122.0	0	1175	632	100
BH7	8.07	172	87.3	102	88.9	101	7.4	522.7	59.4	201.3	0	1070	457	165
BH10	7.2	69	0.2	70	3.1	69	9.0	12.0	4.3	374.4	0	448	317	375
BH11	7.3	71	0.4	64	3.2	68	6.0	15.0	12.6	374.3	0	461	334	375
BH12	7.8	112	< 0.2	76	3.7	138	4.0	263.0	12.3	296.2	0	728	452	298
BH13	7.2	58	< 0.2	53	4.5	54	3.0	62.0	17.4	263.4	0	377	226	265
BH14	7.1	51	0.4	59	3.4	20	3.0	7.0	10.3	308.6	0	332	286	309
BH15	7.5	75	0.2	75	3.3	91	9.0	7.0	4.6	407.0	0	488	314	409
BH16	7.3	87	0.3	102	3.7	54	17.0	148.0	24.5	297.4	0	566	452	298
Visser 1	7.65	81	2.6	22.8	57	71.7	2.1	23.0	6.4	536.8	0	435	439	440
Visser 2	7.58	78	1.1	55.7	85.5	19.5	3.3	4.1	4.6	610	0	478	490	500
Sleepwa	8.57	51	2.3	44.9	34.4	19.7	2.0	76.5	31.9	122.0	6	279	154	110
Knoppieskraal	7.74	45	20.8	32	23.6	37.6	2.4	5.6	18.5	189.1	0	235	22	155
Strydom	7.18	68	2.5	62.9	46.4	33.3	1.7	3.7	5.1	536.8	0	424	349	440
Blockdrift	7.32	77	0.0	76.5	54.0	30.0	1.4	2.0	6.8	494.1	0	439	405	—
Nieuwpoort	7.16	107	13.5	74.3	56.9	76.7	0.3	15.4	80.8	530.7	0	583	420	435
Blaauwbank	8.06	36	63.4	12.3	7.9	18.3	11.4	18.8	10.2	36.6	0	161	23	30
South 1.	6–9	70	6	150	70	100	200	200	250			450	300	
African 2. Limits (Anon., 1993)	6.5–9.5	300	10	200	100	400	400	600	600			2000	650	

Notes

Except for pH and EC (mS m^{-1}), all units are expressed in mg l^{-1}.

1 Maximum limit for no risk.

2 Maximum permissible limit for insignificant risk.

Table 8.12 Rock classification of geochemical and physical parameters for acid mine drainage (AMD) evaluations (After Brodie *et al.*, 1989)

Factor	*Highest chemical activity* = *5*	*4*	*Intermediate chemical activity* = *3*	*2*	*Lowest chemical activity* = *1*	*Relative weight*	*ARD potential*
Sulphide type	Highly reactive, e.g. fine grained, $<5\ \mu$ pyrrhotite		Moderate reactivity, e.g. coarse grained (5–100 μ)		Massive pyrite crystals	6	6
Portion sulphide surface area exposed	Localized (zones) of concentration exposed on fracture surface, e.g. $>$50% of sulphides in stringers or veins		$>$20% of sulphides in zones, stringers or veins with some preferential exposure on fractures		Individual small crystals, uniformly distributed through host rock material	5	15
Alkali type	Highly reactive e.g. $CaCO_3$		Moderate reactivity		Slightly reactive	−4	−9
Alkali surface area exposure	Individual crystals uniformly distributed through the host rock material, or 50% alkali in bedding, fractures or veins which tends to become exposed on handling		$>$20% of alkali in bedding or veins with some preferential exposure fractures		Localized zones of concentration exposed on fracture surfaces e.g. $>$50% of alkali in bedding, fractures or veins which tend not to become exposed on handling	−3	−15
Grain size	$>$20% fines; e.g. $>$ 20% sand size and finer		5% sand size and finer		Little fines; $<$ 1% sand size and finer	2	2
Slaking	Highly slaking; $>$ 20% of rock mass degrades to sand size		Slightly slaking; $>$ 2% of rock degrades to sand size		Non-slaking	2	3
						Total	2

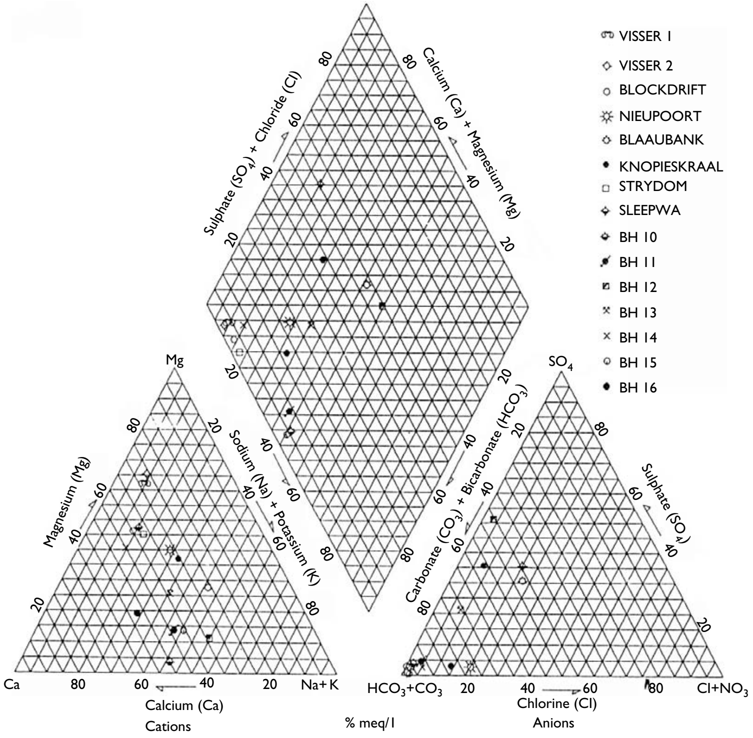

Figure 8.10a Piper diagram of samples of groundwater that is unaffected.

components. From examination of the Piper diagrams of the surface water, natural groundwater and affected groundwater, it is evident that the mixture (in this case the affected groundwater) between the natural groundwater and surface water does not plot on a straight line between these two components and therefore the graphic criterion is not met. Hence, the affected groundwater is not a simple mixture of surface water and natural groundwater. In such a situation the second criterion cannot be satisfied. This implies that the groundwater occurring in the tin field was subjected to different hydrochemical processes. Such processes could include ion exchange, mixing, dissolution and precipitation.

The character of the groundwater was examined with the aid of Stiff diagrams (Stiff, 1951). The advantage of the Stiff diagram is that it presents a better picture of the total salt concentration than other graphic methods. The effects of dilution and concentration are reduced to a minimum, this is

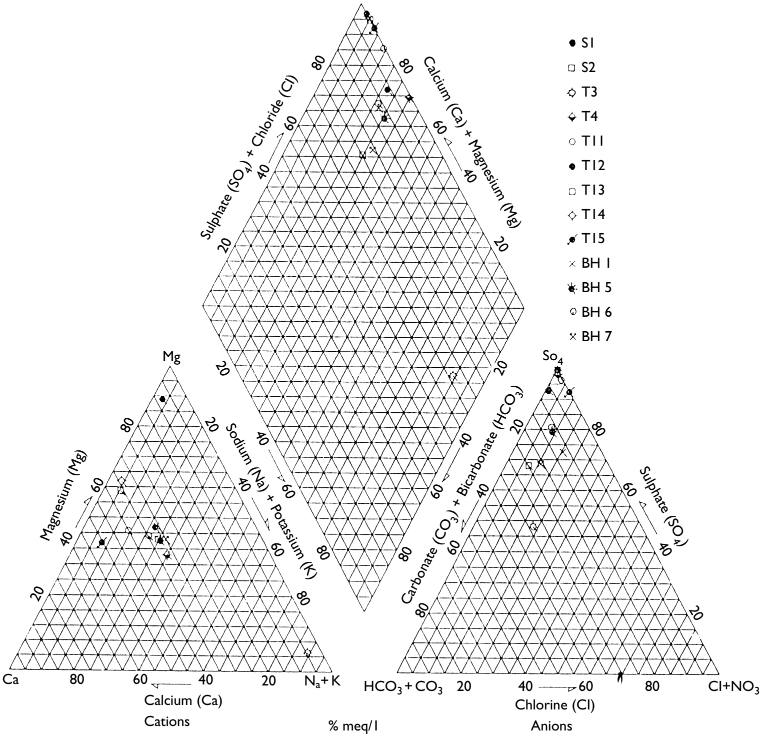

Figure 8.10b Piper diagram of samples of groundwater that is affected.

in contrast to the Piper diagram, which is directly affected by both dilution and concentration. In other words, the Stiff diagram offers a simple, practical means of characterizing and comparing groundwaters.

The use of Stiff diagrams allows a threefold classification of groundwater in the tin field. The natural groundwater has a ‘kite’ shaped tail with HCO_3 being the dominant anion. The Stiff diagrams for boreholes Blaauwbank, Blockdrift, Knoppieskraal, Nieuwport, Strydom, and Visser 1 and 2 offer examples (Fig. 8.11(a)). As the groundwater becomes affected by acid mine drainage, the HCO_3 percentage decreases, and the sulphate anion begins to dominate, leading to a change in the shape of the Stiff diagram. A ‘flat’ tail develops as the tail tends towards the sulphate ion and the HCO_3 percentage decreases. The groundwater from shafts S1 and S2, and from boreholes BH1, BH5 and BH6 provide ‘flat’ tailed Stiff diagrams (Fig. 8.11(b)). Water that is most affected by acid mine drainage has a low pH value, has a very

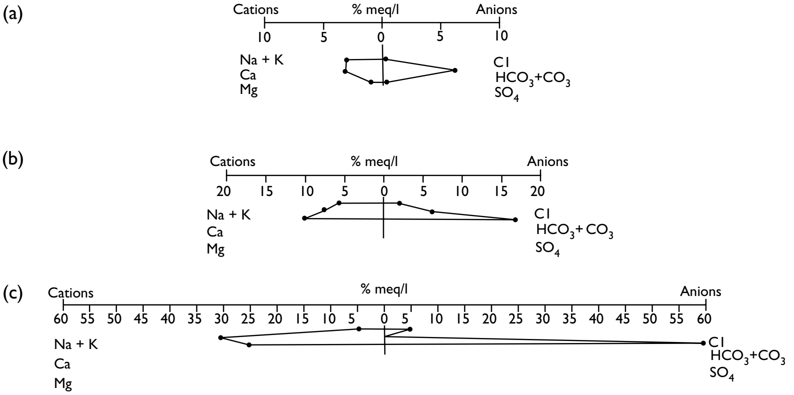

Figure 8.11 Examples of Stiff diagrams (a) borehole 11 (BH11), (b) shaft No 2 (S2), (c) trench No 4 (T4).

low or zero concentration of HCO_3 and an extended 'flat' tail towards a high concentration of sulphate ion. The groundwater sampled from trenches T3, T4, T11, T12, T13 and T15 provide examples of this type of Stiff diagram morphology (Fig. 8.11(c)).

In summary, Class 1 water is unaffected by acid mine drainage and has a 'kite' shaped tail; Class 2 has a 'flat' tail but HCO_3 is still present; and Class 3 water has an extended 'flat' tail, indicating a negligible concentration of HCO_3. Class 3 water has a low pH value and tended to occur close to the surface in the perched water table. Class 2 water, although affected by acid mine drainage, had a pH value near neutral. The neutralizing process was thought to be brought about by the predominance of the cations Ca, Mg, Na and K that were released from clay particles and raised the pH value. The second factor that increased the pH, so neutralizing acidic waters, was the ankerite present in the Boschoffsberg Quartzites.

The groundwater samples also were plotted on trilinear diagrams. Figure 8.12(a) shows the trilinear diagrams for groundwater sampled from the boreholes BH10 to BH16. The major anion diagram indicates that bicarbonate was the dominate ion with minor amounts of sulphate and chloride whereas the cation diagram suggests that calcium, magnesium and sodium were not dominant. Groundwater taken from farm boreholes had a lower concentration of chloride anion and magnesium cation than in the boreholes mentioned previously, but the calcium and sodium concentrations were greater (Fig. 8.12(b)). Trilinear diagrams of groundwater sampled from trenches and subsurface workings are shown in Figure 8.12(c). The anion triangle shows a distinct skewness towards the sulphate ion. The lower

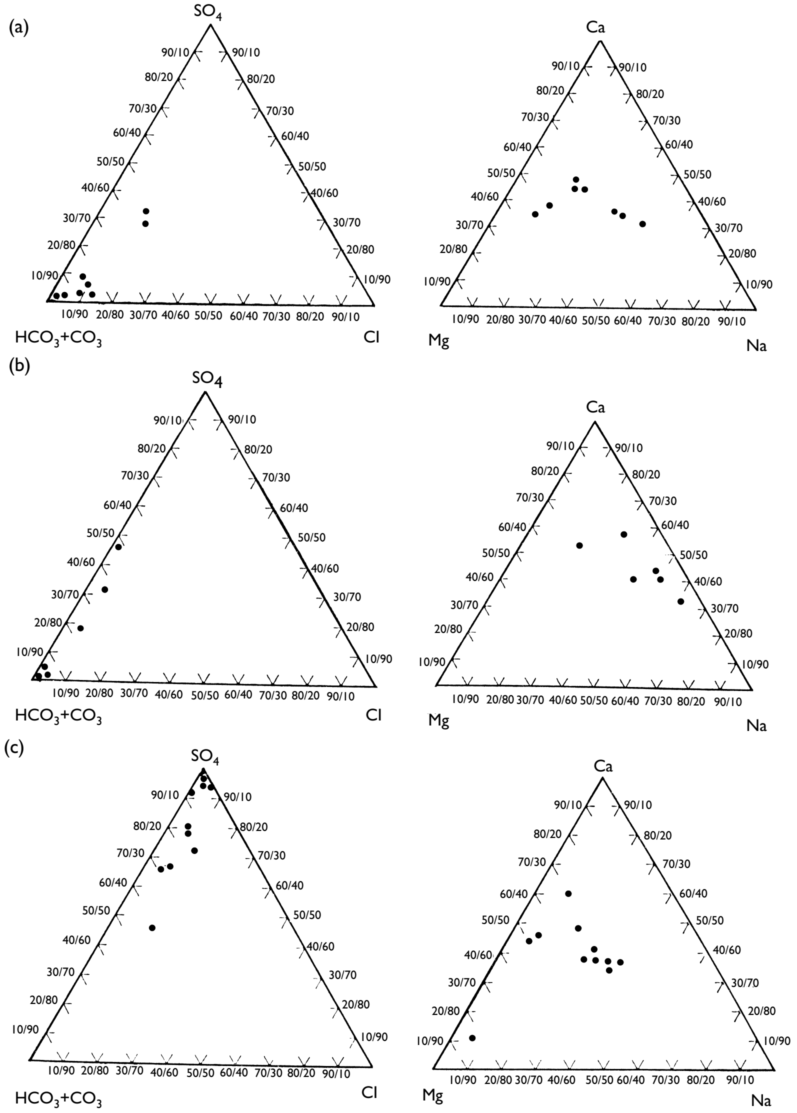

Figure 8.12 Trilinear diagrams for (a) boreholes B10 to B16, (b) boreholes Visser 1 to Blaauwbank, (c) trenches 2 to 15 and underground workings.

bicarbonate concentration and higher sulphate ion concentration was attributed to acid mine drainage. In the cation triangle some samples showed a tendency towards the magnesium ion. This also was attributed to acid mine drainage, magnesium being more soluble in waters with low pH and so was concentrated in the polluted water. Calcium values were relatively high due to cation exchange processes. Cation exchange occurs when subsurface waters containing solutes interact with organic and inorganic adsorbent processes in the soil. In other words, the cation exchange capacity measures the capacity of soils to hold positively charged elements such as calcium, and the ability to resist changes in pH.

Contours of pH value, electrical conductivity and the major cation and anion (Ca, Mg, Na, K, Cl, SO_4) concentrations, derived from groundwater samples, were drawn to provide an overall assessment of groundwater quality in the area around the mine (Fig. 8.13(a)–(h)). The anomalies that are present on the individual maps more or less corresponded with acid mine drainage from the pyrite dumps. In other words, the maps of sulphate concentration, pH values, TDS values, magnesium values and electrical conductivity show that plumes developed away from the dumps in an easterly direction, that is, in the direction of groundwater movement. On the other hand, there was a concentration of sodium on the western side of the dumps, the alkalinity of the groundwater declining eastwards. Calcium values tend to be concentrated beneath the sand dump and spread out fairly evenly from there.

8.5.4. Remedial treatment

The groundwater gradients in the area of the dumps were low, mainly due to the flatness of the surface topography. These low groundwater gradients, together with the presence of a dyke 500 m north of the major dumps and another about 1 km to the south-west, and the relatively impermeable nature of the Boschoffsberg strata, suggested that it would be unlikely that affected groundwater would migrate significant distances from the dumps. Indeed, migration of pollutants probably would be restricted to less than 1000 m from the dumps by these geological conditions.

Be that as it may, the pyrite was removed, it being sold for the manufacture of sulphuric acid. Inevitably, some pyrite was left behind. This remaining material was disposed of in an impoundment on site. The impoundment was designed so that it was isolated from the natural drainage by the construction of cut-off trenches and by the use of clay liners to prevent seepage into the groundwater. Once dumping within the impoundment was completed, it was capped with a clay layer and then completely vegetated. An impoundment also surrounds the slag dump. Part of the rock dump was placed in an abandoned opencast working. The remaining material was levelled. Both areas were covered with top soil and vegetated. The sand dump was stabilized by

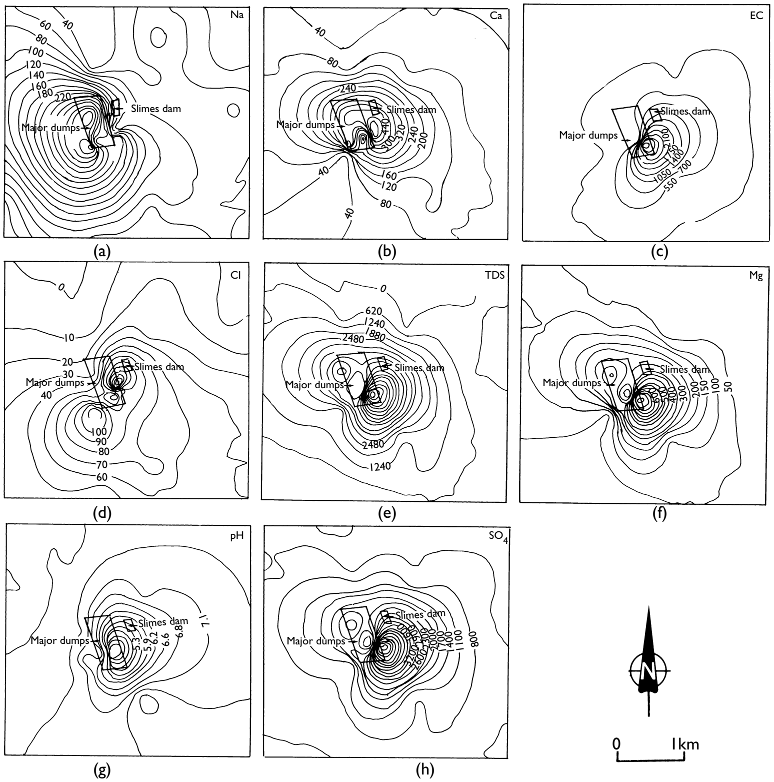

Figure 8.13 Maps showing contoured concentrations of (a) sodium (mg l^{-1}), (b) calcium (mg l^{-1}), (c) electrical conductivity (mS m^{-1}), (d) chloride (mg l^{-1}), (e) total dissolved solids (mg l^{-1}), (f) magnesium (mg l^{-1}), (g) pH value and (h) sulphate (mg l^{-1}).

covering with waste rock from the rock dump or by grassing. However, the latter proved difficult due to the low organic and nutrient content of the sand, its high permeability and excessive surface temperatures. The major tailings dam was relatively well-vegetated and apparently did not represent a principal source of pollution. The other tailings dam was vegetated and isolated from the natural drainage by embankments.

8.6. Case history 2

The Witbank Coalfield is located in the headwaters of the Olifants River in Mpumalanga Province, South Africa. Mining in Witbank Coalfield began in 1906, and there are currently over 50 operating or defunct coal mines. The coal and waste rock associated with the mining operations is pyrite bearing, and therefore acid mine drainage in the area has caused a deterioration in both surface and groundwater qualities. Opencast mining has the greatest impact on groundwater quality, in that the mines are acid generating and associated with heavy metals, which include iron, aluminium, manganese, copper and zinc. Investigations have shown that the average rate of sulphate generation in a backfilled opencast area is between 5 and 10 kg per hectare a day. On the basis of the present scale of opencast mining in the Witbank area this amounts to 70 tonnes per day of sulphate. Recharge to the groundwater in the opencast areas is as high as 20% of rainfall. Sulphate levels in the groundwater around these opencasts mines are typically between 2000 and 3000 mg l^{-1}. There are essentially four water management options at opencast mines. These are selective spoil handling, clay capping of backfilled opencast areas, flushing and containment. Shallow underground mining also has had an affect on regional groundwater quality. Shallow mining has given rise to subsidence leading to small troughs formed by pillar collapse, to open tension cracks and to crown holes at the surface formed by void migration, with the result that rainwater actively recharges the mines. Recharge in these areas has been found to range up to 15% of rainfall. A number of defunct mines west of Witbank are currently decanting extremely acid water to the surface. The decant water may have a pH as low as 1.5 and sulphate levels in excess of 3000 mg l^{-1}. Water quality deterioration is a two-phased phenomenon. First, base exchange occurs as groundwater seeps towards areas of high extraction, resulting in a sodium bicarbonate/chloride water entering these areas. The second phase occurs within the mine in that pyrite oxidation introduces sulphate, then releases calcium and magnesium from carbonates. Groundwater in high abstraction areas therefore tends to have a range of chemistries, depending on the evolutionary stage of the groundwater. Groundwater quality ranges from severely polluted in some instances to negligible in others.

Unfortunately, acid mine drainage is feeding from a number of abandoned mines into the waters of the Blesbokspruit, which is a tributary of the Olifants River. As a result, the water in the Blesbokspruit has a low pH and high total dissolved solids. This has become a matter of concern as far as the Olifants River is concerned, the latter ultimately flowing through Kruger National Park. The catchment area of the Olifants River is not only sensitive from the point of view of tourism and nature conservation but also because much of the river flows through areas of intensive agriculture. Water quality management and any environmental remediation needs to be considered within a regional context and requires cooperation between mining concerns in the area and downstream users. South Africa presently is moving towards regulation based on water quality receiving objectives that take account of the assimilative capacity of the receiving water, as well as the water requirements of the downstream user. A survey was undertaken at one particular abandoned mine (Middelburg Steam Colliery) by Bell *et al.* (2002) to determine the effect of acid mine drainage issuing from it on the Blesbokspruit.

The five recognized coal seams in the Witbank Coalfield occur within a succession some 70 m in thickness. Only one seam was mined during the life of the mine investigated. It occurs at a depth of approximately 18–23 m and ranges in thickness from 3.5 to 6 m. In the east of the mine property, the seam crops out approximately 100 m west of the Blesbokspruit.

The seam was mined primarily by the bord and pillar method from 1908 to 1947. Pillar robbing started in the late 1930s and resulted in the formation of crown holes at the surface due to void migration, and in discontinuous subsidence caused by multiple pillar failure with associated extensive surface fracturing (Bullock and Bell, 1997).

There are two spoil heaps on the site. One covers an area of approximately 56 250 m^2 and the other covers 66 000 m^2. It was assumed that the spoil material reflected the composition of the coal and shale in the old mine. Samples of shale and coal therefore were taken from the spoil heaps for analysis. Samples of coal also were obtained from an opencasted area. The shale was subjected to both chemical (XRF) and mineralogical analysis (XRD). The chemical and mineralogical composition of some samples of shale from the spoil heaps are given in Table 8.13, from which it can be seen that the two principal oxides, as expected, were silica and alumina. Calcium, magnesium, iron, sodium, potassium, titanium and phosphorus oxides are present in small concentrations. The sulphur content of this shale material averages approximately 1.5%. The mineralogical composition of the shale material in the coarse discard consists primarily of kaolinite, quartz and mica. Other minerals present included microcline, illite and jarosite. Table 8.14 indicates that the coal is low-rank bituminous coal. It also shows that the sulphide content, and therefore the pyrite content, frequently is in excess of 2%. The ash content of the coal averaged 24.5%, which is high. When analysed by XRF, silica and alumina were again the chief oxides, with Fe_2O_3 coming a lowly third, averaging 1.1%.

8.6.1. Impact of mining on hydrogeology

The surface subsidence and the associated underground fire at the mine have had impacts on both groundwater and surface water hydrology. These impacts include reduced surface run-off, increased groundwater recharge, and deterioration of water quality. Surface run-off is reduced as rainfall collects in collapsed areas after heavy summer rains. The ponded water percolates through subsidence related tension cracks and crown holes to the underground workings. The workings in the seam concerned act as an aquifer for the percolated water. An anticline in the mine area acts as a

Table 8.13 Analysis of shale (from spoil heaps). (a) Chemical composition; (b) Mineralogical composition (XRD) (After Bell *et al.*, 2002)

(a) Sample no.	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*MgO*	*CaO*	*Na_2O*	*K_2O*	*TiO_2*	*P_2O_5*	*Sulphur content*
1	63.4	32.7	0.96	0.24	0.04	—	1.01	1.43	0.08	0.94
2	80.1	15.7	0.47	0.03	0.03	0.18	0.22	2.64	0.47	1.72
3	51.8	44.0	0.48	0.13	0.02	0.32	0.70	2.19	0.08	1.25
4	65.2	31.0	0.78	0.11	0.07	0.2	0.43	1.59	0.14	2.01

(b) Sample no.	*Quartz*	*Kaolinite*	*Illite*	*Mica*	*Microcline*	*Jarosite*
1	10	68	0	14	0	6
2	18	53	2	21	2	3
3	14	72	4	6	1	2
4	23	66	1	6	0	3
5	29	58	2	4	2	1

water divide. Groundwater collecting on the western side of this regional anticlinal axis flows to the west and dams up against the boundary pillar with the adjacent mine. However, groundwater moving through the workings on the eastern side of the anticlinal axis flows towards the coal sub-outcrop in the vicinity of the Blesbokspruit. Since 1991, after the coal sub-outcrop pillar along the eastern boundary of the working was mined, groundwater, which previously had been retained behind the pillar, began to seep from the workings. This seepage water flows overland in a series of springs, before merging to enter the Blesbokspruit. A V-notch flume was installed to measure flow on the stream and weekly flow readings were recorded for a one-year period from December 1994 to November 1995. The total annual volume of water collecting over the mine site catchment area was derived from the rainfall data. The estimated recharge to the coal seam is around 50% of the volume of rain that falls. Figure 8.14 suggests that there is a lag time between the heaviest rainfall (January) and maximum flow over the V-notch (July).

Rainwater seeping into the old workings is affected by both the oxidation of pyrite and the presence of the underground fire. Table 8.15 includes some examples of water quality analyses of samples of water collected at the V-notch. Samples were obtained both during the summer (the wet season) and in winter (dry season) over a number of years, and are representative of the quality of water seeping from underground. Analyses of samples taken from drillholes sunk into the seam, along with analyses of water from drillholes sunk at adjacent collieries are given in Table 8.16 for comparison.

Inspection of the water quality data at the V-notch and from the mine shows that the waters are highly polluted and that the water in the

Table 8.14 Analysis of coal (a) from spoil heaps, (b) from open cast area. (c) Ash content (XRF) (After Bell *et al.*, 2002)

	Coal from spoil heap 1					*Coal from spoil heap 2*				
(a)	*Sample no.*	*Carbon content*	*Ash content*	*Sulphur content*	*Moisture content*	*Sample no.*	*Carbon content*	*Ash content*	*Sulphur content*	*Moisture content*
	1	64.2	22.1	2.25	5.5	1	66.8	22.7	2.35	2.3
	2	67.3	21.2	1.81	4.7	2	64.5	21.6	1.79	3.6
	3	63.2	24.3	2.31	4.1	3	63.2	29.6	1.85	1.9
	4	67.2	25.6	2.10	4.9	4	67.2	26.0	2.17	3.3
	5	64.6	27.1	2.21	5.2	5	65.7	27.3	2.28	3.9
(b)	*Sample no.*	*Carbon content*	*Ash content*	*Sulphur content*	*Moisture content*	*Sample no.*	*Carbon content*	*Ash content*	*Sulphur content*	*Moisture content*
	1	61.5	25.4	2.57	4.4	6	61.4	31.2	1.26	4.7
	2	66.5	23.9	1.92	3.8	7	58.6	33.0	2.74	3.6
	3	62.7	22.0	2.64	4.1	8	65.1	29.6	2.15	2.9
	4	64.5	26.9	2.79	4.1	9	66.7	27.9	1.98	3.1
	5	62.7	28.5	3.77	3.9	10	68.4	23.8	2.41	4.7
(c)	*Sample no.*	SiO_2	Al_2O_3	Fe_2O_3	*MgO*	*CaO*	Na_2O	K_2O	TiO_2	P_2O_5
	1	52.9	43.3	0.59	—	0.11	0.25	0.76	1.65	0.40
	2	40.6	35.7	1.99	0.06	10.2	0.23	0.35	1.75	8.84
	3	58.6	38.1	0.22	0.05	—	0.27	0.21	1.93	0.08
	4	52.8	43.4	1.48	0.12	0.09	0.12	0.33	1.01	0.21
	5	51.6	40.0	2.01	0.07	0.06	0.14	0.39	1.02	0.56
	6	52.6	41.4	1.90	0.10	1.26	0.22	0.54	1.11	0.32

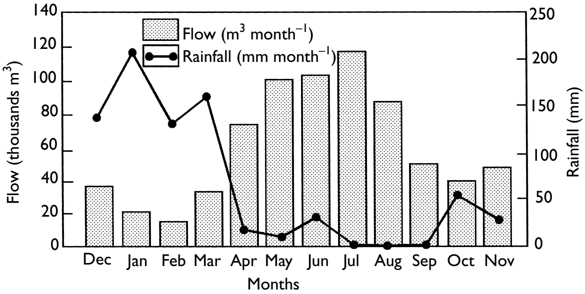

Figure 8.14 Monthly rainfall figures compared with seepage flow over the V-notch.

Blesbokspruit catchment is characterized by low pH and high total dissolved solids. As such, it is capable of mobilizing toxic metal concentrations. The pH values are well below and the total dissolved solids values significantly above the respective crisis limits recommended by the South African guidelines for domestic water (Anon., 1993). At such values there is a danger to health due to dissolved metal ions. Low pH values can be attributed to the formation of sulphuric acid as a product of reactions involving the oxidation of pyrite with the production of acid mine drainage. In this case, the oxidation of pyrite is enhanced by higher temperatures attributable to burning coal in the old mine. This is supported by the sulphate content, which in all the analyses is above the crisis limit guidelines and in some instances is twice that limit. The high sulphate content is not unexpected when compared with the high sulphur content in the coal and associated shale (Tables 8.13 and 8.14). Table 8.15 also shows that the concentrations of aluminium and iron far exceed the crisis limits for drinking water quality in South Africa. Most of the other constituents are around or exceed the maximum permissible limits.

The effect of the time lag between the period of maximum precipitation and maximum flow from the workings is reflected in TDS concentrations. Consequently, the salt concentrations for the wettest months, when flow is lowest due to the time lag mentioned, are generally greater than for the dry months when flow is highest. The increased volume of water therefore has a dilution effect on the concentration of dissolved salts in the water.

In an attempt to ameloriate the impact of underground water entering the Blesbokspruit, a series of four pollution control ponds were constructed (Fig. 8.15). A side stream of the seepage water was directed into the upper reservoir while the remaining flow entered the nearby stream below the ponds. Residence time in the ponds is not known but is likely to vary with

Table 8.15 Examples of the chemical composition of acid mine water collected from the V-notch (location W4 in Fig. 8.16) and South African guidelines for drinking water quality (Anon., 1993; after Bell *et al.*, 2002)

Determinand ($mg\,l^{-1}$)	*Sample 1 May 1990*	*Sample 2 June 1990*	*Sample 3 July 1990*	*Sample 4 Dec 1990*	*Sample 5 Jan 1991*	*Sample 6 Mar 1991*	*Sample 7 Dec 1993*	*Sample 8 Jan 1994*	*Sample 9 Feb 1994*	*Sample 10 Dec 1995*	*Sample 11 Aug 1996*	*Sample 12 Aug 1996*	*Sample 13 Aug 1996*	*Recommended limit (no risk)*	*Maximum permissible limit (insignificant risk)*	*Crisis limit (max limit for low risk)*
TDS	2749	2575	2575	2843	2760	2082	3376	3038	3575	4844	2968	3202	3604			
EC ($mS\,m^{-1}$)	293	327	465	421	379	298	424	463	418	471	430	443	340	70	300	400
pH value	2.3	2.4	3.0	1.8	1.9	2.0	2.8	6.6	2.8	1.9	2.4	2.95	2.8	6–9	5.5–9.5	>4 or <11
Nitrate NO_3 as N	0.05						0.04	0.02	0.18	0.1	0.1	0.1	0.1			
Chloride	91	84	186	120	106	124	179	174	170	310	431	406	611	250	600	1200
Fluoride										0.6	0.5	0.33	0.84	1	1.5	3
Sulphate as SO_4	2361	2239	2697	2462	2330	1692	2722	2378	2897	3250	1610	1730	1440	20	600	1200
Total hardness as $CaCO_3$											484	411	377			
Calcium hardness as $CaCO_3$											285	310		20–300	650	1300
Magnesium hardness as $CaCO_3$											199	101				
Calcium	135	115	176	76	132	98	162	179	186	173.8	114.0	124	84	150	200	400
Magnesium	56	50	90	41	55	40	84	90	83	89.4	48.4	49.5	31	70	100	200
Sodium	102	65	200	116	138	114	194	185	200	247.0	326.0	311	399	100	400	800
Potassium									9.4	7.3	9.4	8.9		200	400	800
Iron			140						128	248.3	128	140	193	0.1	1	2
Manganese			18						15	17.9	15	9.9	9.3	0.05	1.0	2.0
Aluminium			86						124		124		84	0.15	0.5	1.0

Table 8.16 Chemical composition of acid mine water from drillholes sunk at Middelburg Steam and adjacent collieries (After Bell *et al.*, 2002)

Determinand ($mg\,l^{-1}$)	*Middelburg Steam Colliery (1)*	*Middelburg Steam Colliery (2)*	*Witbank Colliery (1)*	*Witbank Colliery (2)*	*Tavistock Colliery (1)*	*Tavistock Colliery (2)*
TDS	3604	5778	3048	3354	5778	7158
EC ($mS\,m^{-1}$)	340	355	389	403	355	368
pH value	2.8	2.8	2.65	2.7	2.8	2.9
Nitrate NO_3 as N	0.1	0.19	0.29	0.29	0.21	0.28
Chloride	611	184	951	989	18	4.8
Sulphate	1440	3233	910	1306	3253	3840
Total hardness as $CaCO_3$	377	214	106	161	2461	1977
Calcium	84	509	42	40	509	462
Magnesium	31	289	14.9	14.8	289	200
Sodium	399	47	620	775	47	32
Iron	193	198	122	99	198	726
Manganese	9.3	49	5.9	3.9	49	30
Aluminium	84	32	81	87	32	38

Figure 8.15 Pollution control pond, one of four.

season. Comparison of water quality data, especially of samples W7 and W8 (see Table 8.17; Fig. 8.16), show that the effect of cascading part of the seepage water through the decantation ponds is negligible. Indeed, it would appear that aluminium is being leached from soil particles in the ponds as aluminium concentrations leaving the lowest pond are about double those of water at the V-notch flume.

Table 8.17 Analyses of waters in the Blesbokspruit and its catchment (After Bell *et al*., 2002)

Determinand (mg l^{-1})	*W1*	*W2*	*W3*	*W4*	*W5*	*W6*	*W7*	*W8*	*W9*	*W10*	*W11*	*W12*	*W13*	*W14*	*W15*	*W16*	*W17*	*W18*
TDS	578	2280	1748	2097	2356	2625	2295	2341	2504	2164	2526	2215	2225	2232	1070	360	230	180
EC (mS m^{-1})	84	357	371	373	329	390	363	364	378	308	438	316	330	330	166	126	33	23
pH	3.5	2.6	2.7	2.6	2.8	2.7	2.7	2.7	2.6	2.7	2.7	2.8	2.8	2.8	3.1	3.2	7.4	7.3
Chloride	111	468	220	397	486	572	363	380	552	366	425	319	299	271	127	89.6	50.5	48.5
Fluoride	1.1	1.2	1.2	1.2	2.0	1.3	1.3	1.2	1.3	1.3	0.04	1.4	1.5	2.1	1.7	1.2	0.1	0.08
Sulphate	284	1345	987	1226	1416	1512	1509	1511	1470	1417	1587	1487	1512	1510	716	128	45.8	22.9
Alkalinity	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	73.8	41.1
Calcium[a]	49.2	110	116	117	139	145	136	134	122	111	169	120	151	158	72.8	52.1	23.5	10.6
Magnesium[a]	24.7	43.1	47.1	45.4	56.7	56.9	51.9	51.3	47.0	44.6	64.5	51	64.4	81.4	36.4	25.7	11.6	7.4
Sodium[a]	101	296	360	294	248	302	229	228	298	213	266	228	188	199	111	56.4	23	18.2
Potassium[a]	4.5	11.5	13.4	11.2	4.85	24.5	2.34	33.0	10.5	5.01	8.9	6.7	5.9	7.4	4.3	4.5	3.3	1.9
Iron[a]	1.3	31.6	25.5	46.2	29.6	38.6	34.6	74.4	36.1	27.2	87.1	7.4	19.9	7.0	4.7	1.6	0.61	0.59
Manganese[a]	2.9	10.6	11.5	13.4	12.4	12.4	13.8	12.7	13.4	12	13.7	13.5	19.2	23.1	9.5	6.5	0.09	0.08
Aluminium[a]	7.9	89.4	115	101	96.1	153	190	189	111	132	233	137	161	152	60.3	39.6	0.33	0.27
Silicon[a]	7.8	44.8	44	42.2	31.7	59.9	54.3	55.5	42.2	41.2	64.8	39.4	39.8	36.8	17.1	13.0	0.75	2.67
Copper[a]	1.0	1.4	0.96	1.1	1.0	1.4	1.5	1.1	1.42	1.4	1.5	1.0	1.1	1.0	1.0	0.97	0.94	0.95
Nickel[a]	0.87	1.9	1.8	1.9	1.71	2.2	2.1	2.2	1.9	1.9	2.6	1.8	2.0	1.9	1.3	1.1	BDL	1.1
Lead[a]	1.2	1.6	1.5	1.4	1.4	1.6	1.4	1.4	1.4	1.6	1.6	1.6	1.4	1.7	1.1	1.3	0.96	1.1
Zinc[a]	0.74	2.4	2.7	2.6	1.9	2.3	3.4	2.8	2.6	2.3	4.3	2.2	2.7	2.8	1.4	1.1	0.4	0.4

Notes

See Figure 8.16 for sample locations. All samples from the Blesbokspruit (including W16) except those noted below.

W2 and W3 samples of seepage water.

W4 sample of water from V-notch.

W5, W6, W7 and W8 samples of water from the decantation ponds.

W15 sample of water from the wetland.

W17 and W18 samples of water from the uncontaminated Prison stream.

W16 sample of water from downstream of the confluence with Prison stream.

a Determined by ICP-AES.

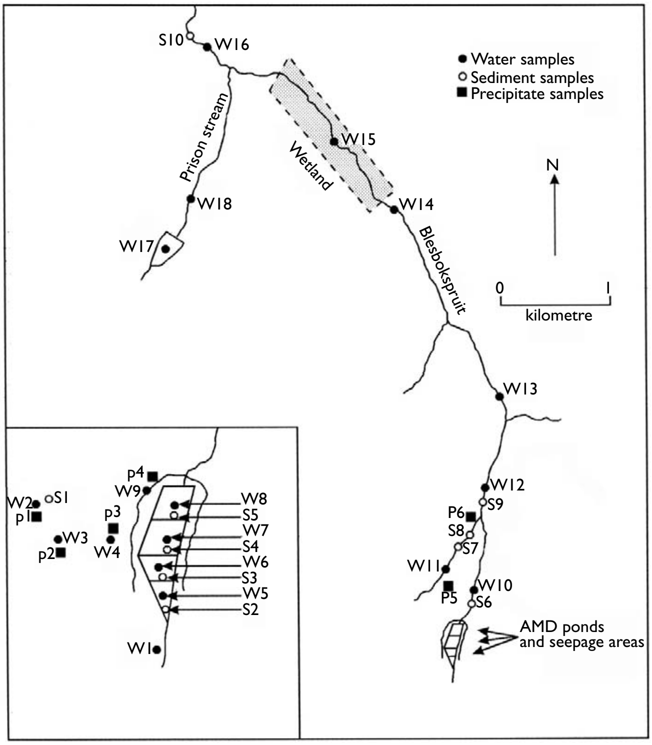

Figure 8.16 Location of water samples and wetland.

8.6.2. Aqueous geochemistry of the Blesbokspruit catchment

The pH value of the waters of the Blesbokspruit varied from pH 2.6 near where the water issued from the mine to pH 3.2 downstream of the wetland, which contained reed beds (Fig. 8.16; Table 8.17). By comparison, two samples taken from the unaffected tributary of the Blesbokspruit, namely, the Prison Stream, had values of pH above 7 (Table 8.17). The very low values of pH that characterized the rest of the Blesbokspruit catchment indicated a lack of neutralizing capacity in the mine workings and the catchment. The values of electrical conductivity were above 300 mS m^{-1} for water with a pH less than 3.0 (Fig. 8.17), whereas the unaffected water of the tributary stream had low electrical conductivity values (Table 8.17). This is a reflection of the TDS content.

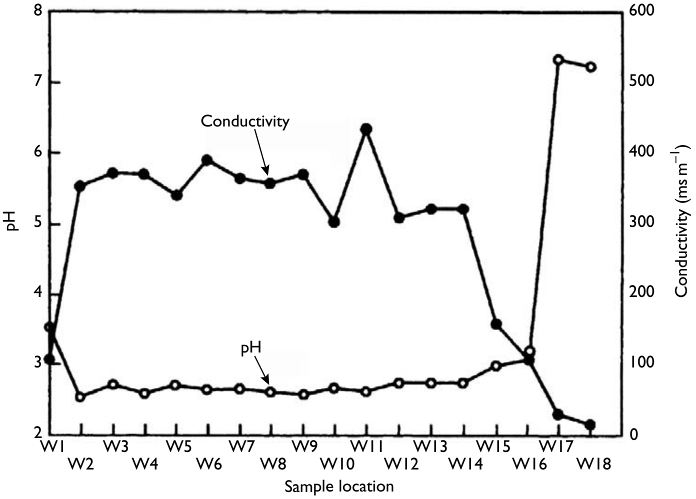

Figure 8.17 Relationship of electrical conductivity and pH value of water samples along the Blesbokspruit.

High concentrations of aluminium are typical of acid mine drainage water and presumably are derived from alumino-silicate minerals such as kaolinite and mica in shales associated with coal seams. The content of aluminium in the Blesbokspruit varied between 80 and 240 mg l^{-1} compared with 0.59–0.8 mg l^{-1} for stream water that was not contaminated. There was a twofold to fourfold decrease in Al concentration in the wetland.

The iron content of the Blesbokspruit was lower than that found in the waters obtained from drillholes, suggesting that much of the dissolved iron has been precipitated as a result of oxidation and hydrolysis. The equilibrium of iron, according to Karathanasis *et al.* (1988), is modified in an acid sulphate system. Although goethite ($HFeO_2$) and amorphous $Fe(OH)_3$ control Fe levels in most natural aquatic systems, the control of dissolved Fe in acid sulphate rich solutions appears to be more consistent with the solubility of the iron sulphate mineral jarosite [$KFe_3(OH)_6(SO_4)_2$].

Sulphate was the dominant anion in the Blesbokspruit, with concentrations up to 1587 mg l^{-1}. The high concentrations of sulphate are characteristic of water contaminated by acid mine drainage in this area. Once the sulphate rich acid mine drainage entered the Blesbokspruit the concentration remained fairly constant until it was diluted somewhat by uncontaminated water from the Prison Stream.

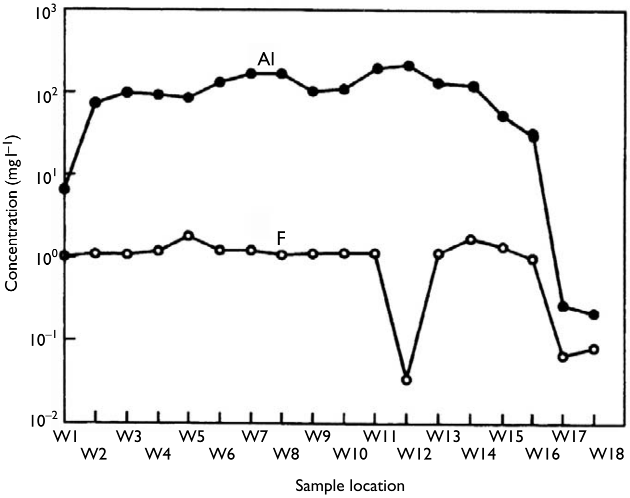

Figure 8.18 Changes in the concentration of fluoride compared with aluminium in water samples along the Blesbokspruit.

The chloride ion concentration up to about 580 mg l^{-1}. It, like sulphate, was derived from the coal and shale in the mine. It would be expected that the sodium and chloride present would have a similar origin. However, the higher values of chloride would suggest that the removal of dissolved sodium was occurring as a result of the precipitation of Na-jarosite. Calcium and magnesium had similar concentrations in the Blesbokspruit. The maximum concentration of manganese was 81 mg l^{-1} and the Blesbokspruit contained significant concentrations of lead and zinc (Table 8.17). As far as fluoride was concerned, its concentration fluctuated according to the changes in aluminium in the water (Fig. 8.18), aluminium-fluoride complexes presumably explain this fluctuation.

The waters of Blesbokspruit contained high concentrations of elements typical of acid mine drainage (Table 8.17). However, the concentration of elements decreased as the Blesbokspruit flowed through the small wetland. The reduction in the concentration of some elements can be attributed to element retention reactions involving adsorption, precipitation and co-precipitation. Dilution of the water exiting the wetland by uncontaminated water from the Prison Stream, further decreased the elemental concentrations of the Blesbokspruit. In particular, the precipitation of jarosite and goethite probably accounted for the removal of iron. However, the solubility of aluminium sulphate minerals under acidic conditions would seem to explain the high concentration of aluminium in the water downstream of the wetland.

If natural water is at saturation equilibrium, then the ion activity product (IAP) should be the same as the solubility product constant (K). The logarithm of this ratio is referred to as the saturation index (SI). A negative saturation index implies that the waters are unsaturated with respect to a particular mineral phase and the mineral should be expected to remain in solution. On the other hand, supersaturated waters have a positive saturation index, the mineral phase being expected to precipitate out of solution. Saturation indices of around zero indicate that the water is in equilibrium with a particular mineral phase. The MINTEQA2 program was used to determine the saturation indices (Allison *et al.*, 1991). Saturation indices of selected minerals were plotted as a function of pH in order to investigate the effects of dissolution or precipitation of minerals on the concentrations of metals in the Blesbokspruit. Water with a low pH is undersaturated with respect to kaolinite [$Al_2O_3 \cdot 2SiO_2 2H_2O$] and saturated with respect to quartz [SiO_2] (Fig. 8.19(a)). High concentrations of silica and aluminium correspond with low pH values where kaolinite is undersaturated. Most water samples with a pH value of less than 3 appear to be supersaturated with respect to jarosite [$KFe_3(OH)_6(SO_4)_2$] and goethite [$HFeO_2$], and undersaturated with respect to ferrihydrite [$Fe_2O_3 \cdot nH_2O$] (Fig. 8.19(b)). Gypsum [$CaSO_4 \cdot nH_2O$], alunite [$KAl_3(OH)_6(SO_4)_2$] and jurbanite [$AlOHSO_4$] may be at equilibrium or slightly undersaturated in water with a low pH (Fig. 8.19(c)). Waters with a pH exceeding 7 are undersaturated with respect to gypsum and jurbanite and supersaturated with respect to kaolinite, jarosite, ferrihydrite, goethite and alunite. The Blesbokspruit was slightly undersaturated with respect to anglesite ($PbSO_4$), indicating that lead remains in solution in these waters. In fact, the low pH of the water would counteract Pb adsorption to hydrous ferric oxides such as goethite and result in Pb concentrations remaining high (Schwertmann and Taylor, 1989).

8.6.3. Effect of acid mine drainage on vegetation and influence of algae

Most plants cannot tolerate low pH water because the high concentration of hydrogen ions causes inactivation of enzyme systems, restricting respiration and root uptake of mineral salts and water (Bradshaw *et al.*, 1982). A denuded area of approximately 3 ha exists in the coal sub-outcrop area between the eastern boundary of the mine and the decantation ponds. In this area, almost all vegetation has been killed and an algal mat has developed over part of the area (Fig. 8.20). Dissolved aluminium ions also are regarded as a major cause of plant toxicity in acid soils. As the total aluminium concentration in the seepage water is over 100 mg l^{-1}, aluminium is also likely to have played a significant role in the destruction of vegetation

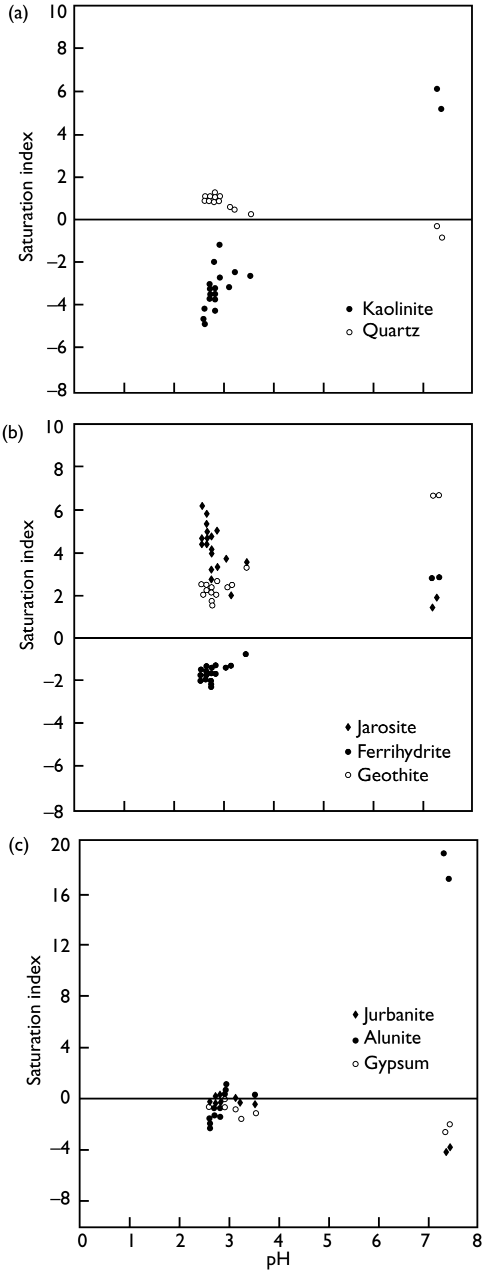

Figure 8.19 Saturation indices in relation to pH for (a) kaolinite and quartz, (b) ferrihydrite, goethite and jarosite, (c) gypsum, alunite and jurbanite in the waters of the Blesbokspruit.

Figure 8.20 Part of seepage area where vegetation has been decimated and an algal mat developed.

in this area. Only species of algae appear to exist in the seepage area, in the pollution control ponds and in the headwaters of the Blesbokspruit.

Many species of algae are known to tolerate acid mine drainage and they appear to play a role in metal attenuation. Intensive algal growth occurs in the seepage area. The green algae belongs to the genus Mongeotia and the red algae to the genus Microspora. There are several processes by which algae can remove metals from acid mine drainage water, including physical trapping of suspended metal particles and subsequent chemical binding (chelation) to the numerous anionic sites within the cell walls of the algae. The polymers that constitute the cell walls are rich in phosphoryl, carboxyl, hydroxyl and aromatic groups with cationic metals. In addition, the presence of micro-organisms that grow epiphytically on green algae filaments can result in mineral deposition on the cell walls of algae and algae can accumulate metals by intracellular uptake (Brady *et al.*, 1994).

High concentrations of Fe_2O_3 were detected by XRF in both types of algae, Mongeotia containing 77% by weight whilst Microspora contained 40% by weight (Table 8.18). This indicates that the algae take part in biomineralization of Fe from the iron rich acid water. The concentration of Al_2O_3 in the algae may be attributed to either the adsorption of aluminium to the precipitate crust or to the accumulation of aluminium due to the increased availability of the metal in low pH water. The amount of CaO and K_2O in Microspora is some six times higher than that of Mongeotia whereas the latter contained much more P_2O_5. There also is a significant difference in the chloride concentration.

Table 8.18 XRF analyses of algae (After Bell *et al.*, 2002)

Major oxides (weight %)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Cl	SO_3	TiO_2	P_2O_5
Mongeotia	3.5	1.9	77	0.68	0.35	0.75	0.51	0.98	9.8	0.02	2.3
Microspora	3.0	1.5	40	3.9	0.44	1.1	3.1	2.9	12	0.14	0.06
Precipitate (1)	2.1	4.3	79	0.06	0.02	0.12	0.06	0.22	9	0.02	1.2

Trace elements ($mg\ kg^{-1}$)	*Zn*	*Cu*	*Ni*	*V*	*Cr*	*Mn*	*Co*	*Mo*	*Zr*	*Y*	*Sr*	*Rb*	*Th*	*Pb*
Mongeotia	91	52	9.0	797	81	221	13	0.4	7.1	17	4.9	14	2.0	4.3
Microspora	230	14	63	79	337	789	33	0.5	17.1	22	33	165	2.3	6.5
Precipitate (1)	17	9.4	<0.8	800	69	37	6.4	0.3	7	4.5	1.4	3.5	3.7	19

The contents of zinc, copper, nickel, manganese and lead in both types of algae exceeded those found in the acid drainage water seeping from the mine. Hence, both algae would appear to have the ability to abstract and concentrate these trace metals. Furthermore, these algae, especially Mongeotia, presumably play an important role in the formation of precipitate material. Iron rich encrustations occurred on dead algae, notably ferrihydrite, and can result in the co-precipitation of heavy metals.

High concentrations of zinc were detected in the algae, with Microspora containing the higher concentration (Table 8.18). Zinc can be adsorbed to negatively charged cell walls of algae or may be co-precipitated with iron minerals (Kiekens, 1995). An antagonistic zinc–copper relationship would appear to occur in the case of Microspora where the ratio of the two metals is 16.4, which compares with a Zn:Cu ratio of 1.7 in Mongeotia. This suggests that the presence of zinc inhibits the uptake of copper in Microspora, which may indicate that the latter algae have the same carrier sites in adsorption mechanisms for both metals.

Microspora contained significantly higher concentrations of chromium than Mongeotia. On the other hand, Mongeotia possessed more or less 10 times a much vanadium as did Microspora (Table 8.18). In fact, Mongeotia contained similar concentrations to that of precipitate material from near the seepage point of the acid mine drainage. Arnon and Wessels (1953) noted that high values of vanadium in acidic conditions were attributable to it being an essential micro-nutrient for certain green algae and that the presence of aluminium and ferric ions caused precipitation of vanadium. Subsequently, Edwards *et al.* (1995) mentioned that V^{3+} has a similar ionic radius to that of Fe^{3+} and that it therefore may replace Fe^{3+} in iron minerals, resulting in vanadium enrichment.

According to Heier and Billings (1970), rubidium is easily taken up by algae and may substitute for potassium sites. Mongeotia had a K/Rb ratio of 320 and that of Microspora was 155. However, potassium was present in the cytoplasm of the latter. These differences in the ratios could indicate different metal accumulation mechanisms and/or different rates of metal accumulation between the two types of algae.

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