

CHAPTER 1

INTRODUCTION

South Africa is particularly rich in mineral resources and has been one of the leading raw material exporters in the world for more than a century. The mineral industry has made an important contribution to the national economy, has achieved a high degree of technical expertise and has the ability to mobilize capital for new development.

The main raw minerals are gold, coal, diamonds, platinum, chromium, vanadium, manganese, uranium and iron ore. Coal is second only to gold in the economy of South Africa in total sales value and foreign exchange earnings. Coal continues to play a major role in the production of essential products for development such as electricity, liquid fuels and chemicals (South Africa Department of Minerals, 1998).

The requirements for effective control of water in the mining industry are increasing as mines become deeper and larger and as the environmental controls became more stringent. Mining is implicated as a contributor to water pollution, because most of the geological formations, which are mined, contain pyrites. Mines that contain ore rich in pyrites often produce poor quality water with a low pH and a variety of metal ions. Pyrite is formed from the reaction of sulphur with ferrous sulphide (FeS) to form a highly insoluble crystalline structure, which is very common in bituminous coals and many ore bodies (Brock and Madigan, 1991). Pyrite, when exposed to air and water, produces water high in iron and sulphate concentrations, generally referred to as Acid Mine Drainage (AMD), shown in Plate 1.

Thomas (1970) described AMD as one of South Africa's major pollution problems. It is primarily associated with the mining of coal, although the mining of ores containing other minerals can also lead to the formation of acid drainage (Walsh, 1978). Sulphuric acid is the major pollutant, resulting in mine water with a pH as low as 1.0 in certain instances. The release of acid drainage into water systems increases the acidity, the hardness, the metal ion and suspended solids concentrations.

Lundgren *et al.* (1972) estimated that 3.6×10^9 kg of acid is produced each year in South Africa. It was also noted that 90% of the produced pollutants are released into water systems. In addition, concentrations as high as 2.3×10^6 kg acid per day were observed in certain mining effluents (Walsh, 1978).



Plate 1: Acid Mine Drainage

AMD is a serious problem since mixing of acidic mine water with natural waters in rivers and lakes can cause severe degradation in the quality of the natural water bodies. This can be ascribed to the fact that both the acid and the dissolved metals are toxic to aquatic life. Such polluted waters are unsuitable for human consumption and industrial use. Collecting and treating mine water to a quality where it can be re-used without restrictions can prevent this source of pollution. Traditionally, iron (II) rich acid mine water was treated with lime using the High Density Sludge (HDS) process. Iron (II) is oxidised at a fast rate through aeration when the pH is raised with lime to pH 7.2 and higher. Recently, lime was replaced with limestone, which has a number of advantages, as:

1. limestone is more readily available,
2. the process control is simplified as no pH-control is required since limestone dissolution essentially occurs at pH-values below 7,
3. limestone is non-hazardous and easy to store.

The raw material can be stockpiled in the open air because CaCO_3 is not readily soluble in neutral water. The pH of iron (II)-rich water can only be raised to pH 6 using limestone. During treatment of acid mine water, the iron (II) component needs to be oxidised to iron (III), in order to prevent downstream oxidation of iron (II), which will result in re-acidification of the treated water when exposed to the atmosphere. The following processes were developed to achieve iron (II) oxidation without raising the pH to 7.2.

- **The integrated iron (II) oxidation and limestone neutralization**

In this process, powdered calcium carbonate together with aeration is used to oxidise iron (II) to iron (III), to neutralize acid water and to allow for gypsum crystallization in one reactor (Maree, *et al.*, 1999). In this process the milled limestone (particle size less than 0.1 mm) precipitated to calcium carbonate (e.g. a by product produced by the paper industry).

- **The fluidized-bed limestone neutralization**

In this process crushed limestone (particle size less than 4 mm) is used for neutralization of acid water in a fluidised-bed reactor after iron (II) has been oxidised to iron (III) at low pH. This oxidation process is needed as limestone particles are scaled with a layer of ferric hydroxide and gypsum when iron (II) rich water is fed directly to the limestone neutralization plant. Complete neutralisation of discard leachate containing, 10 g/L CaCO_3 and 4 g/L iron (II) can be achieved in a limestone neutralisation fluidised-bed reactor, provided that the iron (II) is oxidised beforehand (Maree, *et al.*, 1998a). This can be achieved through biological iron (II) oxidation at low pH. It was shown that the iron (II) oxidation rate is related to the surface area of

the support medium: when plastic medium (surface area 200 m²/m³) was used as support medium a reaction time of 18 h is required to oxidise 4 g/l iron (II) to iron (III) (Maree, *et al.*, 1998b).

1.1 APPLICATIONS FOR IRON (II) OXIDATION

Iron plays an important role in environmental and industrial processes as indicated below:

- Pyrite oxidation in ore. The pyrite oxidation reaction occurs underground during or after mining activities and on the surface of mine dumps that contain pyrite. Pyrite oxidation can occur through direct bacterial attack or through an indirect chemical bacterial mechanism whereby ferric iron oxidizes the pyrite (Silverman, 1967) (Reaction 1):



- Bacterial leaching of gold and other minerals from pyrites rich ore.
- Desulphurization of coal. The microbial oxidation of pyrite present in coal can be represented by the following reaction



The ferric ions can oxidise pyrite to ferrous ions and sulphate ions. The ferrous ions formed can be oxidized to ferric ions by the by *T. ferrooxidans* bacteria, and these ferric ions react with more pyrite. Thus there is a progressive, rapidly increasing rate at which pyrite is oxidized, called the *propagation cycle*.

- Metal bioleaching (Nemati *et al.*, 1998). Microbial leaching is generally applicable to both metal sulphides and uranium ores in a slightly acidic

aqueous sulphate solution. The dissolution of metal sulphides is achieved by a series of reactions involving both direct and indirect mechanisms. An important reaction that describes the dissolution of metal sulphide (MeS) ore in an acidic, ferric sulphate medium is:



- Sulphur production from H₂S. H₂S gas is produced during anaerobic treatment of sulphate-rich water, during oil refinery and by the coal-to-fuel-industry. Sulphur can be produced from H₂S by placing H₂S gas in contact with an iron (III) solution (Reaction 4). The produced iron (II) can be back oxidised to iron (III) at low pH (Reaction 5)



- Desulphurization of sour gasses and flue gasses (Nemati *et al.*, 1998). Hydrogen sulphide is a highly undesirable component of natural gas and biogas. Removal of H₂S from sour gas is required for reasons of health, safety and corrosion during transmission and distribution, and to prevent sulphur dioxide pollution upon combustion of the gasses. At present, well-established physicochemical techniques for the removal of H₂S dominate the market. These include treatment with alkanolamine and the Claus processes. The continuing search for more economical processes has led to investigation into microbiological solutions for purifying H₂S and gasses containing SO₂ as well as coal and petroleum. Microbiological processes operate around ambient temperature and atmospheric pressure, thus eliminating the need for heat and pressurization power, cutting the energy cost to a minimum. The relatively high chemical, catalyst and disposal cost of conventional processes are important drawbacks, which may be overcome partly in a biological process as described above.