

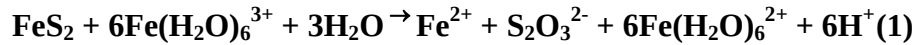
CHAPTER 4 - ACID MINE DRAINAGE (AMD)

4.1 AMD Chemistry

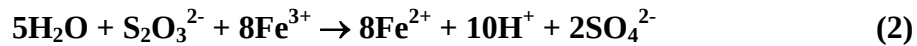
Iron sulphides in mine tailings (waste products generated during mining and milling operations), usually pyrite, oxidise to form soluble hydrous iron sulphates. Water dissolves these sulphates to form AMD.

Oxidation of pyrite produces acidic drainages rich with high concentrations of Fe, Mn, Al, SO₄, and heavy metals such as Pb, Hg, and Cd. Pyrite oxidation occurs when the mineral is exposed to air and water. This process involves chemical, biological and electrochemical reactions and varies with environmental conditions. The rate of oxidation is determined by factors such as pH, morphology of pyrite, presence or absence of bacteria and clay minerals as well as hydrological factors (Geller *et al*, 1998).

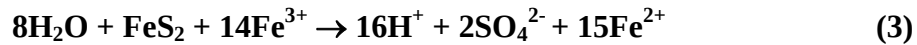
Pyrite oxidation is a two-step process – formation of a pyrite/surface free radicle and transfer of oxygen atom from the pyrite/surface-adsorbed water to the sulphur on the pyrite surface (Geller *et al*, 1998).



The transfer of six electrons from pyretic sulphur to six Fe³⁺ produces one S₂O₃²⁻ and six H⁺. In the presence of excess Fe³⁺, S₂O₃²⁻ is changed to SO₄ through the transfer of eight more electrons as follows:



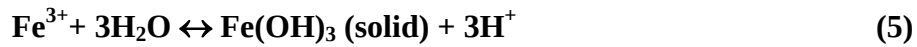
Equation (1) and (2) give:



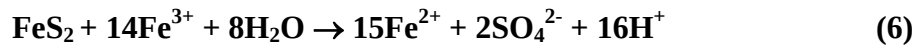
The dissolved Fe^{2+} , SO_4^{2-} , and H^+ represent an increase in the total dissolved solids (TDS) and acidity of the water and unless neutralized the increasing acidity is often associated with a decrease in pH. If the surrounding environment is sufficiently oxidizing much of the ferrous iron will oxidize to Fe^{3+} (Audouin, 1997):



At pH above 2.3 – 3.5 the Fe^{3+} iron will precipitate as $\text{Fe}(\text{OH})_3$, leaving little Fe^{3+} in solution while lowering pH at the same time:



Any Fe^{3+} that does not precipitate from solution through the above reaction may be used to oxidize additional pyrite:



The pyrite oxidation process can be bacterially mediated, primarily by *Thiobacillus ferrooxidans*, and both temperature and moisture affect the rate of the reaction (SRK, 1989). At pH 4.5 *T. ferrooxidans* increases initial acidification; below pH 4.5, it allows acidification to continue by oxidising Fe^{2+} . *Thiobacillus ferrooxidans* is most active in waters with pH around 3.2. Below pH of approximately 2.5, the activity of Fe^{3+} is significant and results in steady state cycling between oxidation of pyrite by Fe^{3+} and bacterial oxidation of Fe^{2+} (Kleinmann *et al*, 1981). As soon as acidity is initiated acid production becomes increasingly rapid (Minerals Council of Australia, 1997). If conditions are not favourable, the bacterial influence on acid generation will be minimal. Biological oxidation of pyrite depends on, among other variables, the particular variant of *T. ferrooxidans*.

Oxidation of sulphide minerals in the walls of the mine workings during operations may result in mine water with a depressed pH. Upon closure, flooding of the abandoned

workings below the water table may result in dissolution of minerals from the walls. Additionally, further oxidation of sulphide minerals in the abandoned workings above the water table may occur. The principal acid cations are hydrogen, iron and aluminium species. There are also large variations in the state in which iron is present and this is important since on neutralisation all of Fe^{3+} is precipitated below pH 6, whereas precipitation of Fe^{2+} was found to be complete at about pH 7.8 (Thompson, 1980).

Most of the acid waters from gold mine dumps have a light brown to dark brown colour and the iron is almost entirely in the Fe^{3+} state due to contact with atmospheric oxygen. It is generally accepted that the formation of acid sulphate waters from pyrite is fundamentally a process involving oxidation. It is thus logical to expect that iron will be predominantly in the Fe^{3+} state.

Metal solubility and contaminant migration are controlled by a number of physical, chemical and biological properties of mine waste facilities. The mobilisation of metals is principally controlled by chemical factors while the processes that occur along the migration route are governed by both physical and chemical factors. The important physical factors include climatic conditions, waste permeability and porosity, availability of pore water, pore water pressure and the processes or mechanisms of movement (Audouin, 1997). Generally, the physical properties of the underlying subsurface strata tend to contrast quite significantly with the overlying waste material, resulting in a number of contaminant fronts which all migrate at different rates. The primary chemical factors which determine the rate of acid generation are pH, temperature, availability of oxygen in the gaseous phase, availability of oxygen in the water phase, chemical activity of Fe^{3+} , surface area of exposed metal sulphide, and chemical activation energy required to initiate acid generation. The low pH of AMD mobilises the heavy metals occurring naturally in water, and it is these mobilised substances which are most harmful to the environment (Miller, 1994).

As the water moves through the acidic material, oxidation of reactive sulphide occurs, generating acidity which can be neutralised initially by alkalinity in the groundwater. If

more acid is generated than the initial alkalinity of the water, the alkalinity will be consumed and acid water will result. If sufficient oxygen is present, the amount of acidity generated is determined by the amount of reactive sulphides in the material. The Minerals Council of Australia (1997) reports that in the absence of mining, acid waters are uncommon because dissolved oxygen in the groundwater is insufficient to produce acidity greater than the alkalinity of the groundwater. During mining, gaseous oxygen is introduced as the rock is broken up, and water movement through the system is accelerated.

The large scale exposure of pyrite occurring in the mineral deposits of South African gold mines have consequences for both surface and groundwater quality. The ferrous iron is oxidised to the Fe^{3+} state. The Fe^{3+} hydrolyses in water to form Fe^{3+} hydroxide. Fe^{3+} hydroxide is a yellowish-orange precipitate that turns the acidic runoff in the streams an orange or red colour and covers the streambed with a slimy coating (Colorado School of Mines, 1999). Mine effluents can therefore be very acidic and sulphate-rich. Various chemical and biological reactions at the source of acid generation and along the drainage path from the source to the environment govern the quality and rate of release of AMD.

4.2 Environmental Impacts of AMD

The environmental impact of AMD is a function of time and is dependent on drainage quality, baseline environmental conditions and the natural dilution and neutralising capacities of the environment. The dilution capacity of the environment depends on the magnitude of flow of the receiving water in relation to the contaminated drainage. Stream flows are generally a function of precipitation in the catchment area (SRK, 1989).

Rainfall seeping through the mine or mine waste may carry the acid to nearby streams, destroying the aquatic life and contaminating surface water supplies. It may also infiltrate the ground and contaminate groundwater. AMD is characterised by high concentrations of mineral acids, ions of iron, sulphate and the precipitation of a smothering blanket of iron salts on the streambed. It can have deleterious effects on

aquatic life in streams and can preclude water use by other water users (Supervising Scientist Group, 1997). Drainage with a pH below 5 often gives rise to odour problems by releasing hydrogen sulphide from the river mud. The process of acid generation renders the pore-water capable of mobilising heavy metals and other soluble constituents contained in the waste. It is the high metal loadings in the water emerging from the waste which is most harmful to the environment (Audouin, 1997). Heavy metals may be lethal even at low concentrations if ingested regularly. The more evolved the organism, the greater its susceptibility to heavy metal pollution (Thompson, 1980).

4.3 Tailings Dams as a Potential Source of AMD

Tailings vary considerably in their physical, chemical, and mineralogical characteristics. Particular characteristics can affect tailings behaviour in a storage area and ultimately affect drainage water from the latter, seeping into either surface water or groundwater systems.

Physical properties of the tailings are important in determining how the material will behave in the storage area, its resistance to wind and water erosion, and the extent to which the tailings themselves can be used for construction. The US Environmental Protection Agency (1995) states that mineral content of the tailings will determine the specific gravity of the tailings particles which will in turn have an impact on particle segregation and consolidation. Oxidised tailings can also have poor settling and consolidation characteristics. Chemical properties of tailings need to be determined in order to define the characteristics of the waste and the nature of potential contaminants. This is needed to assess the potential for drainage waters to affect the beneficial uses of ground and surface waters, and to assess limits to revegetation of the tailings storage after closure (Environment Protection Agency, 1995).

Cyanide compounds have many useful purposes. Due to its toxic nature, it has been used as a fumigant and poison. Cyanide is also used in the manufacture of nylon, plastic, glass, perfume, soaps, fertilizers, paints, animal food supplements, pharmaceuticals, and

electroplating. However, its most common use is in the mining industry (Laberge Environmental Services, 2001). Cyanide forms stable compounds with several metals hence its use in the extraction of gold, silver, copper, zinc and molybdenum from ores. It plays an important role in the mining industry because it allows the recovery of microscopic metals from low grade ore. In gold mining industry it is used to dissolve gold in ore.

Cyanide is a fast acting poison capable of killing a person within minutes if they are exposed to a lethal dose without prompt first aid treatment (Laberge Environmental Services, 2001). Poisoning occurs through inhalation, skin absorption or swallowing. In humans and mammals it binds to key iron-containing enzymes required for cells to utilize oxygen. The tissues are then unable to take up oxygen from the blood, this results in suffocation ((Laberge Environmental Services, 2001).

Cyanide is seldom persistent in surface water and soil due to sedimentation, microbial metabolism and loss from volatilization, but may persist in the groundwater for extended periods of time (Laberge Environmental Services, 2001). Aquatic organisms are very sensitive to cyanide. Fish is the most sensitive aquatic organism followed by invertebrates. Elevated concentrations inhibit respiration and can lead to death. Migratory birds have suffered cyanide poisoning associated with tailings ponds. Small mammals, such as rodents, foxes, rabbits, and bats have been found near cyanide containing tailings ponds they used as a source of drinking water (Laberge Environmental Services, 2001).

Most of the gold is contained in sulphide minerals such as pyrite (FeS_2) or arsenopyrite (FeAsS). Pyrite is therefore one of the major by-products of gold processing. The concentration of pyrite in the dumps is high. When initially deposited, the tailings are alkaline (pH greater than 10), but it drops to between 2 and 4 as the pyrite becomes oxidised (Bradshaw, 1980). Acid generation and drainage affect both surface water and groundwater. The sources of surface water contamination are leachate from mine openings, seepage and discharges from waste rock, tailings, ground water seepage, and surface water runoff from waste rock and tailings piles. Mined materials such as waste

rock or tailings used for construction or other purposes (for example, road beds, rock drains, fill material) can also develop acid mine drainage. The receptors of contaminated surface water include birds, fish, and other aquatic organisms. Humans can also be affected by direct ingestion of contaminated surface water or direct contact through outdoor activities such as swimming (Environmental Protection Agency, accessed on 28th August, 2005).

Potential for seepage from the tailings into groundwater is a major issue with many tailings disposal operations. It is often necessary to carry out extensive studies of the hydrogeological and geochemical regimes before selecting a site and designing a storage area in order to predict and minimise its impact, and to develop a monitoring programme to assess performance during and after the operating life of the mine. Synthetically lined dams always leak even if the dams do not fail (Moran, 2001).

Tailings have a particle size distribution that falls in the fine sand and coarse to medium silt size ranges. They tend to retain water by capillarity and, at depths of more than a metre or so below the surface, remain almost saturated for long periods (Blight & du Preez, 1997). Water erosion occurs on the slopes of the tailings dams. It is possible that some acid leachate escapes from the hydraulic fill tailings impoundments as a result of the formation of erosion gulleys. The slopes of gold tailings impoundments are often hard and crusted with iron hydroxides resulting from pyrite oxidation.

Seepage can occur through the walls and through the floor of a tailings storage facility. Infiltration through the floor of a tailings storage facility usually decreases with time as tailings are deposited in successive layers and form a retardant to vertical flow. In the long-term the majority of the tailings water seepage occurs through the dam wall and via infiltration through the ground surface on which the wall is built (Minerals Council of Australia, 1997).

The rate of vertical migration of water through the tailings and into the underlying groundwater is determined principally by the vertical permeability of the tailings and the

permeability of the underlying foundation materials (SRK, 1989). The severity of the problem is dependant on factors such as geology and hydrogeology of the site, ore mineralogy and chemistry, metallurgical processes, waste disposal method, climate and microbiology (Geldenhuis & Harpley, 1989). The effect of seepage from a tailings dam on the local groundwater flow will depend on the relative quantity of water flow from the tailings to the total flow in the underlying groundwater system. The low permeability of many tailings deposits and the flooding that occurs in both operating and abandoned tailings impoundments limit the rate of AMD generation and release. Thus the full potential effect of the very large deposits of more recent acid generating tailings may not yet have developed. Many such these facilities are still under active use and maintenance and any potential impacts of AMD are controlled. The concern is often that AMD may occur after abandonment. Drainage of waters placed with the tailings will occur for some period after the tailings are no longer being deposited. Also, seepage derived from precipitation on the surface will continue indefinitely. Covers (in the form of 60 cm of low permeability material such as clay and the synthetic membrane) are often placed on inactive tailings to minimise long term seepage from precipitation. These layers may be of limited benefit in limiting inflow to the tailings, particularly in arid and semi-arid climates. The low permeability layer creates an increase in effective storage and therefore an increase in evapotranspiration. These covers can limit acid production in tailings containing pyrite and little or no carbonates (McWhorter, D.B. 1989).