3.1 An introduction to acid mine drainage

Iron pyrite, FeS2, also known as 'fool's gold', is the most important source of nearly all water pollution originating from mines and their residue deposits. When pyrite is exposed to air and water, it oxidises to form sulphuric acid and iron oxides and hydroxides ('yellow boy'), which causes the pH of the resultant leachate to drop to about 4. This oxidation reaction is accelerated and extended by bacteria. The most important of these bacteria is *Thiobacillus ferrooxidans*. This causes the pH of the solution to drop to as low as 1.5. The acid that is produced reacts with bases in the country rock or residue deposit to form salts and to mobilise heavy metals that may be contained in the rock or residue. During this reaction, the acidity is often neutralised. The resultant drainage contains elevated levels of salts (primarily calcium and magnesium sulphates) and metals (mainly iron). According to Sullivan and Yelton (1988) the greatest contribution to acid mine drainage (AMD) can be ascribed to residue deposits and spoil heaps. The longer water is in contact with the pyrite, the more chance the oxidation reaction has of proceeding and the more chance bacteria have of speeding it up and producing more acid. Coal discard (with exposed pyrite due to processing the coal) and old workings (due to long time exposure) produce the highest concentration of AMD (Fuggle and Rabie, 1992).

Depending on the bulk composition, an acid-generating mine can become a 'perpetual pollution machine'. In the USA, AMD from abandoned mines has polluted 180 000 acres of reservoirs and lakes and 12 000 miles of streams and rivers. It is estimated that cleaning up these waterways will cost US taxpayers between $32 billion and $72 billion. Not only is AMD treatment and collection
very costly to the environment, it is a big bill for industry. Site rehabilitation costs in the USA can be as high as $410 000 per hectare. The US Bureau of Mines estimates that the US industry spends over $1 million each day to treat acidic mine water. Once it starts, AMD can effectively sterilise an entire water system for generations to come – turning it into a biological wasteland and a huge economic burden (Salomons, 1995).

3.2 Sources of acid mine drainage

The sources of acid drainage from mining operations include:

- Drainage from underground workings
- Surface runoff from open pit mine faces and pit workings
- Waste rock dumps from metal mines and spoil piles from coal mines
- Tailings deposits
- Ore stockpiles and spent ore piles from heap-leach operations.

The acid drainage from underground workings generally occurs as point discharges of substantial flows of low pH water. Many of the earliest sources were drainage tunnels or mine adits.

The effects and consequences of acid drainage from open pit mines have become a concern far more recently. The large areas of exposed rock in open pits can result in large volumes of acid drainage. Long-term slope deterioration can result in a continual exposure of fresh rock to the natural elements and hence acid drainage generation.

Waste rock is generated by the excavation and construction operations undertaken to gain access to the ore being mined. These wastes are subsequently exposed to precipitation, runoff and possibly seepage. Rock wastes that contain sulphides are a large source of acid drainage. The quantities
of rock waste from earlier underground mining operations were proportionately less than the more recent large open pit mining operations. Thus the potential for acid drainage generation is on the increase.

Spoil piles are wastes generated by coal strip mining in order to gain access to the coal deposit. Sulphur exists in three chemical forms in coal-bearing rocks: sulphides, sulphate and organic sulphur. Pyrite (FeS₂) is the most predominant acid-producing sulphur mineral present within coal and the overburden strata. Due to the extreme variability in the geochemical properties of overburden strata it is very difficult to predict the acid-generating potential of the eventual spoil piles.

The potential for acid generation in tailings has long been recognised. The concern is generally that acid drainage may develop after the mine has been abandoned, when the facilities are no longer in use or maintained.

The ability of a particular rock sample to generate net acidity is a function of the relative content of acid-generating and acid-consuming minerals. It is important to consider the scale of examination when investigating acid drainage. A rock, which generates pH-neutral conditions in water flowing over it, may have acid generation occurring in microenvironments around sulphide grains. The resulting acidic water may be neutralised by the remainder of the sample as it leaves that particular microenvironment. The time interval between initial disturbance of the rock and the peak rate of acid generation may range from days to years, depending on a number of environmental factors and the neutralisation potential of the rock. As a result, acid generation is not a simple process; rather, it is a complex set of chemical reactions changing through time (Pulles et al, 1996).

The problem of flooding of abandoned workings, either naturally or artificially, is that it causes widespread AMD. Water coming into contact with remnant coal pillars or an underground surface littered with coal from a collapsed roof or pillars
may become rapidly acidified. This is the result of the presence of pyrite in the coal, which is readily oxidised in the presence of air. In addition, this acidification process may be accelerated by fluctuations in water level or heat from burning coal pillars in the vicinity. Where this water decants from the mine it is generally extremely acidic and rich in sulphates and metals. This water causes acidification and/or sterilisation of soil with which it interacts. Vegetation is also ultimately killed. Such acid mine water is characterised by its orange brown colour. Associated precipitates include 'mela
anterite' (a turquoise-coloured iron sulphate) and 'yellow boy' (a yellow ferric hydroxide).

Although discard dumps have been identified as a source of acid mine drainage, not all dumps produce acid water. This is probably related to the type of pyrite present i.e. fine, porous and granular pyrite vs. pyrite that is mostly compact and crystalline. Burnt dumps are also more likely to create acid water than those that have not burned owing to the presence of water soluble sulphates that are more amenable to leaching and oxidation (Viljoen, 1991).

3.3 Chemical and biological reactions related to acid generation

The primary ingredients for acid generation are:

- Sulphide minerals
- Water, or a humid atmosphere
- An oxidant, particularly oxygen from the atmosphere or from chemical sources

The first important reaction is the oxidation of the sulphide mineral, producing dissolved iron, sulphate and protons:

\[ \text{FeS}_2 + \frac{7}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \]
The dissolved products represent an increase in the total dissolved solids (TDS) and acidity of the water. If the surrounding environment is sufficiently oxidising, much of the ferrous iron will oxidise to ferric iron:

$$\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \leftrightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O}$$

At pH values of 2.3 to 3.5, the ferric iron will precipitate as iron hydroxide, leaving little ferric iron in solution, while lowering pH at the same time:

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3 \text{ (solid)} + 3\text{H}^+$$

Any Fe$^{3+}$ that does not precipitate from solution may be used to oxidise additional pyrite:

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+$$

Acid generation may be represented by a combination of the above reactions:

$$\text{FeS}_2 + 15/4 \text{O}_2 + 7/2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+$$

The above reactions assume that the oxidised mineral is pyrite and that the oxidant is oxygen. It is important to note that other sulphide minerals have other ratios of metal:sulphur and other dissolved metals will be produced.

Following the oxidation of a sulphide mineral the resulting acid products may be flushed away from the sulphide mineral and eventually encounter an acid-consuming mineral. The most common acid-consuming mineral is calcite, which consumes acidity through the following reaction:

$$\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{2+} + \text{HCO}_3^-$$

and

$$\text{CaCO}_3 + 2\text{H}^+ \rightarrow \text{Ca}^{2+} + \text{H}_2\text{CO}_3^0$$

(Pulles et al, 1996)

Ca$^{2+}$ will combine with SO$_4^{2-}$ to form CaSO$_4$, which is sparingly soluble and the carbonic acid will decompose by liberating carbon dioxide.
3.4 Rate of acid generation

The primary factors, which determine the rate of acid generation, are the following:

- A low pH (although the initial oxidation can take place under neutral conditions)
- Temperature
- Oxygen content of the gas phase
- Oxygen concentration in the water phase
- Degree of saturation with water
- Chemical activity of Fe$^{3+}$
- Surface area of exposed metal sulphide
- Chemical activation energy required to initiate acid generation
- Presence of certain bacteria that promote sulphur and/or iron oxidation e.g. *Thiobacillus ferrooxidans*

In certain instances where bacterial acceleration is significant, there are additional factors, which determine bacterial activity and the associated acid generation:

- Biological activation energy
- Population density of bacteria
- Rate of population growth, which depends on temperature, pH, the presence of nutrients e.g. nitrate concentration, potassium concentration, ammonia concentration, phosphorus concentration, carbon dioxide content and the concentrations of any bacterial inhibitors e.g. certain trace elements and certain fungi that consume bacterial nutrients.
3.5 Case studies

Gélinas et al (1992) conducted a study to monitor AMD in a waste rock dump. The findings of this study were as follows:

- There is a good relationship between mineralogical and textural properties of the different rock types and their relative AMD generation potential.
- Air convection is an important mechanism for oxygen supply.
- Mineralogical and chemical data should be used to describe the mechanisms of chemical leachate transformation within and outside of the dump.

According to Kwong (1992), natural attenuation in a small pond receiving acidic drainage near the Mount Washington Mine, Vancouver Island, is effected by dilution and bacterial sulphate reduction. In this case, reclamation activities have focussed on reducing the supply of oxygen and water to the acid-generating waste-rock dump. The natural acid and metal attenuation capacity of a series of wetlands downstream from the site should perhaps be developed and utilised.

Phinney (1992), argues that the present state of knowledge of the acid generation process allows proposed mine developments to be evaluated and planned with confidence. However, the reclamation of historical sites will remain an economically and technically difficult task.

3.6 Mine planning and acid generation

Considerations related to AMD arise during the later phases of exploration. Cores can be carefully examined by a mineralogist and samples taken for acid-base accounting. Samples of both sulphide- and non-sulphide- bearing rocks should be analysed. Elevated levels of sulphate in drill hole water, springs and seepages are an excellent indicator of acid-generating activity. The acid-
generating history of the geological region is perhaps the most important indicator of potential for acid mine drainage (Prévost, 1996).

During the bulk sampling / test mining phase, acid-generating characteristics of the deposit may be confirmed. However, as acid generation develops over an extended time span, there are a number of instances where acid generation situations have not been predicted on the basis of bulk sampling (Robertson and Ferguson, 1995).

During the operation phase, if there is any potential for acid generation, the acid generation must be assumed to occur and the mine should be developed accordingly. The control of acid generation and an effective reclamation plan can be assured if the following guidelines are applied:

- The treatment system for acidic waters must be capable of being expanded in phases to meet increased chemical requirements and sludge generation.
- Waste rock removed during mining must be carefully separated and stored in accordance with its potential for acid generation.
- The reclamation method must be designed to minimise the rate at which atmospheric oxygen can be transported to the reactive sulphides. (Robertson and Ferguson, 1995).