Waste Production and Utilization in the Metal Extraction Industry

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Mining and Beneficiation Waste Production and Utilization

3.1 Introduction

Mining operations consist of excavation (extraction in pits and underground mine workings) to remove ore; beneficiation units, such as mills and processing facilities for upgrading or concentrating the ore; refining facilities for further purification of the metal and manufacturing of finished products. However, mining operations generate extremely large quantities of wastes some of which is shown in Table 2.1 of Chapter 2. This chapter deals with mining waste resulting from extraction and beneficiation processes. The chapter also covers acid mine drainage, a phenomenon which occurs from the dissolution and mobilization of metals from waste rock and tailings into surface water and groundwater. Other types of waste such as that emanating from the refining and manufacturing processes are discussed in Chapters 4 through 8.

3.2 Mine Overburden and Waste Rock

Mining is largely divided into open-pit (surface) and underground mining. Open-pit is the most common technique in modern metal ore extraction. In open-pit metal extraction, the soil and vegetation are first removed from the mine site. Bulk ore is then blasted so as to loosen the bedrock. In underground mining, shafts are sunk into the ore deposits, passages are opened off the shaft and the ore is then broken up and brought to the surface.

Overburden and waste rock are the non-liquid wastes generated in the largest volumes by extraction activities (EPA, 1994). Overburden includes the soil and rock that is removed to gain access to the ore deposits in open pit mines (Fraser Institute, 2012). On the other hand, waste rock consists of rock that is mined, but contains minerals in concentrations considered too low to be extracted at a profit and is, therefore, removed ahead of processing (IIED, 2002).

Overburden and waste rocks have limited potential for reuse because of their high impurity content or remote location and are thus disposed of. However, some of it may be favourably located and of interest because of contained metals and minerals or inherent physical and chemical characteristics. Therefore, the utilization of overburden and waste rocks is an attractive alternative to disposal because disposal costs and potential pollution problems are reduced or even eliminated and resources are conserved. Waste rock and/or overburden could be used as landfill; in roadbed and dam construction; as railroad ballast; as an aggregate in concrete and asphalt mixes, and, for the finer sizes of waste, as
Waste Production and Utilization in the Metal Extraction Industry

construction sand; as an additive to concrete and asphalt mixes; in brick and block manufacture; in the manufacture of thermal insulation; for the recovery of valuable metals or minerals and as mineral fillers.

3.3 Mineral Beneficiation Waste

Mineral beneficiation is the first step after mining in the minerals and metal value chain. Mineral beneficiation consists of the manipulation of the physical properties of the ore to (1) produce desired particle sizes for a final product (2) liberate and concentrate the value mineral from the gangue material. The process consists of a number of steps, the first being comminution which involves size reduction of minerals by crushing and grinding. This process is normally followed by the concentration or enrichment step which is achieved by the separation of valuable minerals from the gangue using various techniques that are based on the physical and chemical properties of the minerals. Some of the techniques applied in the minerals concentration/enrichment step includes sorting which makes use of optical or other properties of the mineral or gangue. This could be done by hand or machines. Separation using density properties is also common; the methods include gravity concentrators and dense media separators. Separation can also be achieved using surface properties of the minerals, for example froth flotation. Magnetic and electrical conductivity properties can also be exploited to effect separation.

The initial comminution process is usually dry during crushing and is mostly wet during grinding. However, for most of the enrichment processes, the ore is normally handled in slurry form making dewatering one of the essential steps. The water removal step is undertaken using specific unit operations like thickening and filtration which prepare the ore material for downstream processing. Once the ore is concentrated, it can be processed further using chemical methods, which can include hydrometallurgy or pyrometallurgy to extract the valuable metals.

Figure 3.1 gives a general overview of the process flowsheet options from run-of-mine (ROM) ore to concentrate.

Some of the processes highlighted in Figure 3.1 are described briefly in the following section.

3.3.1 Mineral Beneficiation Methods and Techniques

This section gives a brief description of some of the typical mineral beneficiation methods and techniques. As has just been discussed, mineral beneficiation techniques involve both size reduction and concentration. Size reduction usually occurs through comminution processes that involve crushing and grinding. There are, however, a number of techniques and methods used in the enrichment or concentration process. The choice of the method applied is largely dependent on the chemical and physical characteristics of the material being treated.

3.3.1.1 Comminution

Comminution aims to reduce the size of solid particles so as to liberate the valuable minerals from the gangue and to increase the surface area for chemical reaction in subsequent processes (Wills and Napier-Munn, 2006). The process involves the use of crushers and
grinding mills. Crushing is normally the first mechanical size reduction stage following ore extraction and can process feed particle sizes as large as 1.5 m. Crushing can occur in several stages, that is, primary, secondary and tertiary crushing. Primary crushing is normally done underground to reduce the particle size of the ROM to a size that is suitable for transportation. The typical examples of primary crushers employed in mineral beneficiation include gyratory and jaw crushers. The product of the primary crusher is further processed in secondary or tertiary crushers, for example cone, roll and impact crushers (Wills and Napier-Munn, 2006).

Crushing equipment generally has a specific reduction ratio and this ultimately means each crushing stage has a size limitation in terms of the final products. This suggests that the number of crushing stages can be reduced or increased depending on the feed size accepted by the primary grinding stage (Wills and Napier-Munn, 2006). Smaller and finer-sized particles, mostly below 5–20 mm, are achieved in a subsequent step known as grinding (Wills and Napier-Munn, 2006).

According to Metso (2016), the grinding process serves two main objectives:

1. To liberate individual minerals of interest trapped in the matrix of gangue within the ore thereby opening them up for subsequent separation or enrichment processes.
2. To produce fines from mineral fractions so as to increase the specific surface area. The specific surface area is a very important component in the subsequent metal extraction processes, such as flotation if relevant and leaching as practiced in the hydrometallurgical plant.
Grinding takes place in equipment such as ball mills, rod mills and autogenous (AG) or semi-autogenous (SAG) mills; the name given to each milling machine is related to the grinding media used. For instance, in ball milling, grinding media is composed of steel balls, while in rod milling the grinding media is made up of steel rods. In AG milling the size reduction is accomplished through attrition effects taking place between the particles of the raw feed. In SAG milling the grinding media used is the feed plus about 4%–18% ball charges (ball diameter 100–125 mm). In general, the control of particle sizes in the comminution circuit is done through classifiers such as screens and cyclones. Figure 3.2 shows a typical comminution circuit.

After the liberation of all individual minerals in the ore feed by crushing and grinding, separation is undertaken using some of the typical classical methods as discussed in the subsequent sections.

### 3.3.1.1.1 Gravity and Dense Media Separation

Gravity concentration uses the differences in the size and shapes of particles and the specific gravities of minerals to enable separation by force of gravity or by centrifugal forces. Gravity concentrators are characterised by the applied medium (air or water) and are widely used in the processing and recycling industry. Dense medium separation on the other hand not only exploits the difference between the specific gravity of the particles, but also utilizes the variation in the effective specific gravity of the material of a fluid medium.

For separation to occur there has to be differences in the densities between the gangue material and the value mineral. However, the effectiveness of separation is not only dependent on the density of the minerals, but also on the size and shape of the particles. The larger the particle sizes, the higher the gravity separation efficiency. If a feed material has similar densities but different particle sizes, then classification is a more relevant type of separation, and the separation would be based on cut-off particle sizes. If a feed material has similar particle sizes, but different densities, then concentration is a more relevant basis for separation, and the separation would be based on cut-off density. If a feed material has different particle sizes and densities, then a combination of classification and concentration is more relevant, where a screen can be used to narrow the size ranges and then a concentration step can follow (Grewal, 2016). There are a number of gravity concentrators that are used in industry. These include separation in water media through the use of equipment such as jigs (coal, gold, chromite, galena), shaking tables (tin, copper, gold, lead, zinc, tungsten) and
spirals (coal, beach sands, chromite, iron), and separation in a heavy medium such as in dense medium separation (DMS).

From practice, the particle sizes of the feed to the gravity concentrator must be closely controlled so that the size effect is eliminated and the separation is only dependent on the specific gravities (Wills and Napier-Munn, 2006).

**Centrifugal gravity concentrators:** Centrifugal gravity concentrators have dominated in the gold industry for a number of years although the technology has recently expanded to encompass the processing of other heavy minerals. The Knelson and Falcon concentrators are the two most predominant commercially applied units today for the recovery of fine particles of free gold, which do not require the application of the cyanidation process for recovery. The centrifugal concentrator consists of a rifled cone that spins at high speed to create forces that are in excess of gravity. The feed material in slurry form typically from a ball mill or cyclone discharge is introduced into the centre of the cone from above. During operation, the centrifugal force produced by rotation drives the solids towards the walls of the cone. The slurry migrates up along the wall where heavier particles are captured within the riffles (Grewal, 2016).

**Jigs:** The jig operates by dilating a bed containing the mixture of minerals under treatment allowing heavier particles to fall through. The process consists of two actions; one is the effect of hindered settling meaning that a heavier particle will settle faster than a lighter particle. The other action relies heavily on the density properties in which an upward flow of water separates the particles based on their densities. These two actions are combined in a jig by slurry pulses generated mechanically or by air. In the processing of most heavy minerals, the denser material would be the desired mineral and the rest would be discarded as float or tailings. Jigging is an efficient process even within close specific gravities, whereas with larger specific gravity differences, separation improves significantly.

**Spirals:** The spiral concentrator is one of the most common and cost-effective gravity concentrators and has found wide spread application in the processing of minerals such as coal and chromite ores. It uses a flowing film principle based on the size and specific gravity difference present in a suite of minerals. The device consists of one or more helical profiled troughs supported on a central column. As slurry travels down the spiral, high and low density particles are stratified and separated at the bottom end of the spiral with a set of adjustable bars, channels or splitters. The lighter minerals are recovered on the outer walls of the spirals and become more diluted as it contains the bulk of the liquid. The heavy minerals that form the concentrate part are selectively directed into the inside of the spiral surface through the use of adjustable product splitters.

**Shaking tables:** These consist of a cross stream of water which transports material over the table to riffles running perpendicular to the direction of feed. Particles build up behind each riffle and stratification occurs with heavier particles sinking to the bottom. The light particles are carried over each riffle to the tailings zone. The shaking action of the tables carries the heavy particles along the back of each riffle to the concentrate discharge. Shaking tables have been commonly used in the concentration of gold and the recovery of tin and tungsten minerals. The technique can also be used in conjunction with other gravity concentration techniques.
equipment such as spirals and jigs, especially downstream to help generate a much cleaner product.

Dense Media Separation (DMS) is a beneficiation technology that takes place in fluid media possessing a density between that of the light and heavy fractions to be separated. The process results in two products, the floats and the sinks. Particles much more dense than the specific gravity of the separating medium sink while the lighter ones float. The process is more efficient when there is a significant distinct density difference between the valuable minerals and waste materials, thus allowing for a clearer cut-off between the two minerals being separated. Furthermore, the separation process works very well when the valuable material is liberated from the gangue minerals. Thus, for this reason, comminution processes tend to precede the DMS processes. The commonly used media for the separation process are powdered ferrosilicon, commonly known in industry as FeSi, and magnetite (Fe₃O₄). This mixture acts as a high density medium and its density can be varied by changing the ratio of water and powder in the mixture. The popularity of ferrosilicon and magnetite in industrial application lie in their magnetic properties which make them easy to recover and re-circulate within the plant, thus saving on operational costs.

3.3.1.1.2 Magnetic Separation

The separation of minerals based on their magnetic susceptibility is a widely used technique that can be very efficient separation process. Magnetic separation is extensively used in the mining industry in the processing of, for example, iron ore, ilmenite, chromite, mineral sands, silica, fluorspar, kaolin and talc. The magnetic separation processes are generally classified into two (Balakrishnan et al., 2013; Grewal, 2016):

1. Strongly magnetic particles commonly classified as ferromagnetic, such as iron and magnetite that can be easily separated from other minerals by the application of a low intensity magnetic field.

2. Weakly magnetic particles, commonly classified as paramagnetic and diamagnetic. These are not magnetic but differ in how they interact with magnetic fields. Paramagnetic minerals are weakly attracted whereas diamagnetic minerals are weakly repelled along the lines of magnetic forces. These minerals require a high intensity magnetic field for separation. Typical examples are rutile, ilmenite and chromite.

The magnetic separation process is generally a low-cost method of recovery unless high intensity separators are required. The process can be accomplished under wet or dry conditions.

3.3.1.1.3 Flotation

Flotation is the process which utilizes differences in surface properties of wanted and unwanted minerals (Wills and Napier-Munn, 2006). In other words, the separation of the required minerals from the ore is achieved by the difference in surface properties (Gupta, 2003). According to Wills and Napier-Munn (2006), the process of recovering valuable minerals from the ore by flotation consists of mechanisms such as

- Attachment of valuable minerals to air bubbles
- Chemistry of carrying valuable particles in the pulp
- Physical attraction between particles in the froth that stick to air bubbles
Valuable mineral attachment to air bubbles is considered as the main mechanism during flotation (Wills and Napier-Munn, 2006). It follows after the separation of valuable minerals from gangue minerals. The separation of minerals depends on the degree of physical entrapment and entrainment (Gupta, 2003). The entrainment of gangue minerals affects the quality of valuable concentrate. In order to increase the recovery of the valuable concentrate, more than one flotation stage is required. An increase in number of flotation stages results in an increase in the recovery of valuable material which simultaneously results in a decreased production of tails. Figure 3.3 shows a typical flotation circuit for the beneficiation and upgrading of metal concentrates.

The basic flotation circuit is divided into:

**Roughing**: Designed to remove the easily recoverable liberated valuable minerals.

**Scavenging**: The emphasis here is recovery and scavenging is designed to extract the entire remaining valuable minerals that are economically justifiable to recover. Scavenger concentrates are known as the middlings, that is, unliberated particles, and thus tend to go through the process of regrinding before being fed back into the flotation stream.

**Cleaners**: The emphasis here is on grade and cleaners are designed to clean the stream of any misplaced liberated waste particles. Since the grade is achieved at the expense of recovery, tailings are, therefore, recycled.

A number of flotation reagents are used in the process. These serve two purposes: to prepare the mineral surfaces for attachment to the air bubbles and to impart stability to the froth once particle attachment has occurred. Typical classes of reagents used in the plant are

- **Collectors**: These adsorb on the surfaces of the mineral rendering the minerals hydrophobic and thus, promoting the adhesion of the mineral surfaces to the air bubbles.
• **Modifiers**: These are divided into (1) depressants that inhibit the adhesion of mineral to air bubbles to promote selective flotation and (2) activators that work in conjunction with collectors and precondition the surface to facilitate the subsequent adsorption of collectors.

• **Frothers**: These help maintain a steady froth phase and prevent air bubble particle breakage once attachment has occurred.

The flotation circuit is clearly an enrichment process, upgrading the concentration of the valuable metals by separating them from the gangue material. This process results in the production of two major exit streams, the float concentrate that proceeds to the next processing stage (pyro or hydrometallurgical processing) and the waste material taken for disposal, for example, into the tailings dam.

### 3.3.2 Characterization of Tailings

Most beneficiation technologies as described in the preceding sections, especially those immediately upstream from the initial processing operation in a production sequence, generate a high volume of solid waste streams. Despite the fact that valuable constituents have been removed, the remaining material (tailings) is often earthen in character, physically and chemically similar to the raw ore fed into the processing circuit, except for the changes in particle sizes arising from the comminution processes. Tailings may also contain trace or substantial quantities of compounds added during the beneficiation process, such as flotation chemicals and media used in the DMS process.

The quality and composition of tailings can vary widely depending on the source material. Hence, when considering tailings material for utilization in alternative applications, attention should be given to the chemical and physical properties of the tailings as the properties play a significant role on the potential impacts on the environment of application. According to Bian et al. (2012), the mineralogical and chemical characteristics of mining wastes are, for example, useful in forecasting the leachability of potentially harmful compounds found within the waste material. The successful utilization of waste may be prevented if it is likely to create a potential or actual environmental hazard (Collins and Miller, 1979). For example, waste material largely sulphidic in nature cannot be considered for application in aggregates because of potential oxidation and subsequent acid production causing a reaction with cement and leading to concrete decay. Characterization of the waste and assessing any potential technical difficulties that could arise in its proposed environment of application in addition to establishing a market for the product are thus, an essential prerequisite. According to Collins and Miller (1979), the waste material should be evaluated in the same way and detail as a primary resource.

Table 3.1 provides chemical composition data for selected samples of copper, gold, iron and platinum group metals (PGMs).

In general most tailings materials contain a significant amount of silica, iron, alumina and other oxide minerals. Although the main chemical constituents are largely the same from one tailing stream to another of the same metallic component, the percentage quantity can vary slightly depending on the primary deposit and the efficiency of the processing methods. For example, in the work done by Malatse and Ndlovu (2015) in the production of bricks using gold tailings from the South African Witwatersrand Basin, the silica content was about 77.7%. This is quite high compared to the 51%–56% indicated by the gold tailings from India shown in Table 3.1. The composition of the tailings has a great
role to play in the choice of potential alternative application of the tailings. This will be highlighted in the subsequent section on the utilization of tailings.

### 3.3.3 Potential Utilization of Tailings

The large volumes of the tailings produced at mining operations are expensive to manage and are frequently cited as an obstacle in the environmental sustainability of mining. For example, tailings that contain a significant amount of iron sulphides play a role in the generation of one of the most environmentally damaging products, acid mine drainage. Acid mine drainage is discussed in detail in Section 3.4. Therefore, the drive for most mining operations at the moment is to reduce the costs associated with the development of processes and procedures that have to be put in place to make sure that the tailings discharged meet the required environmental standards. As a result, the mining industry is moving towards making use of its own waste materials. In fact, the concept of the utilization of tailings embraces the basic principles of increased reuse, recycling, reprocessing and converting these materials to value-added products as an alternative management strategy (Dean et al., 1986; Edraki et al., 2014; Liu et al., 2014). Furthermore, Dean et al. (1986) and Yellishetty (2008) observed that the utilization of mine tailings in the downstream economic activities and industries can alleviate the socio-economic issues of mine closure associated with loss of employment.

Some typical examples of tailings utilization include the following:

- Reprocessing to extract minerals and metals
- Sand-rich tailings mixed with cement used as backfill in underground mines
- Use of Mn-rich tailings in agroforestry, building and construction materials and coatings

### TABLE 3.1

<table>
<thead>
<tr>
<th>Composition %</th>
<th>Gold</th>
<th>Copper</th>
<th>Iron</th>
<th>PGMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>51.8–56</td>
<td>75.0</td>
<td>47.39</td>
<td>47.16</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>10.2–18.9</td>
<td>3.60</td>
<td>24.82</td>
<td>8.23</td>
</tr>
<tr>
<td>CaO</td>
<td>7.6–8.4</td>
<td>0.16</td>
<td>8.85</td>
<td>7.81</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>8.2–11.9</td>
<td>12.16</td>
<td>7.42</td>
<td>16.90</td>
</tr>
<tr>
<td>MgO</td>
<td>6.3–8.6</td>
<td>0.49</td>
<td>0.097</td>
<td>13.31</td>
</tr>
<tr>
<td>Na₂O</td>
<td>–</td>
<td>4.29</td>
<td>0.32</td>
<td>1.33</td>
</tr>
<tr>
<td>K₂O</td>
<td>–</td>
<td>1.85</td>
<td>0.7</td>
<td>1.43</td>
</tr>
<tr>
<td>CuO</td>
<td>0.32</td>
<td>–</td>
<td>–</td>
<td>0.24</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.013</td>
<td>–</td>
<td>–</td>
<td>3.69</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>2.0–3.9</td>
<td>2.10</td>
<td>10.40</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Tailings source
- Kolar Gold Fields, Karnataka, India
- Hindustan Copper Limited, Khetri, Rajasthan, India
- Anshan of Liaoning Province, China
- Waterval, South Africa

Reference
- Roy et al. (2007)
- Thomas et al. (2013)
- Li et al. (2010b)
- Amponsah-Dacosta and Reid (2014)
• Cast resin products, glass, ceramics and glazes
• Cu-rich tailings as extenders for paints
• Fe-rich tailings mixed with fly ash and sewage sludge as lightweight ceramics
• Clay-rich tailings as an amendment to sandy soils and for the manufacturing of bricks, cement, floor tiles, sanitary ware and porcelains

The following sections look at some of the potential applications of copper, gold, PGMs and iron-rich tailings. Since Table 3.1 indicates a commonality in terms of the tailings chemical composition, it is also expected that there will be some similarities in the application of the tailings generated from the processing of different minerals.

3.3.3.1 Reprocessing of Tailings for Metal Recovery

The growing interest towards metal recovery from wastes is due to the depletion of mineral resources in the most industrialized countries along with the rapid development of technologies enabling the beneficiation of ores even from the poorest deposits. For example, the processing of refractory sulphide and complex material has always presented a challenge in the minerals and metal extraction industry, resulting in most of the valuable metals being left behind in the tailings. The major problems that have existed in the past with regards to the reprocessing of such tailings have been the availability of more efficient, effective and economical processes for obtaining high metal recoveries at high production rates from the once-processed material. However, advances in process technology has seen some of the challenges being overcome, leading to renewed interest in the processing of tailings in order to recover valuable metals. Reprocessing of such wastes brings potential financial and waste reduction benefits. In addition, higher metal prices and the stringent environmental regulations and associated penalties further justify the reprocessing of large volumes of tailings across the globe. For example, tailings that contain economic quantities of copper or gold, if reprocessed, could potentially have higher production rates than primary mining operations. The reprocessing of gold-bearing tailings in particular has increased in the recent past due to it being one of the few commodities that has maintained some semblance of price stability within the current prevailing harsh mining environment.

The key drivers for the extraction and reprocessing of metal-bearing tailings can be summarized as follows:

• Tailings are generally considered to require fewer resources when compared to conventional mining. The mining of raw ores requires a lot of capital investing and other related funding for mining of hard rock and crushing and grinding to achieve high metal recoveries, while waste dumps generally require just crushing and grinding as the treatment methods prior to metal extraction. In most cases, some of the existing facilities for the treatment of raw ores can be utilized for the processing of waste materials. This reduces costs related to capital equipment, labour, fuel and maintenance. For example, despite differences in grade, the reprocessing of old, finely ground mill tailings is probably much more economic than treating most newly mined ores. The mining of raw ores requires a lot of capital investing and other related funding, mining of hard rock and crushing and grinding to achieve high metal recoveries, while waste dumps generally require just crushing and grinding as the treatment
methods prior to metal extraction. In addition, in most cases, some of the existing facilities for the treatment of raw ores can be utilized for the processing of these secondary resources, thus lowering the capital investment costs significantly.

- Advances in processing technology result in changes in patterns of metal extraction from both primary sources and waste or secondary material. As processing techniques become more cost-effective and efficient, it becomes more economically beneficial to recover valuable metals from discarded materials which were previously regarded as untreatable.
- The processing of tailings allows for additional production without increasing a mine’s footprint and without requiring additional land permits.
- According to Binnemans et al. (2013), the reprocessing of residues from waste can also positively influence the availability of metals and consequently stabilize their prices in the world market.

Some practical examples in which tailings can be reprocessed so as to recover metals are highlighted in the subsequent sections.

### 3.3.3.2 Reprocessing of Copper Tailings

According to Gordon (2002), mills process ores that contain 0.5%–2% copper into concentrate containing 25%–35% copper leaving a residue (tailings) consisting of the gangue and the unseparated copper-bearing minerals. One of the primary challenges is to efficiently recover copper from the tailings without significant added capital and operating costs (Edraki et al., 2014). For example, Lutandula and Maloba (2013) used flotation to recover copper and cobalt by reprocessing tailings from oxidized ores in the Democratic Republic of the Congo (DRC). However, the excessive consumption of reagents in relation to tailings was found to be of major concern from a technical and economic standpoint.

Based on the challenges of using conventional tailings reprocessing techniques such as flotation, there has been a focus on applying bioleaching as an alternative reprocessing technique. Bioleaching has been the process of choice for the treatment of most copper sulphide tailings. The importance of this technique in the treatment of waste material is due to its associated low cost and its environmental friendliness. For example, research has been conducted on the potential for the application of an integrated complete bioprocessing route for copper extraction from flotation tailings generated at the Neves Covo mining site in Portugal (Duarte et al., 2006). These tailings constituted mainly metal sulphides, pyrite and chalcopyrite with a very high copper content. The researchers proposed bioleaching using thermophilic bacteria to recover copper and other valuable metals. This was followed by the application of sulphate-reducing bacteria to remediate the final discharge solutions. Figure 3.4 shows the typical flowsheet that would be expected.

The integrated process not only looks at value recovery through the treatment of the copper tailings generated from the beneficiation process, but also considers the bioremediation of the final effluent discharge solution so as to lessen its impact on the environment. As already stated, biohydrometallurgical processes are generally considered to be environmentally friendly and cost-effective. Thus, an integrated process would work very well for the treatment of tailings materials which are considered as low-value feed.

Bioleaching has also been used at the Copper Mine Bor in Sebia. The process makes use of the abundant and highly acidic water of Lake Robule as a lixiviant to leach the copper
flotation tailings (Stanković et al., 2015). The widespread open-pit acidic lakes in the mining region also present a potential source of acidophilic microorganisms that can be used for the bioleaching of copper. Studies by Stanković et al. (2015) showed the presence of acidophilic heterotrophic bacteria, *Acidiphilium cryptum*, and the autotrophic iron oxidizers *Leptospirillum ferrooxidans*, in the lake water. There was also a relatively small number of autotrophic iron- and sulphur-oxidizers, *Acidithiobacillus ferrooxidans*. The obtained results showed that bioleaching could be more efficient than inorganic acid leaching for copper extraction from flotation tailings with higher sulphide contents.

Fraser Alexander, one of the companies making inroads into the operation and management of tailings dams for precious metals, base metals and coal industries internationally, undertakes re-mining projects mostly through hydro-sluicing (Wilkins, 2013). The company operates a copper re-mining solution for Vedanta’s Konkola copper mine near Chingola on the Zambian Copperbelt. For a significant amount of metal recovery to be realized from the processing of these tailings, the volumes of material being processed should, however, be extremely high (Wilkins, 2013).

The significant impact of mining can also be understood through the large quantity of copper mining tailings that have accumulated at the Morenci mine complex in Arizona (Tilton and Landsberg, 1997). When the depression in the price of copper in 1892 threatened many copper mining companies, the Morenci Mine implemented the leach–cementation process in 1893 to recover copper lost in mill tailings (Gordon, 2002). The leach–cementation process was seen to be a more cost-effective and simple to implement process at that particular time. This operation remained in place till late 1977. The process treated an average of 60 kt of the mill tailings containing about 0.2% copper per day, and recovered about 40% copper (McKinney and Graves, 1977). Copper was recovered from the resulting cement copper by feeding it into the smelter together with the sulphide concentrates. However, each kilogram of copper made by cementation consumed 3 of iron (Gordon, 2002). When the price of the iron metal used in the recycling process became high, the leach–cementation process became uneconomic. An alternative cost-effective and much more efficient technology could have prolonged the treatment of the tailings at the Morenci mine. In general, the leach–cementation
process did not prove popular for companies that did not have smelter facilities as building a smelter is capital intensive.

According to Hancock and Pon (1999), the copper mining activities in Zambia from early 1913 have resulted in the generation of waste ponds that contain about $1.2 \times 10^9$ tonnes of copper tailings. It is, therefore, no wonder that one of the most well-known commercial copper tailings reprocessing plant in Southern Africa is the Nchanga tailings leach plant located in Zambia. The plant produces copper cathodes from concentrator tailings and reclaimed tailings. The process was initially based on the acid leach–cementation process. However, the advent of the solvent extraction technology led to the plant being upgraded in 1973/1974 which greatly increased the utility of hydrometallurgy in the extraction of copper (Chisakuta et al., 2005). Through the introduction of solvent extraction, the Nchanga mill in Zambia went from a copper loss to its tailings of about 54 kt a year, to recovering 100 kt of copper per year through the treatment of 10 million metric tonnes (Mt) of tailings per year (White, 1979).

Another company making significant progress in the processing of tailings is the Canadian company, Amerigo Resources, which focusses on old and new copper/molybdenum tailings on a very large scale from one of the world’s great copper mines – Codelco’s El Teniente, the world’s largest underground copper mine in Chile (Henderson, 2013). Amerigo’s wholly owned subsidiary, Minera Valle Central (MVC) is re-treating all the tailings from El Teniente’s present production and has the right to treat high grade old tailings from a 200 Mt *in-situ* tailings impoundment, Colihues, which is located next to MVC’s plant (Williams, 2010). There are two additional major tailings impoundments at El Teniente: the Cauquenes tailings dam, which contains an estimated 500 Mt of additional high grade tailings, and Barahona, which is similar in size to Colihues and located closer to El Teniente mine (Henderson, 2013). Amerigo hopes to obtain the rights to process tailings from these additional sources, although Colihues alone has sufficient material to keep the plant running at its existing production rate for around 20 years (Williams, 2010).

The Roan Tailings retreatment project in the DRC involves the reprocessing of oxide tailings produced by the mineral concentrator in Kolwezi. This concentrator processed high grade copper cobalt ores from nearby mines from 1952 and, thus, significant volumes of tailings were generated. The tailings were previously deposited in the Kingamyambo tailings dam and in the Musonoi river valley. The tailings dams have the potential to be the source of the world’s largest cobalt producers at much lower costs. These tailings dams contain copper and cobalt at an average grade of 1.49% and 0.32% respectively, making these metals economically viable to recover.

One future prospect in copper tailings reprocessing in South Africa lies with Xtract Resources. The company has invested in the development of the Carolusberg and O’Kiep project, which looks at the potential processing of a sulphide copper tailings dam located in the Northern Cape close to the town of Springbok. The project is estimated to contain 33.8 Mt of sulphide tailings material that was mined between 1980 and 2010 by O’Kiep Copper Company. The Carolusberg tailings dam represents 28 Mt of material grading at 0.19% Cu and the O’Kiep tailings dam represents 5.8 Mt of material grading at 0.23% copper.

### 3.3.3.3 Reprocessing of Gold Tailings for Metal Recovery

The gold industry is a typical example where the reprocessing of mine tailings has been extensively reported. According to Wilkins (2013), the high cost of deep level mining combined with low recoveries, fractious labour in certain countries with South Africa being a typical example, has resulted in some mining companies exploring alternative avenues to maintain margins and to unlock profits hidden in substantial volumes of tailings. This is also
largely driven by technological advances coupled with the rising price of gold over the past
decade that has made it both possible and profitable for mining companies to extract micro-
scopic gold from already worked rock. There has also been a trend towards the consolidation
of smaller tailings dams into single tailings facilities in order to better manage reprocessing
and rehabilitation. Reports by Nummi (2015) and Wilkins (2013) cite a number of examples
showing the extensive reprocessing of tailings being undertaken by gold mining companies.
Typical examples of projects in operation and/or being piloted include the following:

- DRD Gold is one of the first South African companies who, with the advent of new
technologies, have abandoned traditional mining to focus on extracting gold from
tailings. Recoveries of up to 40% of the gold from tailings have been reported.
- Mintails processes about 350,000 tonnes of tailings from its extensive gold tailings
dams. It expects to recover 58 kg of gold per month and has declared that it has
enough gold tailings to last until 2025.
- Goldfields has developed a new technology for the processing of about 12,000
tonnes of new tailings and 88,000 tonnes of old tailings a month.
- Gold One Group purchased an 83 million tonnes tailings dump from Rand Uranium
at the beginning of 2012 with the intention of recovering uranium, gold and sulphur
from the tailings dumps. The company estimates that 0.8 million ounces of gold and
34 million pounds of uranium will be recovered from the dump over a 17-year
period.
- The Australian company, Carbine Resources, investigating the extraction of an esti-
mated million ounces of gold left in the tailings from the Mt. Morgan mine, while
also fixing a huge environmental problem at the former mine site (Calderwood,
2014). The mine is an open-pit and has, in the past few years, filled with water that
has also turned acidic. Despite a water treatment plant being run at the mine, the pit
at one time overflowed and spilled acidic water into a nearby river.
- Las Lagunas Gold Tailings is another retreatment project involving the application
of the Albion oxidation technology for the reprocessing of previously unrecovered
gold and silver refractory tailings from the Pueblo Viejo mine in the Dominican
Republic (Barradas, 2012).

3.3.3.4 Reprocessing of Iron Tailings

The increasing demand for heavy construction material like steel and iron has led to the
establishment of many iron ore mining activities, subsequently leading to the generation
of a large amount of iron ore tailings. The iron ore tailings in most cases are fine materials,
containing mostly silica together with some fines of iron oxides, alumina and other minor
minerals (da Silva et al., 2014). This composition places these tailings as a potential raw
feed for aggregated materials of mortar and concrete in the civil construction industry. Iron
ore tailings have also served as secondary resource of iron ore. The reprocessing of iron
tailings streams has been accomplished mostly through gravity, magnetic, flotation separa-
tion and direct reduction techniques.

Praes et al. (2013) studied the concentration by flotation of a fraction of iron ore from
the magnetic separation tailings having an Fe content of about 35% and SiO₂ generally
above 40%. The study was carried out in a flotation column at a pilot plant unit scale and
produced a concentrate of Fe and SiO₂ content of about 66% and 1.0%, respectively,
which met the standards required for commercialization.
Ajaka (2009) investigated the reprocessing of iron ore tailings produced in the Itakpe iron ore processing plant in Nigeria. The tailings contained up to 22% iron minerals, mostly natural fines in the ore and fines produced inevitably during comminution. Ajaka (2009) analysed the existing circuit and undertook specific recovery tests on the tailing material using simple hindered settling and flotation process for the recovery of iron minerals in the tailings. The results showed that concentrates of grades ranging from 41% to 62% could be attained with the selected processes.

Sakthivel et al. (2010) used iron ore tailings containing 15.98% Fe₂O₃, 83.36% SiO₂ and 0.44% Al₂O₃ to produce magnetite powder. The process involved the production of Fe(III) solution by the digestion of the tailings with HCl followed by the separation of the acid-insoluble residue. In the presence of NaHB₄ used as the reducing agent, Fe(III) solution was then used to synthesize magnetite via the formation of metallic iron and with NaHB₄ used as the reducing agent.

Although laboratory research and development on the recovery of iron from tailings is quite substantial, the industrial application remains limited due to the associated high production cost (Li et al., 2010a). The content of iron in the tailings is generally very low, making the reprocessing and reuse very uneconomic. Since the amount of iron recovered from the tailings is low, a large volume of the residue is attained after the iron removal process creating another problem of storage and secondary pollution. With these challenges in mind, Li et al. (2010a) investigated the comprehensive utilization of iron tailings by first recovering the iron from the tailings as magnetite. This was accomplished by using magnetizing roasting to reduce hematite in the iron ore tailings to magnetite followed by separation using a low intensity magnetic separation method. Using this process, a magnetic concentrate of 61.3% Fe at a recovery rate of 88.2% was achieved. The residue obtained after the iron removal process was then used to prepare a cementitious material (Li et al., 2010b). The results from the test work showed that up to 30% of raw material could be replaced by this residue, with 34% blast furnace slag, 30% clinker and 6% gypsum making the other balance to produce a cementitious material with mechanical properties comparable to those of ordinary Portland cement according to Chinese GB175-2007 standard. This approach allows for a more economic, environmentally friendly and comprehensive utilization of iron tailings (Argane et al., 2016).

On the commercial front, in 2009 Xstrata Copper announced the development of the Ernest Henry Mine (EHM) magnetite extraction plant as part of the life of mine extension program for Ernest Henry Mine and also as part of a strategic objective aimed at maximizing the value of the existing resources (Siliezar et al., 2011). The EHM magnetite plant extracts the magnetite from the copper concentrator’s tailings stream. It produces approximately 1.2 Mt of magnetite concentrate per annum at full capacity for export to Asia, making EHM Queensland’s first iron ore concentrate exporter.

Outotec has also developed the SLon® high gradient magnetic separator for the reprocessing of iron ore tailings in order to recover iron metal (Jain, 2015). The SLon® separator utilizes a combination of magnetic force, pulsating fluid and gravity to continuously separate the magnetic from the non-magnetic minerals (Jain, 2015). Outotec highlights some of the advantages of the equipment as the high beneficiation ratio, high recovery, adaptability to varying particle sizes and minimized matrix blocking. The feasibility for its application has been tested in iron ore processing companies in Brazil, the United States, Africa and Russia. The technology can be applied not only for the concentration of iron ore, but also for ilmenite, chromite ore and other paramagnetic materials.

Magnetation LLC is another company that has been making inroads into the processing of tailings from open-pit mines in the Minnesota area, USA (Magnetation, 2016).
Waste Production and Utilization in the Metal Extraction Industry

The company uses a patented Rev3™ Separator technology to separate weakly magnetic particles from waste minerals with high efficiency and throughput. According to Magnatation (2016) the Rev3 process is designed specifically for high volume and high availability iron ore applications to produce high quality hematite concentrates. The product is then used as a primary raw material supply for North American blast furnaces in the steel making process.

3.3.3.5 Reprocessing of Chrome Tailings for PGMs and Chrome Recovery

South Africa accounts for 96% of the known global reserves of PGMs with the Bushveld Igneous Complex in South Africa being host to some of the world’s major PGM ore deposits including the Merensky Reef, UG2 Reef and Platreef (Mohale et al., 2015; Sameera et al., 2016). South Africa’s reputation as one of the leading producers of PGMs worldwide consequently makes it one of the largest producers of mine waste compared to other mining industries. The country’s mining operations associated with the primary production of PGMs from deposits generates over 77 Mt of fresh tailings per annum (Vogeli et al., 2011).

Though the incorporation of PGM tailings into building materials, road aggregates, agricultural applications, landfills, manufactured fillers and many other schemes have been proposed, these high-tonnage waste materials also contain elevated concentrations of valuable minerals and could, therefore, be regarded as an economic resource rather than a waste, provided suitable economically viable processes can be developed.

The reprocessing of chrome tailings to recover PGMs is one of the recent developments in the mining industry being applied to try to meet the ever-growing demand in the fuel cell technology, jewellery market in the Far East and the automobile catalytic converters. With the South African platinum industry being the world’s largest producer of platinum and the world’s second largest producer of palladium, it follows therefore, that a number of developments in tailings treatment processes have been initiated in the country. According to Van Niekirk and Viljoen (2005), the large volumes of tailings produced in the country also require active planning and management to prevent major environmental or social impacts such as tailings dam failures, for example the 1974 Bafokeng tailings disaster; acid mine drainage or other problems, such as dust and environmental health issues.

In December 2003, Anglo Platinum commissioned the first purpose built tailings retreatment facility for PGMs recovery in South Africa. The Western Limb Tailings Retreatment (WLTR) project near Rustenburg takes advantage of modern technology, such as fine grinding, to economically recover PGMs from material historically considered as waste (Buys et al., 2004). The flowsheet includes the recovery of tailings by high pressure water monitoring, ball milling, rougher flotation, rougher concentrate regrinding and cleaner/recleaner flotation. The rougher concentrate is reground in a mill allowing smeltable concentrate grades to be produced from the oxidized, slow floating tailings.

In 2013, the Two Rivers Platinum Mine, also located in South Africa, commissioned a recovery plant to reprocess its UG2 tailings to recover chrome (Implats, 2015; Sameera et al., 2016). The tailings dams at Two Rivers currently contain about 24 Mt of milled and processed ore with an average Cr₂O₃ grade of about 17%.

In 2014, Jubilee Platinum executed a Tailings Access Agreement with ASA Metals Proprietary Limited (ASA) and its subsidiary Limpopo-based Dilokong Chrome Mine (DCM) for the recovery of platinum group metals and chrome from tailings dams (Odendaal, 2014). The agreement offered Jubilee the option to construct, in partnership with ASA, a dedicated chrome and PGM processing plant for the treatment of the tailings.
Mining and Beneficiation Waste Production and Utilization

on ASA’s DCM property. The agreement gave Jubilee exclusive access to an estimated 800,000 t of PGM-bearing chromite tailings (Odendaal, 2014).

Sylvania Platinum Limited in South Africa operates the Sylvania Dump Operations (SDO), which focuses on the re-treatment of PGM-rich chrome tailings material from mines in the region in order to recover chrome and PGM concentrate (Sylvania Platinum Report, 2016). The SDO currently includes seven fully operational chrome tailings processing complexes on the western limb of the Bushveld Igneous Complex (BIC) and a few others on the eastern limb.

The PGMs from tailings constitute an important secondary resource of PGMs for the global market and it is clear that South Africa is playing a significant role in this development. Although this section has highlighted a myriad of the commercial developments in South Africa, it is important to note that the recovery of PGMs from tailings is also being practiced in other platinum-producing countries such as Russia and Zimbabwe (Glaister and Mudd, 2010).

3.3.3.6 Tailings Utilization in the Construction Industry

The large amount of mine tailings generated in the mining industry each year provides a large new source of raw material for utilization in the construction and building industry. The utilization of mine tailings as construction material can reduce the volume of disposable mine tailings and thus, saving the land required for the disposal impoundments and the related high monetary costs. It can also lead to a reduction in the environmental and ecological costs and lower the demand for virgin materials that would need quarrying, thus, prolonging the life of natural resources. The following section looks at the potential use of tailings in different sectors of building and construction.

3.3.3.6.1 Utilization as Aggregates for Concrete Mix

Aggregates make up about 70%–80% of a concrete mix (Shetty et al., 2014). As the natural granite quarries for aggregates are gradually decreasing, there is a need for alternative materials to be used as aggregates in concrete. If mine tailings are considered as a partial or complete replacement of natural aggregates in concrete, a majority of these tailings could be recycled and used sustainably, thereby turning the tailings into useful resource and providing cheaper alternatives in concrete production (Ugama et al., 2014). However, many mineral processing waste materials have limited potential for use as aggregates because of their fineness, variable metal compositions, leachability of some of the trace metals and the propensity for acid generation, especially for sulphide-containing materials. Further to this, these potential raw material resources tend to be found in remote locations, that is, away from aggregate markets (Collins and Miller, 1979). However, when the location and material property characteristics are favourable, coarse tailings may be suitable for use in the production of cement concrete aggregate, asphalt aggregate, flowable fill aggregate. In addition, if these tailings are segregated properly, both fine and coarse aggregates for concrete can be obtained.

3.3.3.6.1.1 Iron Ore Tailings

The processing activities associated with the iron ore beneficiation is such that it results in the tailings with particle sizes ranging from fine to coarse (Kuranchie et al., 2014). Therefore, by proper segregation of the tailings, the iron ore mining companies could incorporate comprehensive utilization of the tailings in their operation, leading to cleaner production and sustainable development (Haibin and Zhenling, 2010). Research has shown that the most comprehensive use of iron tailings is through the
production of building and construction materials such as concrete aggregate, as a substitute for Portland cement and as bricks.

Iron ore tailings have been used as a replacement material in the making of Portland cement (Li et al., 2010b). The researchers used the residue obtained after iron removal (Li et al., 2010a) from iron ore tailings to produce cement of high quality standard. Luo et al. (2016) further successfully utilized iron ore tailings to replace clay as alumina silicate raw material for the production of Portland cement clinker. The key to the success of this application was found to be the rich iron (III) oxide content in the form (Fe₂O₃) which can be effectively used as raw material in cement clinker production (Oluwasola et al., 2014).

Kuranchie et al. (2015) studied the feasibility of using Australian iron ore tailings as both fine and coarse aggregates in making concrete. The authors evaluated the technical and environmental characteristics of the concrete with the main aim being the recycling and addition of economic value to the iron ore tailings for use as cheaper alternative materials for concrete aggregates. The compressive strength of the concrete with iron ore tailings aggregates at 28 days showed an improvement of 11.56% over the concrete with conventional aggregates. However, the split tensile strength exhibited by the concrete with tailings aggregates at 28 days was slightly lower than for the concrete with conventional aggregates by 16%. This was due to higher quantity of fines in the iron ore tailings as compared with the natural sand in the control mix. Nevertheless, the tensile strength increased favourably with ageing. In addition, the concrete with tailings aggregates had a lower potential for corrosion and a low vulnerability to acid attack due to high pH values of the resulting mix.

Ugama et al. (2014) investigated the strength characteristics of control concrete and concrete made with iron ore tailings and determined the optimum replacement level for iron ore tailings content in concrete beam production to be about 20%. It was observed that concrete workability decreased with an increase in the percentage of iron ore tailings in the mix. This was attributed to the fineness and therefore, large surface area of the iron ore tailings which resulted in the need for a large amount of water to wet all the particles in the mix. The iron ore tailings were classified as a heavy aggregate and would therefore, produce concrete pieces of heavier weight. The high density of the waste was related to the high content of iron, which could not be removed by a magnetic separation process. It was further noted that these iron tailings would be suitable as an aggregate for the production of concrete for paving directly on the ground due to higher self-weight and it being less subject to deformation due to external loads.

Kumar et al. (2014) also used the iron ore tailings as a replacement material for fine aggregates in cement concrete pavements. Their results showed that 40% iron ore tailings could be used as replacement to give an optimum compressive strength. It was suggested that the concrete so-generated could be used for pavements and village roads.

The information given in this section suggests that the utilization of iron ore tailings as a raw material in the construction industry is a more attractive and effective solution for management of these tailings. This approach not only utilises a large amount of the iron ore tailings but also provides an added advantage of protecting the natural resources.

3.3.3.6.1.2 Copper Tailings Copper ore tailings are classified as a good quality class-N natural pozzolana and can, thus, be used as a pozzolanic material in the construction industry (Prahallada and Shanthappa, 2014). According to Prahallada and Shanthappa, (2014), copper ore tailings utilization in concrete production has a number of environmental benefits such as increasing the life of pavements and structures by improving the stability of the soil, reduction in the adverse air emissions when used in copper tailing bricks and stabilized blocks, etc. In the studies by Prahallada and Shanthappa, (2014), the suitability of
copper ore tailings as an additive mixture in the preparation of concrete was tested by replacing the ordinary Portland cement in different percentages. The results showed that the replacements of ordinary Portland cement with copper ore tailings was safe up to 20% considering average minimum field strength. If characteristic strength was considered, replacement copper ore tailings up to 30% could be considered as safe.

Thomas et al. (2013) looked at the use of copper tailings as a partial replacement of natural river sand in the preparation of a concrete mix. The results indicated that copper tailings could be utilized for the partial replacement of up to 60% of natural fine aggregates, with the water–cement ratios of 0.4, 0.45 and 0.50. The so-produced copper tailings concrete exhibited good strength and durability characteristics and was further found to be suitable for applications in a number of construction activities.

Onuaguluchi and Eren (2012a) investigated the potential application of copper tailings as an additive in concrete mix. The results indicated that copper tailings have a slight negative impact on the slump, porosity and setting time of concrete mixtures. However, when compared to the control specimen, there was a noticeable improvement in mechanical strength and abrasion resistance and reduced chloride permeability. The conclusion was that a minimum of 5% copper tailings could be introduced into concrete as an environment-friendly and zero cost material. Onuaguluchi and Eren (2016) further investigated the time to initiation of corrosion and deterioration in copper tailings blended concrete mixtures. The results showed that the use of copper tailings as an additive in concrete was more effective in delaying the commencement of corrosion compared to when the copper tailings were used to replace some of the cement raw material. The researchers further undertook an economic analysis by comparing the cost efficiency of using copper tailings either as a cement replacement material or as a cement additive in concrete. Based on the corrosion performance and cost efficiency of mixtures, utilization as a cement additive was found to be the best reuse option for copper tailings in concrete.

The work by Huang et al. (2012) looked at the utilization of Chinese skarn-type copper tailings to prepare autoclaved aerated concrete (AAC). The AAC samples were prepared by completely substituting lime by skarn-type copper tailings and blast furnace slag. The results showed that AAC samples with a dry density of 610.2 kg/m³ and compressive strength of 4.0 MPa could be prepared at a laboratory scale. The patented work by Koumal (1994) also focussed on the use of copper tailings from the Arizona copper mine to produce AAC which could be further utilized as building material for the production of building blocks and prefabricated walls. The mine tailings material was used as a substitute for the processed silica sand during the formation of the AAC building material.

### 3.3.3.7 Tailings Utilization in Brick Making

The conventional production of bricks usually utilizes clay and shale as the source materials and requires high temperature (900°C–1000°C) kiln firing (Muller et al., 2008). Clay and shale are sourced through quarrying operations which are energy intensive, adversely affect the landscape, and can release a large quantity of waste materials (Bennet et al., 2013; Zhang, 2013). The bricks are produced by mixing ground clay with water, forming the clay into the desired shape followed by drying and firing. The major disadvantage of the conventional high temperature kiln firing process is that it not only consumes significant amounts of energy but also releases a substantial quantity of greenhouse gases (Zhang, 2013). Furthermore, in many areas of the world, there is already a shortage of natural resource material for the conventional brick making processes which has led to restrictions in terms of clay brick production. For instance, countries such as China
have started to limit the use of bricks made from clay and have instead been actively advocating for the development of eco-friendly building materials and processes (Zhang, 2013) in order to protect the environment and sustain development.

The use of mine tailings to produce bricks offers an alternative raw material for the building industry. The popularity in the application of these tailings for the production of bricks is largely due to the fact that the composition of these waste materials is closely similar to that of the typical clay material used in conventional brick making. Table 3.2 shows the typical composition of the clay material that is used in brick making.

It can be noted that the tailings material in Table 3.1 primarily have a high composition of silica, alumina, calcium oxide and hematite which are all essential constituents in the brick making process as shown in Table 3.2. In addition, the source material must have some plasticity that can allow it to be shaped or moulded when it is mixed with water.

The use of mine tailings in the production of bricks and blocks was investigated as early as 1979 by Collins and Miller as part of an intensive research into waste utilization in the United States. Copper, lead, zinc and iron ore tailings from various U.S. sources were evaluated in the production of cemented blocks. Base metal mine tailings were on the other hand, also evaluated for the production of concrete blocks during tailings recycling research in Melbourne, Australia (Struthers, 1999). These blocks were shown to be superior in compressive strength compared to conventional blocks. However, Struthers (1999) further observed that tailings are often too fine to work successfully in a commercial high-speed production system. They would instead, be suited to slower, intermediate technology methods and are ideal for the production of complex concrete formwork.

The production of bricks using mine tailings can be divided into three general categories based on the production methods – firing, cementing and geopolymerization.

### 3.3.3.7.1 Production of Bricks through Firing

In the firing process, the waste material is substitute partially or entirely for clay and follows the traditional method of kiln firing (Malaste and Ndlovu, 2015). Chen et al. (2011) studied the feasibility of utilizing hematite tailings from the Western Hubei Province of China as the main raw material in the production of fired bricks. Clay and Class F fly ash were used as additives to improve the brick quality. It was found that the percentage of tailings used could be up to 84% of the total weight. The firing temperature applied ranged from 980°C to 1030°C over a period of 2 h. The mechanical

### Table 3.2

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight %</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>50–60</td>
<td>Prevents cracking, shrinking and warping and thus imparts uniform shape to the bricks</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>20–30</td>
<td>Imparts plasticity to the clay so that it can be moulded</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>5–6</td>
<td>Helps to fuse sand and also imparts a red colour to the bricks</td>
</tr>
<tr>
<td>CaO</td>
<td>2–5</td>
<td>Helps to fuse sand and also prevents the shrinkage of raw bricks</td>
</tr>
<tr>
<td>MgO</td>
<td>&lt;1</td>
<td>Imparts a yellow tint to the bricks and decreases shrinkage</td>
</tr>
</tbody>
</table>

strength, water absorption and other physical properties and durability of the reddish fired specimens were found to conform to the Chinese Fired Common Bricks Standard (GB/T5101-2003).

Gold tailings from Kolar Gold Fields, in Karnataka, India were also evaluated for the production of bricks through the firing method (Roy et al., 2007). In this work, different amounts of gold mill tailings ranging from 0% to 75% were mixed with black cotton soils or red soils. After drying, the bricks were fired in an electric furnace at three different temperatures, 750°C, 850°C and 950°C. The results indicated that 65%, 75%, 50% and 45% of tailings could be used to produce bricks that pass the quality assessment in terms of compressive strength, water absorption and linear shrinkage.

### 3.3.3.7.2 Production of Bricks through Cementing

The production of bricks through the cementing method relies on the cementing properties or cementing reactions within the waste material itself or other added cementing material(s) such as ordinary Portland cement (OPC) and lime. In this process, there is no kiln firing involved. The process depends on the presence of C–S–H and C–A–S–H phases for matrix formation and strength (Zhao et al., 2012; Zhang, 2013). If the process is based on the waste material providing the cementing properties, then the waste material has to contain a large amount of calcium or any calcium-containing material (Zhao et al., 2012).

The work by Onuaguluchi and Eren (2012b) showed that copper tailings have the potential to enhance the durability properties of cement-based materials. Comparative tests showed that the addition of copper tailings to concrete led to higher compressive strengths of the produced concrete blocks compared to that of copper tailings–free concrete blocks. The production of bricks by Morchhale et al. (2006) showed that a high compressive strength and lower water absorption capacity of the bricks could be obtained with an increase in the OPC content. The work by Prahallada and Shanthappa, (2014) further showed that the replacement of OPC with copper tailings was safe up to only 30% as thereafter, a further increase in percentage tailings led to a decrease in the strength of the concrete blocks.

Fang et al. (2011) studied the utilization of copper tailings with a low silica content to partially replace sand in the production of autoclaved sand–lime bricks. The copper mine tailings were mixed with river sand and sand powder at different proportions. The mixture was then pressed in a mould and autoclaved under a pressure of 20 MPa, forming moulded bricks. The results showed that in order to produce autoclaved sand–lime bricks meeting the China National Standard for Mu 15 sand–lime brick, the proportion of the copper tailings in the brick batch should be limited to below 50% (% by mass). However, appropriate proportions of river sand and sand powder had to be added to compensate for the low silica content.

In addition to making fired bricks, Roy et al. (2007) tested the viability of a mixture of gold mill tailings, OPC, black cotton soils and red soils in different proportions to make cement bricks. The bricks were cured by immersing them in water for different periods of time followed by the determination of the compressive strengths. The most significant parameter levels for bricks of acceptable standard were found to be 20% cement and 14 days of curing. Gold mine tailings have also been used to produce autoclaved calcium silicate bricks (Jain et al., 1983). The bricks are cured under saturated steam, and in the process, lime reacts with silica grains to form a cementing material known as calcium silicate hydrate. Malatse and Ndlovu (2015) also tested the feasibility of using gold tailings to produce bricks through the cementing method. Different ratios of gold tailings, cement and water were used. The bricks were cured under different environments, sun dried,
oven dried and water cured for different periods of time. The tailings bricks were found to require more cement in order to give compressive strengths comparable to that of commercial bricks. This was explained as being due to the possible lack of plasticity in the gold tailings used. Although a cost analysis done by both Malatse and Ndlovu (2015) and Roy et al. (2007) showed that bricks made from tailings cost more than conventional bricks because of the higher quantity of cement used, the tailings brick manufacturing process was found to be more conservative in water consumption. Overall, the results indicated that gold mine tailings have a high potential to substitute for the natural materials currently used in brick making.

Zhao et al. (2012) investigated the possibility of using hematite tailings as the main raw material for the production of high strength autoclaved bricks. The results indicated that a mixture of 70% hematite tailings, 15% lime and 15% sand and an autoclave pressure and time of 1.2 MPa and 6 h, respectively, produced bricks with mechanical strength and durability conforming to the China Autoclaved Lime–Sand Brick Standard (GB11945-1999) for MU20 autoclaved bricks.

From the analysis given in this section on the production of bricks using waste material through the cementing process, it is apparent that the optimum strength and durability is mostly obtained using a higher content of OPC or lime. This is a disadvantage since cement and lime production is expensive; a lot of energy is consumed and a large amount of greenhouse gases are also generated during the production process (Zhao et al., 2012). There is thus, a need to investigate cheaper alternative additives that have a high plasticity or binding properties that can be used in the place of cement (Malatse and Ndlovu, 2015).

3.3.3.7.3 Production of Bricks through Geopolymerization

Geopolymerization is a technology that relies on the chemical reaction of amorphous silica and alumina-rich solid with a high alkaline solution at ambient or slightly elevated temperatures to form an amorphous to semi-crystalline aluminosilicate inorganic polymer or geopolymer (Zhao et al., 2012). During the synthesizing process, silicon–aluminium bonds are formed that are chemically and structurally comparable to those binding the natural rocks (Bennet et al., 2013), giving geopolymer binder–based bricks advantages such as rapid strength gain and good durability, especially in acidic environments. Previous research has shown that geopolymers are cheap to produce, especially since they can be made by mixing naturally occurring materials (i.e. material in possession of a high Si–O–Al framework) with NaOH and water (Davidovits, 1988; Smith and Comrie, 1988). This process consumes less energy, releases less greenhouse gases and is much more environmentally friendly than conventional brick making (Ahmari and Zhang, 2012).

The geopolymerization technology has been applied in the utilization of copper tailings from Mission Mine operations of ASARCO LLC in Tucson, Arizona in the United States for the production of eco-friendly bricks (Ahmari and Zhang, 2012). These copper mine tailings are rich in silica and alumina and can thus, be used as a feed material for the production of geopolymer bricks. The procedure for producing the bricks involves mixing the tailings with an alkaline solution (NaOH), forming the brick by compressing the mixture within a mould under specific pressure and curing the brick at a slightly elevated temperature. Research by Ahmari and Zhang (2012) has indicated that by carefully selecting the right level of parameters such as different initial water content, NaOH concentration, forming pressure and curing temperature, copper mine tailings can be used to produce eco-friendly geopolymer bricks that meet ASTM requirements.
Research into geopolymer bricks has also incorporated the use of copper mine tailings and cement kiln dust (CKD) (Ahmari and Zhang, 2013; Bennet et al., 2013). The work by Ahmari and Zhang (2013) showed that a significant improvement of unconfined compressive strength and durability could be attained when CKD was mixed with the copper tailings. The enhancement of unconfined compressive strength and durability was attributed to the improving effect of CKD on the dissolution of aluminosilicate species, formation of CaCO$_3$ and integration of Ca into the geopolymer gel (Ahmari and Zhang, 2013). Water absorption was however, found to, slightly increase due to the hydration of Ca in the added CKD.

Kiventerä et al. (2016) looked at the use of sulphidic gold mine tailings from a site in Northern Finland together with granulated blast furnace slag (GBFS) for the generation of a geopolymer product which could be used in the construction industry. The tailings were activated using NaOH solution and the GBFS was used as a co-binder. The results showed that the alkaline activation of the pure mine tailings in the presence of the GBFS co-binder allowed the production of specimens with sufficient compressive strength for potential use as a backfill in mining sites or raw material in the construction industry.

Although much research has been conducted on the application of mine tailings in the production of bricks, the commercial production of bricks from waste materials is still very limited. The possible reasons are related to the methods for producing bricks from waste materials, the potential in-use contamination from the applied waste materials, the absence of relevant standards, the economic potential and the slow acceptance of waste materials-based bricks by industry and public (Zhang, 2013). According to Zhang (2013), there is a significant need for further research and development, not only on the techno-economic and environmental aspects but also on standardization, government policy and public education related to waste recycling and sustainable development before a wide production and application of bricks from waste can be implemented.

### 3.3.3.8 Other Potential Applications

#### 3.3.3.8.1 Copper Tailings

Copper mine tailings have also been tested in the manufacture of tiles and glass-ceramic products. Marghussian and Maghsoodipoor (1999) investigated the production of unglazed tiles by mixing copper tailings with other raw materials. They observed that tiles containing about 40% copper tailings fired at 1025°C for 60 min showed good acid resistance and mechanical properties. In a related work by Çoruh et al. (2006), copper flotation waste was vitrified at 850°C for 2 h. The results showed that glass and glass-ceramic products of acceptable quality and durability could be produced by the vitrification process. Microstructure materials with improved physical and mechanical properties and with a wide range of potential applications especially in the construction industry were obtained after heat treatment at temperatures such as 650°C and 750°C.

Copper tailings have also been investigated for potential utilization and value addition as an extender for the production of paints (Saxena and Dhimole, 2016). Saxena and Dhimole (2016) indicated that copper tailings waste had a good potential to be used as an extender in paints with respect to oil absorption, pH and specific gravity. The copper tailings were found to be superior in enhancing the physicochemical properties such as film-like hardness, impact resistance, abrasion resistance and adhesion compared to the conventional extender.
3.3.3.8.2 Iron Tailings

Ceramic floor and wall tiles are some of the value-added products where industrial wastes such as iron ore tailings can be used as raw materials and as an inexpensive source of alkaline earth oxides for fast fired tile bodies. As already noted, the iron ore tailings are fine material composed mostly of silica, together with some fines of iron oxides, alumina and other minor minerals. This composition is similar to that of the clays used in the ceramic industry (da Silva et al., 2014). Further, since the tailings are in powder form, they require less grinding time, providing a significant saving on energy costs. In addition, if tailings have a high silicon, potassium and sodium content they could be used as raw materials for glass production. These are all alternative approaches to a cost-effective solution in managing tailings of iron ore and controlling environmental pollution.

Das et al. (2000, 2012) and da Silva et al. (2014) have reported on the possibility of using iron ore tailings as one of the raw materials for ceramic floor and wall tile bodies. Iron ore tailings used in this study contained high percentages of silica and this was noted to contribute advantageously to favourable properties in the development of ceramic tile compositions. The iron ore tailings could be used to a maximum of 40 wt.% and the high silica content was found to favour the formulation of tile body compositions. These tiles were found to have high strength and hardness compared to conventional tiles and also noted to conform to most of the EN standards.

3.3.3.8.3 PGM Tailings

Beside the reprocessing of the PGM tailings for precious metal recovery; recent research has shown the feasibility of the utilization of the tailings generated during the processing of PGM ores in South Africa to potentially sequester significant amounts of CO$_2$ through the mineral carbonation of the waste material. A scoping study by Vogeli et al. (2011) on the potential application of the Bushveld PGM tailings in South Africa showed that these tailings alone have the potential capacity to store 14 Mt of CO$_2$ per annum. The characteristics of the Bushveld PGM tailings are potentially suited for mineral carbonation due to the vast quantities of fine-grained Ca–Mg–Fe-bearing silicate waste material (Meyer et al., 2014). The main advantage of mineral carbonation compared to the other proposed CO$_2$ storage technologies is that it currently represents the only known form of permanent storage with environmentally benign carbonation products (Lackner et al., 1995; Hietkamp et al., 2008).

3.3.4 Summary

The review and information given in this section indicates that there are many opportunities for the utilization of tailings in metal producing and alternative manufacturing industries. These envisaged modes of use of the tailings could significantly reduce the volumes of tailings and could contribute to the sustainability of the mining sector and reduce penalties imposed on mines for waste accumulation. It has also been noted that the largest volume of waste utilization is being realized in the building and construction industry. This is largely because not much material pretreatment is required before its application. However, there has also been a significant increase in the reprocessing of waste materials for metal recovery arising possibly due to the increase in the monetary value of the metal and also the development of new technologies that can treat much lower grade material.
3.4 Acid Mine Drainage

3.4.1 Formation of Acid Mine Drainage

Acid mine drainage (AMD) is a severe environmental pollutant that can contaminate surrounding soil, groundwater and surface water (Higginson and Wheeler, 2010; Pozo-Antonio et al., 2014), thus affecting plant and animal life (Chattopadhyay and Chattopadhyay, 2013). Basically, AMD is characterized as low pH water with elevated concentrations of sulphates, iron and non-ferrous metals whose profile depends on the originating mineral deposit types (Kontopouls, 1988; Sheoran and Sheoran, 2006; Obreque-Contreras et al., 2015). The AMD may be generated from mine waste rocks or tailings or mine structures such as active or closed or abandoned pits and underground workings. A generalized conceptual model of sources, pathways and receiving environments is shown in Figure 3.5. These sources, pathways and receiving environments vary by commodity, climate, mine facility and mine phase (INAP, 2012). It must also be noted that the causes of AMD are not only limited to the mining industry, but can also occur where earthmoving processes have taken place such as in highway and tunnel construction and other deep excavations (Skousen, 1995; Skousen et al., 1998; Zdun, 2001; INAP, 2012). Basically, any activity that disturbs mineralized materials can lead to AMD (Simate and Ndlovu, 2014). In fact, the phenomenon is termed acid rock drainage (ARD) when it occurs naturally without human intervention (Chattopadhyay and Chattopadhyay, 2013).

The formation of AMD is a function of many factors including geology, hydrology, temperature and location (Chattopadhyay and Chattopadhyay, 2013). However, the chemistry of AMD generation is fairly straightforward (Costello, 2003; Manders et al., 2009) and results from a series of complex geochemical and microbial reactions when water comes in contact with sulphide-containing minerals such as pyrite (FeS₂) in the presence of oxygen (Sheoran et al., 2011). Ideally, AMD is produced through a series of reactions when minerals containing reduced forms of sulphur (S) are exposed to oxygen and water (Obreque-Contreras et al., 2015).

Generally, the process that produces AMD is well-illustrated and explained by using the reaction pathways of the oxidation of FeS₂, which is one of the most common sulphide minerals (Banks et al., 1997; Akcil and Koldas, 2006; Ruihua et al., 2011). According to Akcil and Koldas (2006), the initial and most important pyrite (or sulphide) oxidation

reaction that occurs in the presence of atmospheric oxygen produces dissolved iron, sulphate and hydrogen (Equation 3.1).

\[ 2\text{FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{SO}_4^{2-} + 4\text{H}^+ \]  

(3.1)

Oxygen dissolved in water can also result in pyrite oxidation, but due to its limited solubility in water, this process is much less prominent (INAP, 2012). Reaction 3.1 can also occur ‘biologically’ (i.e. mediated through microorganisms), and such reactions have been discussed by many researchers (Eligwe, 1988; Boon et al., 1995; Fowler et al., 2001). Nevertheless, such mechanisms have been replaced by two ‘indirect’ mechanisms (termed the thiosulphate mechanism and polysulphide mechanism) with no evidence for a ‘direct’ biologically mediated process (Schippers et al., 1996; Schippers and Sand, 1999; Hanford and Vargas, 2001; Sand et al., 2001). Figure 3.6 is an illustration of the thiosulphate and polysulphide mechanisms. The thiosulphate mechanism involves solely the chemical reaction of ferric iron with acid-insoluble metal sulphides (FeS₂, MoS₂ and WS₂) producing thiosulphate, while the polysulphide reaction mechanism involves the attack of acid soluble sulphides (ZnS, NiS, CoS, CuFeS₂ and PbS) by ferric iron and protons (Schippers and Sand, 1999). Readers are referred to Schippers et al. (1996), Schippers and Sand (1999), Hanford and Vargas (2001) and Sand et al. (2001) for detailed discussions of the two mechanisms.

In a sufficiently oxidizing environment (dependent on \( \text{O}_2 \) concentration, \( \text{pH} \) greater than 3.5, bacterial activity), ferrous iron (\( \text{Fe}^{2+} \)) released in Equation 3.1 may be oxidized to ferric iron (\( \text{Fe}^{3+} \)) according to the following reaction (Blowes et al., 2003; Akcil and Koldas, 2006):

\[ 4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \leftrightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O} \]  

(3.2)

If oxygen is low, reaction 3.2 will not occur until the pH reaches 8.5 (Fripp et al., 2000). In general under many conditions, reaction 3.2 is the rate-limiting step in pyrite oxidation because the conversion of ferrous to ferric is slow at pH values below 5 under abiotic conditions.

**FIGURE 3.6**

conditions (Skousen et al., 1998). The oxidation of Fe$^{2+}$ to Fe$^{3+}$ can also occur biologically and such reactions have been extensively discussed in literature (Schippers et al., 1996; Schippers and Sand, 1999; Simate and Ndlovu, 2014).

Aqueous Fe$^{3+}$ ions produced in reaction 3.2 can also oxidize pyrite according to the following reaction:

$$\text{FeS}_2 + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (3.3)$$

Reaction 3.3 is considerably faster (2–3 orders of magnitude) than the reaction of pyrite with oxygen and generates substantially more acid per mole of pyrite oxidized (Ritchie, 1994; Dold, 2010; INAP, 2012). In fact, Fe$^{3+}$ ions resulting from the oxidation of Fe$^{2+}$ ions are recognized as a more potent oxidant than oxygen even at circumneutral pH (Zdun, 2001). Luther (1987) attributed this effect to the more efficient electron transfer of Fe$^{3+}$ compared to oxygen. This molecular orbital study by Luther (1987) is consistent with pyrite oxidation data obtained by McKibben and Barnes (1986) and Moses et al. (1987). However, it must be noted that reaction 3.3 is limited to conditions in which significant amounts of dissolved Fe$^{3+}$ ions occur (i.e. acidic conditions) (INAP, 2012). Studies have shown that at pH values between 2.3 and 3.5, Fe$^{3+}$ ions formed in reaction 3.2 may precipitate as Fe(OH)$_3$ (and to a lesser degree as, jarosite, H$_3$OFe$_3$(SO$_4$)$_2$(OH)$_6$), leaving little Fe$^{3+}$ in solution (for pyrite oxidation) while simultaneously lowering pH (Blowes et al., 2003; Akcil and Koldas, 2006) as shown in reaction 3.4.

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow 4\text{Fe(OH)}_3(s) + 3\text{H}^+ \quad (3.4)$$

If pH is less than 2, Fe$^{3+}$ ion hydrolysis products like Fe(OH)$_3$ are not stable and Fe$^{3+}$ remains in solution (Dold, 2010), thus it is available for oxidizing additional pyrite.

It must be noted that other sulphide minerals are also susceptible to oxidation thus, releasing elements such as aluminium, arsenic, cadmium, cobalt, copper, mercury, nickel, lead and zinc into the water flowing through the mine waste (Blowes et al., 2003). However, not all sulphide minerals generate acidity when being oxidized (INAP, 2012). As a general rule, iron sulphides (pyrite, marcasite, pyrrhotite), sulphides with molar metal/sulphur ratios < 1 and sulphosalts (e.g. enargite) generate acid when they react with oxygen and water. Sulphides with molar metal/sulphur ratios = 1 (e.g. sphalerite, galena, chalcopyrite) tend not to produce acidity when oxygen is the oxidant (INAP, 2012). However, when aqueous Fe$^{3+}$ ions are the oxidant, all sulphides are capable of generating acidity. It must also be noted that the oxidation rates vary among sulphide minerals, and research studies have shown that reactivity decreases in the order marcasite → pyrrhotite → sphalerite-galena → pyrite-arsenopyrite → chalcopyrite → magnetite (Kwong and Ferguson, 1990; Jambor, 1994; Lapakko, 2002; Dold, 2010). The oxidation of these minerals will not be discussed any further in this chapter as they have been extensively covered elsewhere (e.g. see Blowes et al., 2003; Dold, 2010; Simate and Ndlovu, 2014).

### 3.4.2 Prevention and Mitigation of Acid Mine Drainage

Environmental damage or pollution associated with AMD is mainly characterized by a decrease in pH and/or elevated concentrations of heavy metals in nearby waters and soils (Costello, 2003). The hazardous effects of such low pH and heavy metals on the health of humans, wildlife, plants and aquatic species have already been discussed in Chapter 2. As AMD and its hazardous effects threaten the environment, a number of measures aimed at
preventing (or minimizing) and mitigating its impact on the environment have been developed (Johnson and Hallberg, 2005). Two categories of AMD control technologies are (1) source control (or prevention) techniques and (2) migration control and/or treatment (or mitigation) techniques.

### 3.4.2.1 Source Control Techniques

Source control techniques are preventive methods that are directed towards controlling the formation of AMD at the source (Egiebor and Oni, 2007; Luptakova et al., 2010). They are based on preventing oxygen and/or water into the system (Skousen et al., 1998; Kuyucak, 1999, 2002; Johnson and Hallberg, 2005) or inhibiting the activity of sulphide-oxidizing microorganisms (Kleinmann, 2006). In other words, preventive techniques act on any of the three elements that are essential in the formation of acidic waters: oxygen, water and oxidizing microorganisms (Pozo-Antonio et al., 2014). As shown by reactions 3.6 through 3.9, oxygen and water are two of the three principal reactants (Skousen et al., 1998). Therefore, removing water (for example) by pumping it out before it contacts pyritic material may minimize the formation of acidic products. In addition, the control and prevention methods which aim to eliminate sulphide oxidation can be achieved by separating sulphide minerals from the waste (Kuyucak, 2002).

Table 3.3 shows some of the various source control techniques that have been evaluated to prevent or minimize the generation of AMD (Kuyucak, 2002; Johnson and Hallberg, 2005). Ideally, these methods can be categorized as (1) barrier methods, methods that are intended to isolate sulphide minerals from weathering reactants or from the hydrologic transport system; (2) chemical methods, methods that alter the composition of AMD solutions, limit reactant availability or serve to passivate the sulphide mineral surfaces so as to limit oxidation and (3) bacterial inhibition methods, methods that represent a class of chemical treatments that disrupt the biologically catalysed cyclic

<table>
<thead>
<tr>
<th>Source Control Measures</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control of water migration</td>
<td>Water is intercepted and diverted away to prevent it from passing through the waste materials with the potential to form AMD.</td>
</tr>
<tr>
<td>Flooding/sealing of underground mines</td>
<td>Sealing the mine to prevent water and air infiltration.</td>
</tr>
<tr>
<td>Underwater storage of mine tailings</td>
<td>Because oxygen has a very low solubility and diffusion rate through water, almost four orders of magnitude less than in air, the oxidation of reactive wastes can be minimized by depositing and storing sulphide-bearing waste underwater.</td>
</tr>
<tr>
<td>Land-based storage in sealed waste heaps</td>
<td>Dry covers, caps and seals (incorporating an organic layer) used to isolate or encapsulate sulphide-bearing waste, thus limiting the access of either oxygen or water, or both.</td>
</tr>
<tr>
<td>Blending of mineral wastes</td>
<td>Blending acid-generating and acid-consuming materials.</td>
</tr>
<tr>
<td>Application of anionic surfactants</td>
<td>Use of anionic surfactants as bactericide inhibit bacterial activity that catalyse the conversion of ferrous iron and, subsequently, prevent acid generation.</td>
</tr>
<tr>
<td>Coating of certain mine wastes</td>
<td>Coating involves the leaching of waste with a phosphate solution containing hydrogen peroxide. Hydrogen peroxide oxidizes the surface portion of the pyrite and releases iron oxides so that phosphate precipitation forms a passive surface coating.</td>
</tr>
</tbody>
</table>

oxidation processes (Kleinmann, 2006). Nevertheless, despite several years of research, attempts to prevent AMD generation have proven to be practically and extremely difficult (Dinardo et al., 1991; Johnson and Hallberg, 2005).

### 3.4.2.2 Migration Control and/Treatment Methods

Migration control and/or treatment methods or processes generally require pH adjustment, oxidizing or reducing (redox) conditions and/or stabilization of wastes. The migration control and/or treatment techniques can be classified as (1) traditional methods and (2) innovative methods. These two categories are also broadly termed as mitigation techniques because they are directed towards the treatment of the resulting drainage (Egiebor and Oni, 2007; Luptakova et al., 2010; Simate and Ndlovu, 2014). In other words, these are corrective techniques that are used to purify the acidic waters produced (Pozo-Antonio et al., 2014). They are conceptually opposed to the preventive techniques, whose main objective is to avoid the formation of the acidic waters. Furthermore, corrective techniques are applied without distinction to underground or surface mines (Pozo-Antonio et al., 2014). The migration control techniques have been extensively studied and reported elsewhere (Gazea et al., 1996; Skousen et al., 1998; Fripp et al., 2000; Costello, 2003; Johnson and Hallberg, 2005; Kalin et al., 2006; Egiebor and Oni, 2007; Caraballo et al., 2011) and thus are only discussed briefly in this chapter.

#### 3.4.2.2.1 Traditional Techniques

Traditional or conventional techniques are methods that follow the pattern of an ordinary wastewater treatment plant, and are often referred to as ‘active’ treatment methods (Costello, 2003). These methods rely on conventional, well-recognized technology to raise pH or create redox conditions. Basically, these treatment systems involve treating AMD with alkaline chemicals to raise pH, neutralize acidity and precipitate metals (Skousen et al., 1998).

A variety of methods fall in this category of ‘active’ techniques, but the predominant one is the ODAS (O = oxidation, DA = dosing with alkali and S = sedimentation), which is similar to that of traditional wastewater treatment plants (Younger et al., 2002; Costello, 2003; Trumm, 2008, 2010). Although the most common order of treatment in industrial wastewater treatment systems is ODAS, for the treatment of AMD, the most common order followed is DAOS (Younger et al., 2002; Trumm, 2008). Dosing with alkali is typically the first step in AMD treatment followed by oxidation and sedimentation (Trumm, 2008). Ideally, the DAOS steps are followed in AMD treatment because oxidation rates for dissolved metals in reduced form such as Fe$^{2+}$ are strongly influenced by pH (Stumm and Morgan, 1996), therefore, it is beneficial to raise the pH prior to the oxidation step in the treatment of AMD (Trumm, 2008). In other words, the main goal of the dosing with alkali step is to add enough neutralizing agent so as to raise the pH and to lower the concentrations of dissolved metals by forming metal hydroxides and oxyhydroxides (Trumm, 2008, 2010). On the other hand, the goal of the oxidation step is to ensure reduced metals such as Fe$^{2+}$ and Mn$^{2+}$ are oxidized to Fe$^{3+}$ and Mn$^{4+}$, respectively, so that they can form hydroxide, oxide and carbonate precipitates and be removed from AMD (Skousen et al., 2000; Younger et al., 2002). However, the oxidation step may not be necessary if the metals are already highly oxidized through the dosing with alkali step (Trumm, 2008, 2010). Sometimes a pretreatment step such as sedimentation precedes DAOS so as to reduce the concentration of total suspended solids (TSS) which can affect the treatment system performance (Trumm, 2008).
Figure 3.7 is a basic flowsheet for selecting a site-specific ‘active’ treatment system for AMD (Trumm, 2008, 2010). As can be seen from Figure 3.7, the selection of such a system is influenced by a number of factors, including TSS content, Mn concentration (mg/L), flow rate (L/s), Fe concentration (mg/L) and the available land area (Trumm, 2008). Once an ‘active’ treatment system has been selected, a computer program such as AMDTreat can be used to design specific components of the system and to determine potential costs (Rajaram et al., 2001; Means et al., 2003; Trumm, 2008, 2010).

Other traditional or ‘active’ methods that are occasionally used for AMD treatment include, (1) sulphidization, (2) biosedimentation, (3) sorption and ion exchange and (4) membrane processes like filtration and reverse osmosis (Younger et al., 2002; Costello, 2003; Trumm, 2010).

3.4.2.2.2 Innovative Techniques

Innovative is defined in the Cambridge English Dictionary as ‘featuring new methods or advanced and original’, and according to Costello (2003), a variety of ‘passive’ treatment methods have become the most dominant innovative treatment techniques. Passive treatment systems do not require continuous chemical inputs, but take advantage of naturally occurring chemical and biological processes to treat AMD (Skousen et al., 1998). In other words, ‘passive’ treatments techniques are methods that treat AMD (or wastewater in general) using enhanced natural processes, in-situ, and require minimal upkeep (Hedin et al., 1994; Younger et al., 2002; Costello, 2003).

Based on the chemistry of AMD generation (i.e. an oxidation process, which results in the dominant contaminant, iron, being present in two states, Fe$^{2+}$ and Fe$^{3+}$), remediation of AMD using ‘passive’ technologies can be classified into two broad categories: oxidizing and reducing strategies (Trumm, 2010). Ideally, the choice between the two strategies is typically based on the water chemistry (mainly dissolved oxygen [DO] content and Fe$^{2+}$/Fe$^{3+}$ ratio). For AMD which is highly oxidized (DO level at saturation and all iron as Fe$^{3+}$), the oxidizing strategy is most appropriate; for AMD with low DO and all iron existing as Fe$^{2+}$, the reducing strategy is usually recommended. However, site limitations, such as available land area, climate and topography, may limit the use of certain systems (Trumm, 2010).

Oxidizing systems remove iron from the AMD by continuing the oxidation process so that all Fe$^{2+}$ is oxidized to Fe$^{3+}$, and once the pH has been raised sufficiently, the iron precipitates out of the AMD as ferric hydroxide (Fe(OH)$_3$). Typical remediation systems that employ the oxidizing strategy are open limestone channels (OLCs), open limestone drains (OLDs), limestone leaching beds (LLBs), slag leaching beds (SLBs) and diversion wells (DWs) (Trumm, 2010). The OLCs and DWs typically require a steep topography in order to generate the necessary aeration and to prevent armouring of limestone by metal hydroxides, which can inhibit the dissolution of limestone (Ziemkiewicz et al., 1997; Trumm, 2010).

As for the reducing systems, the AMD oxidation process is reversed, such that iron and sulphate are reduced, forming compounds like FeS$_2$, FeS and H$_2$S (Trumm, 2010). In this way, dissolved iron and sulphate are all removed from the AMD at the same time. Typical remediation systems that employ the reducing strategy are anaerobic wetlands; anoxic limestone drains (ALDs); bacteria-based sulphate-reducing bioreactors (SRBRs), also known as biogeochemical reactors (BGCRs) and successive alkalinity producing systems (SAPS), also known as vertical flow wetlands (VFWs) or reducing and alkalinity producing systems (RAPS) (Trumm, 2010).
Mining and Beneficiation Waste Production and Utilization

FIGURE 3.7

3.4.3 Opportunities in Acid Mine Drainage

While a wide range of technologies are available for treating AMD before discharge, most of these technologies consider AMD as a nuisance that needs to be quickly disposed of after minimum required treatment. However, in the recent past, there has been an emerging worldwide paradigm towards environmental responsibility and sustainable development. In fact, the economic sustainability of any AMD remediation system is a factor that is becoming increasingly critical in decision-making (Johnson and Hallberg, 2005). Indeed, significant attention should now be directed towards the recovery of industrially and economically useful materials (Simate and Ndlovu, 2014). In fact, when the value of treated water and by-products exceeds the cost of treatment, it is feasible to create enterprises that will provide economic benefits while dealing with the environmental problem (Simate and Ndlovu, 2014). Therefore, this section of Chapter 3 focuses on the recovery of valuable and saleable products such as metals, water, acid and pigments from AMD.

3.4.3.1 Recovery of Metals

The removal of metals as hydroxide precipitates from AMD using alkaline reagents (e.g., NaOH, etc.) has been the most widely used treatment method (Johnson and Hallberg, 2005; Balintova and Petrilakova, 2011). However, this technique is slowly losing popularity due to large volumes of hazardous concentrated sludge generated that require further treatment and controlled final disposal (Macingova and Luptakova, 2012). The other drawback of hydroxide precipitation is that selective extraction of metals is very difficult (Simate and Ndlovu, 2014).

A recent and suitable alternative method recovers metals from AMD in the form of sulphides. The use of sulphides not only allows the production of effluents with metal concentrations in the order of magnitude of ppm and ppb, but also gives the possibility of precipitation at low pH and selective precipitation for metal reuse (Sampaio et al., 2009). Sulphide precipitation can be effected using either solid (FeS and CaS), aqueous (Na₂S, NaHS, NH₄S) or gaseous sulphide sources (H₂S) (Lewis, 2010). There is also the possibility of using the degeneration reaction of sodium thiosulphate (Na₂S₂O₃) as a source of sulphide for metal precipitation (Lewis, 2010). In a study by Sampaio et al. (2009), Cu was continuously and selectively precipitated from Zn using Na₂S. Selective precipitation was based on the control of pS (= −log [S²⁻]) and pH. Here, having the solubility product defined as $K_{SP} = (M^{2+})(S^{2-})$, it means that different sulphide concentrations (S²⁻ potentials) are required to precipitate different metals. Therefore, the addition of sulphide to selectively precipitate heavy metals can be controlled using an ion selective electrode for sulphide (S²⁻), a so-called pS electrode (Sampaio et al., 2009). In this study, the selective precipitation of Cu from Zn was achieved at pS and pH of 25 and 3, respectively.

Another promising approach to the sulphide precipitation method uses sulphate-reducing bacteria (SRB) at anaerobic conditions to generate sulphide. The generation of sulphide by SRB is a favourable method that eliminates safety concerns related to the handling, transportation and storage of precipitating agents. The other advantage of the process is that it uses sulphate which is also present in the AMD. Using discrete chemical and biological stages, Macingova and Luptakova (2012) selectively removed Fe, Cu, Al, Zn and Mn from AMD in a selective sequential precipitation (SSP) process. In this process, Fe was completely removed in two steps by oxidizing ferrous iron using hydrogen followed by precipitation using sodium hydroxide (Macingova and Luptakova, 2012). In the initial stage, a partial precipitation of Fe was achieved due to a decrease in pH during iron oxidation. In the biological stage, sulphate-reducing bacteria were used to produce hydrogen.
sulphide that was later transported to the contactor filled with AMD (in the chemical stage) where the precipitation of metal sulphide occurred. After the filtration of precipitate, the filtrate pH was adjusted to a higher value using sodium hydroxide. The pH adjustment simultaneously precipitated metal hydroxides. After the filtration of metal hydroxide precipitates, the filtrate was returned to the contactor and the whole process was repeated at the higher pH value. Table 3.4 shows the results obtained (Macingova and Luptakova, 2012; Simate and Ndlovu, 2014). As can be seen from the table, the selective recovery of various metal precipitates was achieved.

Adsorption is another method used for the recovery of heavy metals from aqueous solutions and has evolved as the preferred method in many applications (Rao et al., 2007; Nagpal et al., 2013). Most of the adsorbents used in these studies are highly porous materials, providing adequate surface area for adsorption (Hu et al., 2006). However, with the advent of nanotechnology, various types of nanomaterials with large surface areas and small diffusion resistance have been developed and are now receiving considerable attention in water treatment (Zhang, 2003; Hu et al., 2006; Simate, 2012; Simate et al., 2012). For example, several studies have been carried out to assess the technical feasibility of various kinds of raw and surface oxidized carbon nanotubes (CNTs) for the sorption of various metals from aqueous solutions (Rao et al., 2007). The sorption/desorption studies showed that CNTs could be regenerated and reused consecutively several times without significant loss in adsorbent capacity signifying its appropriateness for commercial application.

Some of the metals such as uranium, thorium, rare earth elements (REEs), gold, silver, PGMs, chromium, copper, zinc, nickel, cobalt and tungsten have been recovered and purified on an industrial scale by means of ion exchange (Hubicki and Kołodyńska, 2012). Ion exchange is defined as the exchange of ions between the substrate and surrounding medium (Hubicki and Kołodyńska, 2012). Depending on the type of functional groups, ion exchangers may be classified as strongly acidic, for example, sulphonate (–SO₃H); weakly acidic, for example, carboxylate (–COOH); strongly basic, for example, quaternary ammonium (–N⁺R₃); and weakly basic, for example, tertiary and secondary amine (–N⁺R₂H and –N⁺RH₂) (Hubicki and Kołodyńska, 2012). There are also amphoteric exchangers, which, depending on the pH of the solution, may exchange either cations or anions. These ion exchangers are also called bipolar electrolyte exchange resins (BEE) or zwitterionic ion exchangers (Nesterenko and Haddad, 2000; Hubicki and Kołodyńska, 2012).

In recent past, a method termed cyclic electrowinning/precipitation (CEP) which combines precipitation and electrowinning was developed (Brown University, 2011). In this method, the concentration of metal cations is increased in the first stage followed by electrowinning to recover and separate the metals from wastewater in the second stage. Basically, the operations are as follows: In the first unit the metal-laden water is fed into a

---

**TABLE 3.4**

<table>
<thead>
<tr>
<th>Step</th>
<th>pH</th>
<th>Reagent</th>
<th>Removed metals</th>
<th>Proportion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.8</td>
<td>H₂O₂</td>
<td>Fe</td>
<td>99.99</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>NaOH</td>
<td>Fe</td>
<td>99.99</td>
</tr>
<tr>
<td>3</td>
<td>3.7</td>
<td>H₂S</td>
<td>Cu</td>
<td>99.99</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>NaOH</td>
<td>Al, Zn</td>
<td>98.94:1.05</td>
</tr>
<tr>
<td>5</td>
<td>5.0</td>
<td>H₂S</td>
<td>Zn</td>
<td>99.99</td>
</tr>
<tr>
<td>6</td>
<td>9.5</td>
<td>NaOH</td>
<td>Mn</td>
<td>99.99</td>
</tr>
</tbody>
</table>

tank in which an acid (e.g. H₂SO₄) or a base (e.g. NaOH) is added to change the water pH, thus effectively separating the water from the metal precipitate which settles at the bottom. The clear water is siphoned off and more contaminated water is brought in. The pH swing is applied again, first re-dissolving the precipitate and then re-precipitating all the metals, thus increasing the metal concentration each time (Brown University, 2011). This process is repeated until the concentration of the metal cations has reached a point where electrowinning can be efficiently employed. When that point is reached it is taken to a second device called a spouted particulate electrode, where metal cations are converted to stable metal solids, so that they can be removed (Brown University, 2011). The tested heavy metals were cadmium, copper and nickel. The results showed that cadmium, copper and nickel were reduced to 1.50, 0.23 and 0.37 ppm, respectively, way below the maximum contamination levels allowed by the EPA (Brown University, 2011). The main advantage of this process is that sludge is continuously formed and re-dissolved within the system so that none is left as an environmental contaminant.

Studies by Cheng et al. (2007, 2011) showed the development of an AMD fuel cell based on fuel cell technology, which was capable of abiotic electricity generation from synthetic AMD solutions. Test works conducted using synthetic solutions of similar composition and constituent as typical AMD solutions showed that the device (AMD fuel cell) could efficiently remove dissolved iron from the solution while also generating electricity at power levels similar to conventional microbial fuel cells (MFCs). Though the power and current yields were relatively low, improvements in fuel cell technology will possibly lead to more efficient power generation in the future.

### 3.4.3.2 Recovery of Water

Water is one of the most important substances on earth (Simate, 2016). All plants and animals need water to survive. If there was no water there would be no life on earth. Therefore, it is imperative that the millions of litres of water in AMD are recovered. To respond to this need, a large number of research studies have been devoted to the recovery of water from AMD. For example, the removal of heavy metals from AMD using the technologies discussed earlier simultaneously recovers water (Simate and Ndlovu, 2014). However, the processes have several disadvantages which include pH dependence, which means that the removal of the mixture of heavy metals cannot be achieved at a single pH level. Therefore, other technologies which are not pH-dependent, such as electrodialysis, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and membrane distillation, have been used to recover water from AMD (Simate and Ndlovu, 2014).

Among the different technologies, electrodialysis has been tested and proven to be an effective technology for water recovery from acidic solutions (Wisniewski and Wisniewska, 1999; Cifuentes et al., 2006, 2009; Agrawal and Sahu, 2009). Electrodialysis is a membrane separation process based on the selective migration of aqueous ions through an ion-exchange membrane as a result of an electrical driving force (Rodrigues et al., 2008). It allows the separation of anions and metallic cations, thus electrodialysis possesses the advantages of removing contaminant metals and simultaneously recovering water (Buzzi et al., 2013). A study by Buzzi et al. (2013) has shown that electrodialysis is suitable for recovering water from AMD with contaminant removal efficiencies that are greater than 97%. The recovery of water has also been studied in other acidic systems containing various metals (Wisniewski and Wisniewska, 1999; Agrawal and Sahu, 2009; Cifuentes et al., 2009; Benvenut et al., 2013). In all these studies electrodialysis has been found to be an effective method for water recovery.
Membrane distillation is another technique that has been used to recover water, and concentrate acid and metal values from mining wastewater and process solutions (Kesieme et al., 2012). This process is a combination of the conventional distillation and membrane separation processes (Shirazi et al., 2014a). Unlike other membrane separation processes which are driven by absolute pressure difference (e.g. reverse osmosis, nanofiltration and microfiltration) or an electrical potential gradient (e.g. electrodialysis) or concentration gradient (e.g. dialysis), membrane distillation is a thermally driven separation process that utilizes hydrophobic, microporous membranes as a contactor (Shirazi et al., 2014b). The driving force in the membrane distillation is the vapour pressure difference induced by the temperature difference across the hydrophobic membrane (Alkhudhiri et al., 2012). In other words, the temperature difference existing across the membrane results in a vapour pressure difference, thus vapour molecules are transported from the high vapour pressure side to the low vapour pressure side through the pores of the membrane (Tomaszewska, 2000).

Individual and/or combinations of microfiltration, ultrafiltration, nanofiltration and reverse osmosis membrane processes have also been studied for the recovery of both water and metals (Ahn et al., 1999; Garba et al., 1999; Zhong et al., 2007). For example, Vaclav and Eva (2005) used the reverse osmosis technique to recover good quality water from three different sources of AMD. Günther and Mey (2008) evaluated different water treatment technologies, including the membrane technology with the objective of treating AMD from a coal mine. The results showed that only the biological sulphate removal process and reverse osmosis membranes could be used to produce a high water recovery cost-effectively. Bhagwan (2012) studied the use of a high recovery precipitating reverse osmosis (HiPRO) process for the recovery of low salinity water from mine waters. The main advantage of the developed process is that it makes use of reverse osmosis to concentrate the water and produce supersaturated brine from which the salts can be released in a simple precipitation process.

### 3.4.3.3 Recovery of Sulphuric Acid

AMD is predominantly acidic due to high concentrations of sulphuric acid (Simate and Ndlovu, 2014). In fact, over the past five decades, assiduous efforts have been directed at remediating AMD through acid removal so as to reduce the impact of the acidic water on the environment and produce water suitable for reuse (Johnson and Hallberg, 2005; Simate and Ndlovu, 2014; Nleya et al., 2016). Indeed, apart from the production of reusable water and saleable metals, the recovery of sulphuric acid would also be used to offset the treatment costs (Simate and Ndlovu, 2014). Table 3.5 is a summary of the methods used to recover sulphuric acid from various wastewater solutions, including AMD, showing the recoveries, advantages and disadvantages of the processes (Nleya et al., 2016). Furthermore, a study by Nleya et al. (2016) critically evaluated the technical and economic feasibilities of the processes in Table 3.5 for application to AMD, and the results of the study are given in Table 3.6. Based on the technical and economic feasibility results in Table 3.6, the freeze crystallization and acid retardation processes are expected to be the most suitable technologies for acid recovery from AMD. Several studies on these processes have been conducted in the past, and their fundamentals are well documented (Etter and Langill, 2006; Kim, 2006; Özdemir et al., 2006; Tjus et al., 2006; Agrawal and Sahu, 2009). Furthermore, their use in commercial applications is widely recognized.

Another process, not included in Tables 3.5 and 3.6, which may be used to recover or concentrate sulphuric acid, is the membrane distillation process. Moreover, Tomaszewska (2000) used membrane distillation to recover hydrochloric acid from spent pickling liquors containing residual acid.
### TABLE 3.5

Summary of Methods Used for Sulphuric Acid Recovery

<table>
<thead>
<tr>
<th>Method</th>
<th>Solution Content</th>
<th>$\text{H}_2\text{SO}_4$ Recovery</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rectification</td>
<td>$\text{H}_2\text{SO}_4$, nitro compounds</td>
<td>$R = 98.3%$</td>
<td>Recovery of high purity acid</td>
<td>High energy consumption</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>High operating cost</td>
</tr>
<tr>
<td>Diffusion dialysis</td>
<td>$\text{H}_2\text{SO}_4$, $\text{AlH}_2\text{SO}_4$, Fe, V</td>
<td>$R = 82%-90%$ $R = 84%$</td>
<td>High acid recovery</td>
<td>Not efficient at low acid concentration</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, Ni</td>
<td>$R = 80%$</td>
<td>Low pay back period</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, rare earth sulphates</td>
<td>$R = 70%-80%$</td>
<td>Strong salt rejection</td>
<td></td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>$\text{H}_2\text{SO}_4$, Ni, $\text{H}_2\text{SO}_4$, Fe</td>
<td>$R = 80%-90%$ $R = 90%$</td>
<td>Clean acid product</td>
<td>High operating cost</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, Cu, Sb, As</td>
<td>$R = 80%-90%$ $R = 90%$</td>
<td>Reduced solid waste for disposal</td>
<td>Membrane fouling</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, Fe, Na</td>
<td>$R = \text{Up to} 99%$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid retardation</td>
<td>$\text{H}_2\text{SO}_4$, Fe, $\text{H}_2\text{SO}_4$, Fe</td>
<td>$R = 74%-96%$ $R = 96%$</td>
<td>Low operating cost</td>
<td>Increases product volume</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, Ni</td>
<td>$R = 70%-95%$</td>
<td>High acid recovery</td>
<td>High consumption of fresh water</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Small equipment size and space</td>
<td>Dilute acid product</td>
</tr>
<tr>
<td>Crystallization</td>
<td>$\text{H}_2\text{SO}_4$, Fe</td>
<td></td>
<td>Low cost</td>
<td>Risk of scale formation in crystallizer.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Reduced waste for disposal</td>
<td></td>
</tr>
<tr>
<td>Solvent extraction</td>
<td>$\text{H}_2\text{SO}_4$, $\text{CuH}_2\text{SO}_4$, Fe, Mn</td>
<td>$E = 75%-79%$ $E = 90%$</td>
<td>Can manage great volumes of solutions with high contents of toxic solutes</td>
<td>Chemicals used are hazardous</td>
</tr>
<tr>
<td></td>
<td>$\text{H}_2\text{SO}_4$, Zn</td>
<td>$E = 90%$</td>
<td>Clean acid product</td>
<td>Pretreatment is required to remove impurities</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Only physical separation</td>
<td>Difficulties in stripping from Cyanex 923</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High throughput with compact equipment</td>
<td>Co-extraction of Fe and Zn</td>
</tr>
</tbody>
</table>


Note: $R$, recovery; $E$, percentage extraction.
3.4.3.4 Uses of AMD Treatment Sludge

Despite widespread usage, one of the main drawbacks of the active treatment methods is the use of large amounts of chemicals needed to reduce metals to an acceptable level before discharge. Other disadvantages are its excessive sludge production that requires further treatment, increased costs, slow metal precipitation, poor settling, the aggregation of metal precipitates and the long-term environmental impacts of sludge disposal (Kurniawan et al., 2006). Therefore, in recent years, due to several disadvantages of AMD treatment as stated, concerted effort has been made to investigate the potential use of the sludge which would otherwise be disposed of in a landfill at significant costs. The succeeding sections focus on and cite some of the applications of the AMD treatment sludge, especially with reference to the publication by Simate and Ndlovu (2014).

3.4.3.4.1 Production of Iron Pigments

Studies have shown that the sludge obtained from AMD can be considered for the production of inorganic pigments (Hedin, 1998, 2003; Marcello et al., 2008; Michalkova et al., 2013), and magnetic particles like ferrites (Wei et al., 2008). To produce commercially usable iron oxides as raw material for the production of pigments, additives to ceramics, etc., the treatment of AMD using a two-step selective precipitation process was developed (Hedin, 1998, 2003). The two-step process that uses magnesium oxide and sodium hydroxide results in the ferrous and ferric oxyhydroxide sludge that can be thermally transformed to basic ferric pigment. A study by Hedin (2003), however, indicated that while the end product was of high quality, the costs associated with the process made the materials more costly to produce than mined oxides, although this may be offset when considering the high cost of hydrous ferric oxide disposal. Marcello et al. (2008) investigated the use of hydrous ferric oxides from active coal mine drainage treatment as pigment within ceramic tile glaze. Favourable results occurred when the ferrous hydrous oxides was blended with an industrial standard pigment.

Research by Cheng et al. (2007, 2011) has also shown that fuel cell technologies was not only used for simultaneous AMD treatment and power generation, but also generated iron oxide particles of sizes appropriate for use as pigments and other applications. As already discussed in Section 3.4, a fuel cell called an AMD fuel cell based on an MFC was developed and used during the process. During treatment, ferrous iron was oxidized in the anode chamber under anoxic conditions, while oxygen was reduced to water at the cathode. Ferrous iron was completely removed through oxidation to insoluble ferric iron and precipitated at the bottom of the anode chamber. The particle diameter of the iron oxides

### TABLE 3.6
Summary of Capital and Operating Expenditures of Proposed Process Routes

<table>
<thead>
<tr>
<th>Cost (US$)</th>
<th>Rectification</th>
<th>Diffusion</th>
<th>Dialysis</th>
<th>Electrodialysis</th>
<th>Solvent Extraction</th>
<th>Crystallization</th>
<th>Acid Retardation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed capital cost</td>
<td>1,193,165</td>
<td>381,780</td>
<td>1,523,478</td>
<td>442,956</td>
<td>407,268</td>
<td>307,973</td>
<td></td>
</tr>
<tr>
<td>Total estimated CAPEX</td>
<td>1,372,140</td>
<td>439,047</td>
<td>1,752,000</td>
<td>509,399</td>
<td>468,368</td>
<td>354,169</td>
<td></td>
</tr>
<tr>
<td>Total estimated annual OPEX</td>
<td>427,789</td>
<td>247,752</td>
<td>266,809</td>
<td>125,124</td>
<td>154,798</td>
<td>124,810</td>
<td></td>
</tr>
<tr>
<td>Estimated annual revenue</td>
<td>≈9,800</td>
<td>≈9,800</td>
<td>≈9,800</td>
<td>≈9,800</td>
<td>≈10,320</td>
<td>≈9,800</td>
<td></td>
</tr>
</tbody>
</table>

Waste Production and Utilization in the Metal Extraction Industry

could be controlled by varying the conditions in the fuel cell, especially current density, pH and initial ferrous iron concentration. Upon drying, the iron oxide particles were then transformed to goethite ($\alpha$-FeOOH).

3.4.3.4.2 Building and Construction-Related Materials

Many constituents in sludge are the same as those used in cement manufacturing. For example, calcite, gypsum, silica, Al, Fe and Mn are common raw materials for cement. Therefore, the components that make up AMD treatment sludge such as gypsum, calcite and ferrihydrite can be utilized as raw materials in the manufacturing of construction materials and other products. Levlin (1998) indicated that in order to avoid waste disposal, inorganic components in sludge can be used for the production of building materials. Research by Lubarski et al. (1996), found that the high aluminium content of sludge produced from the treatment of acidic drainage at some coal and gold mines could be used for the production of aluminous cement. Other studies have suggested that sludge can replace up to as much as 30% Portland cement in blended cement (Tay and Show, 1994). In these options, the utilization of sludge reduces the mining of raw materials for the production of building material.

3.4.3.4.3 Adsorbents in Industrial Wastewater Treatment

The standard treatment technology for the removal of impurities such as phosphorus from municipal wastewater involves dosing the wastewater with coagulants such as alum, ferric chloride or lime (Metcalf and Eddy, 1991; Parsons and Smith, 2008), but the costs of these reagents often make their use impractical or uneconomic for the low concentrations and high volumes often encountered in most wastewater. Therefore, it is necessary that alternative coagulants are sought. Given the wide range of studies that successfully removed phosphorous from wastewaters using iron and/or aluminium hydroxide sludges, Wei et al. (2008) hypothesized that the AMD sludge containing a mixture of iron and aluminium hydroxide precipitates would be a suitable medium for the adsorption of dissolved orthophosphate from solution. In other words, sludges produced by the neutralization of AMD could be used for phosphorus sequestration as it is composed primarily of aluminium and iron hydrous oxides, the same chemical forms produced when alum or ferric chloride is added to wastewater at near-neutral pH. In addition, research by Sibrell et al. (2009) and Sibrell and Tucker (2012) has shown that dried AMD sludge, or residuals can be used as a low-cost adsorbent to efficiently remove phosphorus from agricultural and municipal wastewaters. The phosphorus that has been adsorbed by the AMD sludge can later be stripped from the sludge and recycled into fertilizer, and the mine drainage sludge can be regenerated and reused for a number of additional applications.

Studies by Edwards and Benjamin (1989) have also shown that the iron ferrihydrite component of AMD sludge from lime treatment plants can be used as a highly effective adsorbent for the removal of metals from water streams. Similarly metal hydroxide sludge has also been used to remove carcinogenic dyes from wastewater (Netpradit et al., 2003).

3.5 Concluding Remarks

Mining and beneficiation operations produce several tonnages of waste annually. This waste is composed of broken rocks from open pits and underground mines; coarse mill rejects from screening and heavy media separation processes and fine mill tailings from
Mining and Beneficiation Waste Production and Utilization

screening, magnetic separation, flotation processes, etc. The volumes of waste produced in each category are dependent on the geologic characteristics of an ore body, the type of mining (underground versus open pit) and the metal being mined as well as the size of the mining operation. For example, less mine waste is produced from underground mining operations than from open-pit mining operations. Furthermore, less tailings are produced from underground mining as ore grades are higher and tonnages lower. Some of this waste is inert and consequently unlikely to be a significant environmental hazard apart from smothering river beds and the risk of collapse if stored in large quantities. Other fractions, in particular those generated by the non-ferrous metal mining industry, may contain large quantities of dangerous substances, such as heavy metals. However, the sheer volume and chemical composition of mining and beneficiation waste mean that where it is put and how it is managed is very critical.

This chapter discussed various examples of utilizing mining and beneficiation waste. Basically, the utilization of waste is an attractive alternative to disposal because disposal costs and potential pollution problems are reduced or even eliminated and resources are conserved. Some of the industrial uses of overburden and/or waste rock, for example, include use as an aggregate for asphalt roads, road fill, commercial sand-blasting and anti-skid surfacing of bridges. Other waste such as tailings can be used in the recovery of metals, manufacture of building and construction materials, glass and ceramics.

The chapter also showed that acid generation from the oxidation of sulphide minerals, such as pyrite and pyrrhotite, in mining and beneficiation wastes is one of the most significant issues facing the mining industry. The chapter highlighted some of the basic approaches that are normally employed in the controlling or mitigation of AMD, (1) source control where one of the major components of acid drainage formation is eliminated making the possibility of acid generation very small; (2) migration control where acid drainage can still occur, but measures are implemented that controls the migration of the generated acid and (3) treatment where the acid drainage is intercepted and treated. Measures 2 and 3 are interrelated, and thus are normally used interchangeably.

References


Waste Production and Utilization in the Metal Extraction Industry


