## CHAPTER 9.2

# Water Balance

David Love and Leendert (Leon) Lorenzen

## INTRODUCTION

The objective of this chapter is to explore the details of the water balance in the mining and mineral processing industry. This embraces the interaction between the supply of process water, the mining processes, and the environment with regard to effluent reuse or disposal of the resulting wastewater. Specifically, three main water streams are examined in some detail: process water, wastewater, and acid mine drainage. Examples of water treatment options are provided for the processing of gold, base metal, platinum, uranium ores, and coal.

### Process Water

Recently, the water balance in many sites has been restricted and confined from all directions. The quantity and quality of primary water supplies have become limiting. This has resulted in an increasing need to use relatively impure primary water sources to use higher proportions of recycle from tailings dams, thickener overflows, and dewatering processes. Effluent discharge guidelines have also become more stringent. Some mining and mineral processing operations now operate under zero water discharge conditions or are required to control effluent release under much stricter quality control.

Primary water supplies from bores containing high levels of salinity (including calcium, magnesium, and iron salts as potential precipitates) are being used in some remote areas. Treated sewage effluent water with relatively high concentrations (>1,000 mg/L) of total organic carbon (TOC) is being used at some sites for make-up water supply. The return of cyclone underflow from primary grind and regrind operations in several circuits introduces high levels of dissolved species from soluble mineral phases (e.g., pyrrhotite, siderite, brucite, and other metal hydroxides, sulfates, and carbonates).

Variability of pH, dissolved oxygen, suspended solids, and dissolved ionic species in recycle water streams (thickener overflow, tailings dam return) contribute to a varying process water quality. Total dissolved solids (TDS) levels may also be raised by reagent addition for pH control (e.g., lime) and TOC levels increased by recycled organics (e.g., depressants, dispersants, flocculants, collector decomposition products). This variability adds another level of complexity to managing the process water and the ore extraction processes.

### Wastewater Treatment

Figure 1 summarizes the groups of processes that are commonly used to treat wastewater on minerals industry sites, for the following main purposes:

- Recycle for specific end uses on-site
- Return to process water circuits
- Discharge off-site to a suitable environmental discharge point or to disposal

#### *Neutralization*

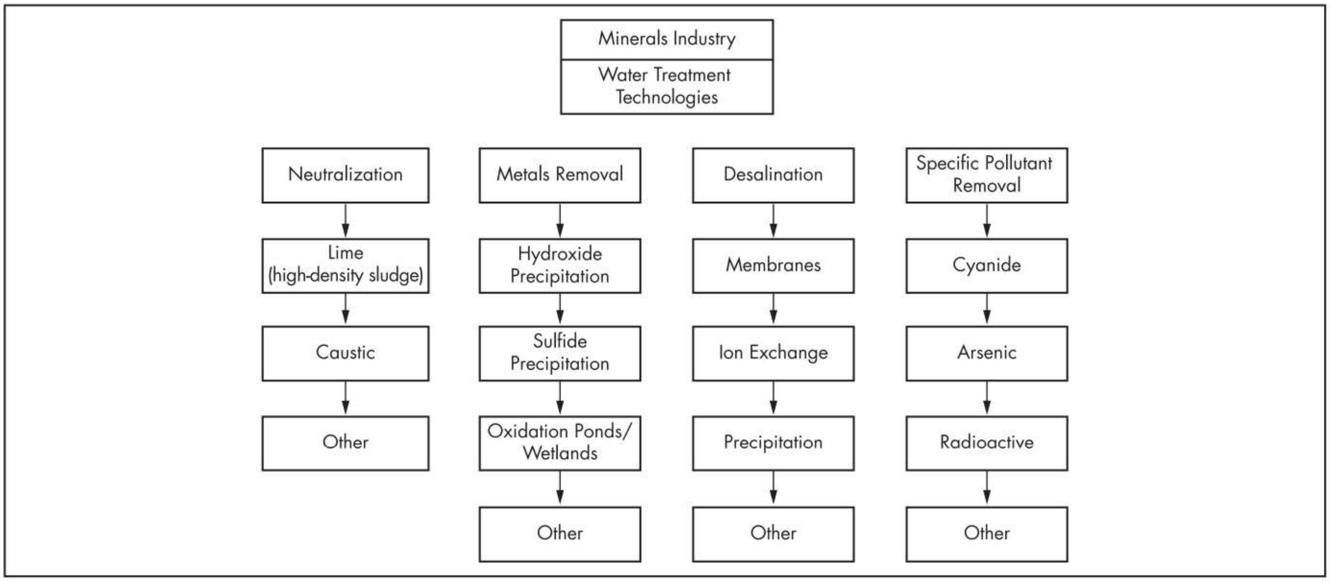
Lime is the most commonly used alkali for neutralization of the acidic wastewater streams that are often generated in mining sites. The net result of lime neutralization is the formation of metal precipitates such as hydroxides and carbonates. The high-density sludge (HDS) process has been commonly used for lime neutralization. The process features premixing of lime with recycled sludge and is operated at a pH of 10–11. The main attraction of the HDS process is the production of dense, high-solids-content waste sludge, which presents several benefits for waste disposal. Many variations of the HDS process have been developed over the years.

More recently, the use of limestone has become more common because it is lower in cost and overcomes some of the process constraints that are present with lime neutralization. Further innovation has been achieved by integration of neutralization and softening. In some cases, neutralization with caustic has been carried out, producing less sludge. This alternative is usually used for smaller facilities, because it is simpler to dose and has lower equipment costs.

#### *Metals Removal*

Mining wastewater often contains a range of dissolved and suspended metal contaminants. Some of these metals are dominant in the wastewater from the mining of certain ores, while other contaminants (e.g., iron) tend to be present in most wastewaters.

David Love, Principal Consultant & Director, Water Logics, Adelaide, Australia
Leendert (Leon) Lorenzen, Managing Director (Professor), Lorenzen Consultants, Mintrex (Stellenbosch Univ.), Perth, Australia (Stellenbosch, South Africa)



Source: Lorenzen 2015

**Figure 1 Process groups used to treat wastewater**

Most dissolved metal ions can be oxidized to their hydroxide forms. These hydroxides exhibit an inverted type of solubility curve that shows solubility decreasing as pH is increased until it reaches a minimum and then increasing again as the pH is raised further. By adjusting pH to that corresponding to the minimum solubility level, it is possible to achieve good removal of most metal ions by precipitation. However, the pH levels at which minimum hydroxide solubility takes place vary from metal ion to metal ion. This can often mean that several stages of neutralization are required to meet metal removal objectives.

In some cases, minimum hydroxide solubility levels are not low enough to meet target metal levels for specific uses. In this case, sulfide precipitation can be used to take advantage of the very low solubilities of metal sulfides. The solubility curves for metal sulfide do not exhibit inversion but continue to decrease as pH is increased. Because of costs and chemical handling safety issues, sulfide precipitation is usually used only when hydroxide precipitation will not meet the removal levels required.

Natural oxidation processes such as oxidation ponds and wetlands can also be used for dissolved and suspended metal reductions. This often requires large surface areas to give enough residence time for the slower oxidation rates that are involved.

### *Desalination*

It is common in mining wastewaters to have significant levels of dissolved cations and anions, resulting in the TDS levels being quite high. This can often create performance issues with the processing of ores, as discussed later. The reduction of TDS levels can be achieved by using semipermeable membranes (e.g., nanofiltration, reverse osmosis) or by adsorption of the ion on resins (ion exchange). For these processes, one or more stages of pretreatment are usually required to reduce contaminants (such as suspended solids) down to low enough levels to avoid fouling or other damage to the membranes or resins. A generic desalination flow sheet is shown in Figure 2.

These processes can produce high-quality treated water that is suitable for high-quality uses on-site. However, they also produce brine waste streams that are very high in TDS. These wastes can be problematic for storage on-site or for transport off-site for disposal. Treatment of these brine wastes can involve using concentration processes such as natural evaporation, thermal evaporation, and crystallization. In the case of thermal evaporation and crystallization, up to 90% of the water can often be recovered for use on-site.

### *Specific Contaminant Removal*

Where specific contaminants of concern are present, it may be necessary to target the treatment approach that is best to deal with removal of these contaminants. Examples include the removal of arsenic, cyanide, and uranium. Specific processes that are used will usually aim to remove significant levels of the contaminants of concern and to accept negligible removals of some other contaminants.

## Acid Mine Drainage

Acid mine drainage (AMD) refers to the outflow of acidic water from metal mines and coal mines. AMD can originate from many locations within the site, such as

- Drainage from underground workings,
- Runoff from open pit workings,
- Seepage from waste rock dumps,
- Drainage from mill tailings,
- Drainage from ore stockpiles, and
- Drainage from heap leach operations.

The primary issues of concern to the environment from these AMD wastes are acidity, metals, and sulfate. Some of the wastewaters sourced from mines are highly acidic, with pH levels of $\leq 5$, and laden with sulfate and metals. These are formed under natural conditions when the geologic strata-containing sulfide minerals (such as aluminum, iron, and manganese) are exposed to the atmosphere or to oxidizing environments.

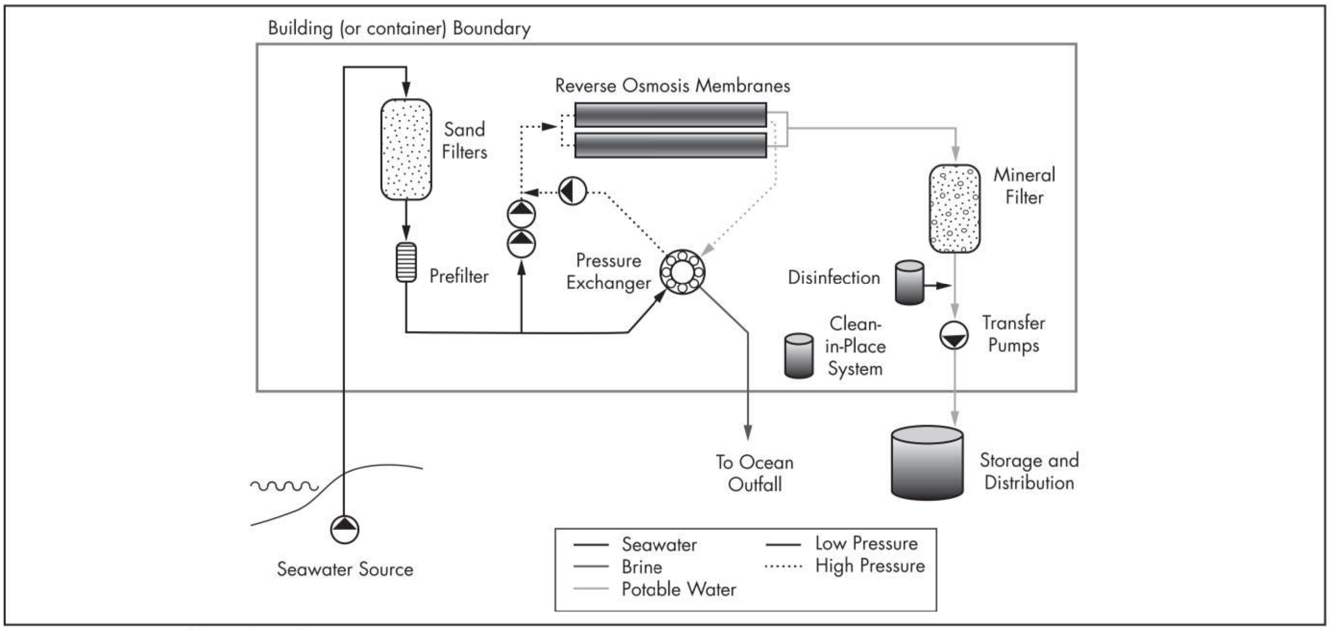


Figure 2 Generic flow sheet for treating seawater

## PROCESS WATER

Raw water used for mining processes can be sourced from underground bores or from surface supplies. It is common for this raw water to be mixed with recycled water arising from treated process water. In many cases, the recycling of process water is desirable both for plant operating reasons and for environmental protection. The main advantages are better use of process chemicals, together with the reduction of polluting species discharged to the environment. However, there are many possible process problems with using recycled process water. Recycling can have a negative impact on the performance of the mining processes, sometimes only becoming evident some months after commencement of the recycling. The resulting quality of the process water, arising from the final water balance, is site specific and dependent on several factors, including the following:

1. **Quality of the incoming raw water.** Because of the remoteness of most mining sites, a main supply of potable quality water is usually not available as a raw water source. Groundwater from a bore system or surface water from a lake or reservoir will likely be used for potable water, cooling, steam generation, and other applications where higher quality is important. In some cases, groundwater can be high in dissolved salts, and surface water can be contaminated with suspended solids and organics.
2. **Extent of effluent treatment to render suitable for recycle.** The processes will often generate a combined effluent stream that varies in quality and quantity over time. Some effluent streams may be suitable for treatment, making them acceptable for recycle back into the process water circuits. This recycle stream may be either sent directly to specific uses or blended with raw water to achieve the required process water quality.
3. **Process water quality limitations set by the mining process.** In the case of many mining processes, process water is in direct contact with the ores or minerals being processed. It forms an integral part of the extraction or treatment processes, and its quality can have a significant impact on process performance.

This section focuses on the effects of item 3 in the preceding list by discussing the specific limitations that the process itself places on the quality of the process water being used. These limitations vary significantly and depend on the type of mining and extraction processes being used.

### Gold Processing

For the extraction of gold, an alkaline cyanide solution (usually sodium cyanide or calcium cyanide) has commonly been used because of its high efficiency and relatively low cost. Dissolution of gold in dilute cyanide solutions (100–500 mg/L) is essentially an electrochemical process. The active cyanide ions react with the fine gold particles to produce a soluble gold cyanide complex $Au(CN)_2^-$.

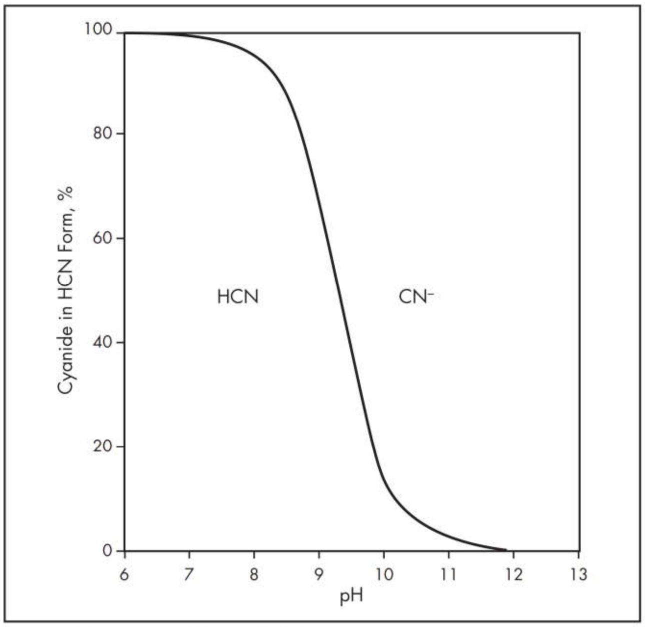
Cyanide is very reactive, forming ionic complexes of varying strengths with numerous other metal and alkali earth cations. The stability of these salts is dependent on the cation and on the pH. The formation of these complexes can tie up cyanide that would otherwise be available to dissolve gold. The cyanide ion can also preferentially combine with free sulfur or sulfide minerals in the ore to form thiocyanate compounds ($SCN^-$).

The key factors requiring consideration for the process water that is used for gold ore processing are pH, magnesium buffering, oxygen compounds, and hydrogen cyanide.

#### *pH*

In water, cyanide ions ($CN^-$) hydrolyze in the following reversible reaction to form hydrogen cyanide (HCN). HCN is a colorless liquid that is highly soluble in water, but its solubility decreases with increased temperature and under highly saline conditions.

$$CN^- + H_2O \leftrightarrow HCN + OH^- \qquad \textbf{(EQ 1)}$$



Source: Marsden and House 2009

**Figure 3 HCN and $CN^-$ as a function of pH**

The extent of hydrolysis of the cyanide ion is pH dependent, with the relative proportions of hydrogen cyanide (HCN) and cyanide ion ($CN^-$) shown in Figure 3. At neutral or acidic pH levels, most of the cyanide ions will be converted to HCN. At a pH of 9.36, 50% of the total cyanide ions that are present will be converted to hydrogen cyanide. When the solution pH is further increased to 10.3 or more, the amount of dissolution will be negligible, and the cyanide ions concentration will be dominant. A good resource is *The Cyanide Compendium* (Mudder et al. 2001).

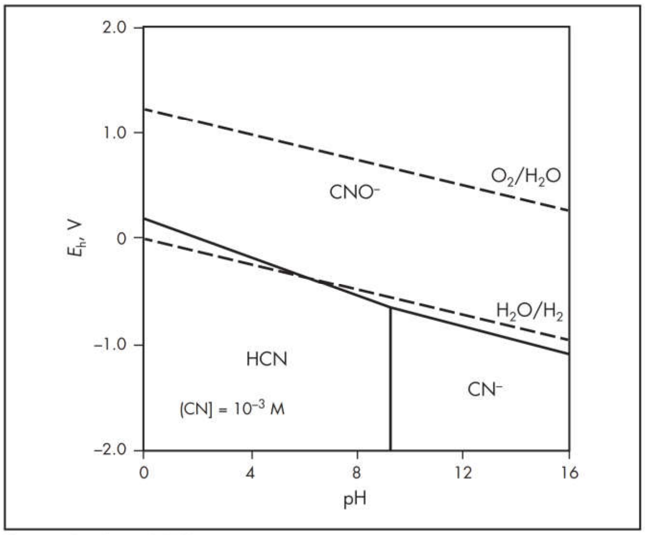
Equation 1 also shows that $OH^-$ ions are produced, which can increase the solution pH above its starting pH. However, if the process water is high in hardness, the high levels of magnesium ions present (sea and hypersaline waters) will remove the $OH^-$ ions by forming insoluble hydroxides. This results in an initial buffering of the solution pH in the range of about 8.8 to 9.5. This means that significantly higher dose rates of alkali will be required to overcome the buffering, as well as to raise the solution pH up to the desirable level of 10.3.

The leaching, or extraction capability, of a cyanide solution is determined by the free cyanide present rather than just the ionized species. The term *free cyanide* refers to both cyanide ions ($CN^-$) and hydrogen cyanide (HCN). Loss of free cyanide from the system can occur by the process of volatilization, where some of the HCN can be lost as a vapor.

The amount of cyanide that is lost by volatilization increases with

- Decreasing pH,
- Increased aeration of the cyanide solution,
- Increasing temperature,
- Ultraviolet (UV) radiation, and
- Increasing salinity.

Volatilization losses from leach tanks and tailings dams were investigated by Lotter (2005). Losses from the leach tanks were less than 10% of the cyanide losses when operating the leaching at normal pH levels. However, volatilization was much greater from tailings dams where climactic conditions on the surface of the dams played a significant role. Botz and Mudder (2000) developed a computer simulation to estimate the losses of free cyanide, weak acid dissociable (WAD) cyanide, and total cyanide due to dissociation, photolysis, and volatilization.



Source: Pourbaix 1974

**Figure 4 Pourbaix (Eh–pH) diagram for cyanide**

This relationship is specifically important because, in gold-cyanide extraction processes that are operated at or above a pH of 10.3, most of the free cyanide in the process slurry water will be present as $CN^-$ ions. Because the ratio of $HCN/CN^-$ is relatively low at this pH, the capacity for cyanide loss by volatilization is low. However, if the pH is decreased down toward 9.4 and less, the ratio of $HCN/CN^-$ increases substantially. As a result, cyanide loss by volatilization becomes more and more problematic, both with regard to the HCN emissions themselves as well as leaving less cyanide available for leaching.

The electrical potential in the leaching circuit can also play an important role in leaching kinetics of gold as well as the HCN and $CN^-$ formation (Figure 4). Thus, an operating control system that is capable of determining the total HCN, pH, and Eh is essential. The slurry may also be subject to other preconditioning such as preoxidation at the head of the circuit before cyanide is added, which will aid in keeping the pH higher.

### *Magnesium Buffering*

Water quality can have a significant impact on slurry pH and HCN formation. If the water supply has high levels of dissolved magnesium salts, it can be very expensive to raise the process pH higher than 9.0 because of the natural buffering action of magnesium (Figure 5). This can force gold processing plants to operate at lower leach pH values, resulting in higher cyanide consumption rates. This leaves only a small margin for error on the pH process control.

The high sulfate levels in the process water can also promote the formation of gypsum, which leads to significant scale issues such as screen blockages, carbon fouling, and pipe blockages. Lower magnesium levels in the feed process water are advantageous from both a chemical cost and extraction

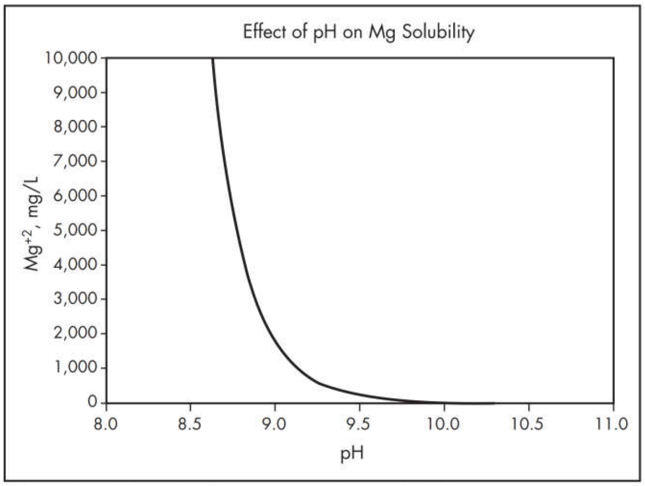


**Figure 5 Effect of pH on magnesium solubility**

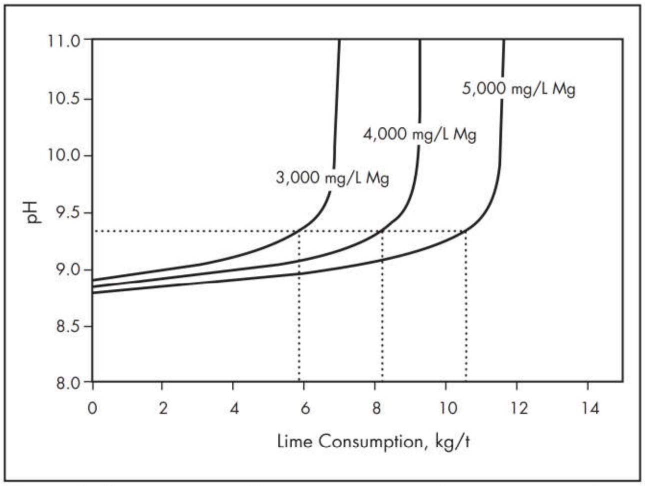


**Figure 6 Lime consumption versus magnesium concentration**

efficiency viewpoint. In certain cases, the removal of some of the magnesium by ion exchange treatment of the process feedwater may be justified. The addition of hydroxyl ions to water containing magnesium results in the precipitation of magnesium hydroxide, thereby removing hydroxyl ions from solution, as shown in the following equation:

$$Mg^{2+} + 2OH^- \rightarrow Mg(OH)_2\downarrow \quad \textbf{(EQ 2)}$$

When sufficient magnesium is precipitated at a pH of ~9.5, the pH increases, and this allows both the hydroxyl (lime) demand of the water and the original concentration of the magnesium to be calculated.

Curves indicating the quantity of lime required to obtain a pH value for various magnesium concentrations can be constructed as shown in Figure 6. These lime demand curves are for a system with a pulp density of 50% solids, 100% available lime, and low salinity. This illustrates a series of theoretical lime consumption versus pH curves for magnesium values within the range typical for raw water supply to Australian mines. In the presence of magnesium, the pH buffers at around 8.75–9.5, and larger quantities of lime are required to obtain a small change in the pH. Conversely, only small changes in the pH set point can dramatically reduce the lime consumption. Decreasing the magnesium content of the raw water, as well as increasing pulp densities, will result in a reduction in lime consumption.

### *Oxygen Compounds*

The use of oxygen or per-oxygen compounds (instead of air) as an oxidant increases the leach rate and decreases the cyanide consumption. This is due to the inactivation of some of the cyanide-consuming species that are present in the slurry. If the pH of the slurry can be raised to about 10 (by dosing lime at the head of the leach circuit), this will ensure that when the cyanide is added, toxic hydrogen cyanide gas is not generated and the cyanide is kept in solution to dissolve the gold.

Cyanate ($CNO^-$) is the primary by-product of treatment using sulfur dioxide or hydrogen peroxide in the process. Cyanate is slowly hydrolyzed to ammonia and does exhibit its own toxicity. In this case, the primary approach in the elimination of cyanate is to select a process that does not form the compound as a by-product.

### *Hydrogen Cyanide*

The presence of hydrogen cyanide (HCN) has far-reaching effects on refinery amine system performance. After hydrocarbon contamination, its presence is one of the primary reasons that amine systems suffer from accelerated corrosion and have operability and reliability problems. When HCN enters the amine system, its hydrolysis produces ammonia and formate, which is a heat-stable salt. Reaction of HCN with oxygen and hydrogen sulfide ($H_2S$) generates thiocyanate, another heat-stable salt. The heat-stable salts are known to chelate iron, which leads to accelerated corrosion. This also leads to faster formation of particulate iron sulfide, which can plug filter elements, foul equipment, produce stable foams, and lower plant capacity.

## Base Metal Processing

Base metals such as copper, lead, and zinc are usually extracted from their sulfide ores by a flotation process. Many investigations have found that the quality of the process water that is used for flotation can have a significant impact on the flotation performance for extraction of each of these base metals.

Muzenda (2010) reported on a study to determine the effect of water quality on the flotation selectivity of complex sulfide minerals. Several water types were tested, from different thickener overflows and sewage effluent water (as process water) and also a potable water source. The water types differed in pH, TDS, total suspended solids (TSS), and conductivity. The process waters reduced both the concentrate recovery and mass pull but increased the concentrate grade. Conversely, the potable water increased the concentrate recovery and mass pull but decreased the concentrate grade. It is proposed that a combination of process water and potable water supply should be used in flotation circuits to balance the different effects that the different water types have on flotation efficiency.

The key factors requiring consideration for the process water that is used for based metal processing are pH and ion content.

### *pH*

Ng'andu (2001) reported on the results of investigations in the Mufulira copper mine in Zambia. The investigation was initiated to find out the reason for the reduction of flotation recovery after changes in the site water balance. Traditionally, the mill water used for flotation consisted of 40% underground water (pH = 7–7.5) and 60% of recycled thickener overflow (pH >10.5).

The percentage of thickener overflow recycled was decreased to only 40%. The study found that the resulting pH in the primary grinding mill decreased from the previous range of 8.5 to 9.5 to less than 8.5. It was found that the lower mill water pH had a deleterious galvanic interaction between the sulfide minerals and the cast-iron grinding media inside the grinding mills. The consumption of oxygen created a strong reducing environment in the slurry fed to the flotation process, adversely affecting the proper adsorption and oxidation of xanthate. Further, the sulfide mineral surfaces, which tend to be cathodic, became prone to covering by hydrolytic oxide layers, hindering the flotation response. Moving the quicklime addition point from downstream of the milling process to the inlet of the primary ball mills had a positive effect and significantly reduced lime consumption.

#### Ion Content

Forssberg and Hallin (1989) carried out studies on the effect of recycle water on flotation process performance and concluded the following:

- The flotation process was stable in terms of sensitivity to different levels of anion and cation content of the recycled water, except the precipitation of gypsum. The calcium and sulfate ion products in excess of the solubility level of gypsum in a flotation system can affect the process.
- The use of recycled water always had an effect on frothing properties.
- There was not any accumulation of the analyzed ions in the recycled water.
- Flotation problems appear to relate to process chemical residues and different types of oils that accumulate in tailings ponds, when conditions for their degradation are poor.
- Naturally occurring organic surface-active substances like bacteria and humus acids can also interfere with the flotation process.

Coetzer et al. (2003) investigated the impact of ions present in various water sources (deionized, simulated circulation, lead concentrate thickener, lead tailings thickener, and borehole) on galena flotation to recover lead. The activation, depression, and selectivity effects were different for each water source. The borehole water had high salt content, which decreased the froth stability, requiring a stronger frother to be used. The water from the lead tailing thickener had the greatest effect (negative) on galena recovery. It was concluded that, to gain the full benefit from all of these water resources, it would be necessary to first remove some of the ions that have the greater negative impact on galena flotation performance.

### Platinum Processing

Water chemistry influences the performance and selectivity of the flotation process because the milled ore is constantly in contact with water. Solution chemistry is extremely complex, and no one rule applies for all systems, or for a circuit as a total. Slatter et al. (2009) summarized several case histories where the process effects of water quality and impact of recycling were evaluated.

The key factors requiring consideration for the process water used for platinum ore processing are dissolved salts, reagent addition, ore dissolution, and organics.

#### Dissolved Salts

Slatter (2001) found that flotation reagents were more effective in process water with a higher TDS level (up to about 5,000 mg/L) rather than at lower TDS levels. In some sites, very little fresh water is available to the process, and so seawater (with TDS of 35,000–45,000 mg/L) or highly saline borehole waters are used in grinding (Dunstan 1999). Flotation in higher-salinity waters appears to cause little or no mineral dissolution, indicating little surface alteration (Shackleton et al. 2001).

At very high TDS levels, high levels of chlorides can have a negative effect on a smelter. To limit these negative effects, the concentrate is often washed with water that is low in chloride before it is sent to the smelter. The chlorides are also responsible for corrosion, and all materials from which the mills, flotation cells, launders, and so forth, are made need to be corrosion resistant, all of which adds to the capital costs of the process.

Research has shown that calcium and thiosulfate ions affect sulfide flotation differently:

- Calcium activates the adsorption of collector ions when the galvanic effect of mill iron is effective. An investigation into the effects of synthetic waters on synthetic minerals indicated that the adsorption of calcium onto pentlandite and pyrrhotite surfaces increased the minerals hydrophilicity. As a result, more xanthate was required to induce hydrophobicity of the minerals (Malysiak et al. 2003). In one process, substituting soda ash for lime decreased the amount of calcium in the process, which increases value recovery because calcium tends to precipitate on the mineral surface, causing depression (Smart et al. 1999).
- Thiosulfate, which also tends to be generated in flotation cells (Forssberg and Hallin 1989), decreases the adsorption of hydrophilic compounds such as metal hydroxides (Kirjavainen et al. 2002).

#### Reagent Addition

Flotation of minerals from gangue and from each other makes the use of their different surface properties (Arnold and Aplan 1986). These surface properties are affected by solution components (e.g., passivation of mineral surfaces may occur due to ion precipitation), and this has a negative effect on flotation because the surface chemistry of the mineral is changed. However, the effect of these components may be somewhat negated by using reagents to modify the surface properties (Smith and Hertzog 1985).

Reagent consumption decreases by about 50% when water from the process is reused compared with potable water (Forssberg and Hallin 1989). However, these recycled waters can cause very stable froths to form; consequently, measures need to be taken to ensure that water causing stable froth formation is not used. Cleaner circuits are the most sensitive to changes in froth properties, as the selectivity between sulfide particles and fine-sized gangue mainly depends on the water content in the froth. When the froth is stable and has a higher water content, selectivity tends to be reduced. MIBC (methyl isobutyl carbinol) has been used as the frother of choice in a closed water system because over-stable froths do not form (Johnson 2003).

### *Ore Dissolution*

Ore dissolution can also cause various elements/compounds to accumulate in solution, which alter the chemistry of the system (Rey and Raffinot 1985). An example of ore dissolution effects is in a complex sulfide flotation plant where small amounts of copper may be dissolved during ore–water interaction. This effect can be further increased as a result of water recycling. Eventually, the level of dissolved copper may become high enough to cause the formation of sphalerite (which should be depressed at the start of the float) to be activated (Smith and Hertzog 1985).

### *Organics*

Some natural organics (humic, fumic, tannic, and stearic acids) have a detrimental effect on flotation (Hoover 1980). High TOC levels also seem to cause frothing problems (Forssberg and Hallin 1989). In some cases, using recycled treated sewage effluent waters caused frothing problems across a flotation bank. Work has been performed showing that a foam fraction may improve the frothing problem but does decrease in metal recovery.

## Uranium Processing

Uranium is extracted from the raw ore by oxidizing and leaching the ore material with an acid or alkaline leaching solution. As discussed in the NRC (2012) publication, the selection of either an acid or alkaline leaching solution depends on the nature of the ore. This requires extensive testing, economic studies, and environmental considerations to decide the final process choice.

Uranium is found in many deposits as uranium dioxide (as $UO_2$ in the +4 oxidation state). Given that uranium dioxide is insoluble, it needs to be converted first into a water-soluble form to enable extraction to take place. The first step in any uranium leaching operation is the oxidation of the uranium oxide from +4 oxidation state to +6. The second step is the stabilization of the uraniferous ions in the leaching solution. The uraniferous ions form stable, soluble complexes with sulfate or carbonate. Therefore, sulfuric acid is added as the source for sulfate ions when acid leaching is used. For alkaline leaching, sodium bicarbonate, sodium carbonate, or carbon dioxide are added to provide a carbonate ion source.

The key factors requiring consideration for the process water that is used for uranium ore processing are acid leaching and alkaline leaching.

### *Acid Leaching*

Acid leaching is usually more effective with the difficult-to-treat uranium ores. Sulfuric acid is typically used because of the good solubility of uranyl sulfate complexes. The reaction is typically performed at slightly elevated temperatures (50°–60°C) and can often release $H_2$, $H_2S$, and carbon dioxide ($CO_2$) gases during the process. The uranium goes through a series of reactions, eventually leading to the formation of the desired uranyl sulfate complex. Oxidizers such as oxygen, hydrogen peroxide, sodium chlorate, or manganese dioxide are used to maintain the presence of the hexavalent $U^{6+}$ cation.

### *Alkaline Leaching*

Alkaline leaching solutions using sodium carbonate (30–60 m/L) and sodium bicarbonate (5–15 m/L) tend to be more selective to uranium minerals, so the leaching solution will contain fewer impurities. Consequently, the uranium oxide can be directly precipitated without further purification. The alkaline solutions are less corrosive and can be recycled without the annoyance of increasing impurity concentrations. However, because of the slower reactivity of the alkaline solutions, increased pressures and temperatures (90°–95°C) are often needed.

Because both acid and alkaline leaching require relatively high concentrations of reagents, it is likely that variations in the quality of the raw water and the process water have little impact on the uranium leaching performance. The ore slurry (with the uranium in solution) requires the separation of the solids from the uranium-containing liquid. This is commonly performed using filters (horizontal belt, pressure, or drum filters) or a series of thickeners or decanters. The slurry is washed with acidified water in the acid leach process, or water only in the case of the alkaline leach option, in what is termed *countercurrent decantation*. The washed solids (now referred to as tailings) are neutralized and then forwarded to a tailings impoundment facility for storage.

## Coal Processing

Raw coal extracted from the mine needs to be cleaned using different physical processes, with or without chemical agents, to

- Remove inorganic material (ash), thus reducing ash handling in plants that are using coal for coke making or power generation;
- Increase the heating value of the coal; and
- Reduce the transportation cost per unit weight of coal.

The availability of good-quality process water in sufficient quantities is seen as an emerging issue in the coal industry in many countries. Potential approaches to meet this challenge are to

- Reduce water consumption in coal preparation,
- Increase recycling, and
- Use saline mine water (if available) on the mine site.

Most of the process water is supplied by thickening units, which settle out ultrafine suspended solids and enable the recycling of the clarified water back into the plant. A small amount of fresh makeup water from an external source is usually required to satisfy the balance between moisture contents of solids entering and exiting the plant. The clarification and recycling of process water provides an effective means of reducing freshwater demands and lowering environmental impacts. However, plant operators are faced with increasing difficulty in avoiding the buildup of contaminants in the process water. Evidence suggests that dissolved ions and suspended solids adversely impact the performance of dewatering processes.

Flotation is commonly used to treat fine coal (typically <500 µm in size). This is a complex process that is controlled by three facets: coal, chemistry, and machine. Flotation is most often used for treating metallurgical coal fines where the value of the product can justify the added treatment cost of cleaning and dewatering the product component. Because of improvements in flotation technology and the dewatering of both product and tailings, this avenue is becoming increasingly attractive for treating thermal coals. Deterioration of process water quality reduces sizing efficiency, lowers flotation recovery, and increases magnetite losses.

The key factors requiring consideration for the process water that is used for coal processing are salinity and suspended solids.

### *Salinity*

Ofori et al. 2009 reported on a study to identify the impacts of using saline mine water as process water for coal preparation. The study examined the interaction between dissolved electrolytes, hydrophobic solids, hydrophilic solids, and air bubbles in terms of how they impacted coal preparation unit operations. The aim was to study the important physical forces that control the behavior of solids, liquid, and air bubbles in coal preparation processes. How the manipulation of these surface forces could mitigate negative effects of saline water use and thus maintain optimum process efficiencies was also studied.

In terms of the process, saline water had a positive impact, resulting in improved flotation recovery and/or reduced flotation reagent consumption. The impact was even greater when higher concentrations of divalent cations such as $Mg^{2+}$ and $Ca^{2+}$ and divalent anions such as $SO_4^{2-}$ were present. The extent of this positive effect was determined to be dependent on the type of coal being processed. However, with regard to filtration and sedimentation rates, the impact of saline water was negative if no flocculent addition was being used. If flocculants were used, it had such an overwhelming positive impact on filtration and sedimentation rates that it overshadowed the negative effect due to salts. In this situation, the presence of the salts (in most cases) resulted in clearer sedimentation overflow, with less residual solids.

### *Suspended Solids*

Physical separation processes such as dense medium cyclones are widely used for washing coal with particle sizes >0.5 mm. Process water used for these physical separation processes requires certain limits on suspended solids levels, depending on the individual equipment requirements. The water quality and size separation is specific to the usage and cannot be generalized. Even a specific duty such as filter cloth spray nozzles requires a drastically different particle cut size, depending on the type and aperture of nozzles used.

Bickert (2013) undertook a review of filtration technologies currently used with the potential to improve process water quality from a solids content perspective. Fully automatic backwash filters with nozzles, suction scanners, and/or mechanical screen cleaning were most suitable and cost-effective for solids removal from process water, where a separation size of 50–500 µm is sufficient. Where it is necessary to have essentially complete solids removal, or where the process contains mineral matter, media filters such as the continuous sand filter should be considered. However, these media filters should be fed with water with <200 mg/L solids, and so coarse screen filters may still be required for pre-filtration. Technologies such as flotation and gravity clarification are less suitable for solids removal from process water, because of their limited performance with low levels of solids in the water.

## WASTEWATER TREATMENT

The main liquid waste streams that are generated from most mining sites arise from the various hydrometallurgical processes such as leaching, thickening, and flotation. The mining wastes include concentration process wastes, heap leaching products, and old slurry tailings from discontinued mining operations. The environmental threat imposed by these effluent streams can be attributed to various chemical compounds, toxic metal ions, and extreme pH variations. Some of these environmental threats exhibit the possibility of contaminating surface and groundwater through one or more of the following mechanisms:

- Acid mine drainage
- Release of residual cyanide and soluble metal species from heap leaching operations
- Mineral dissolution that results in the release of metal species and other anions

The extent to which these processes pose environmental threats highly depend on the process occurrence and containment techniques employed, as well as the nature and concentration of the species.

A detailed understanding of wastewater sources and their characteristics is essential for the purposes of selecting, as well as developing, efficient and reliable water management and wastewater treatment systems. Such knowledge, coupled with effluent design criteria, is utilized in establishing the level, type, and capacity of wastewater treatment that is required to meet the stringent environmental legislations, as prescribed by different environmental protection agencies globally.

The chemical characteristics are dependent on the complex interactions between the metallurgical processes and reagents, ore chemistry, and site hydrology. The fate of the effluent streams can be determined by the following scenarios:

- Suitability for treatment to recycle for specific uses on-site. This will be driven by the process performance factors.
- Treatment to meet stringent limitations for discharge to the environment. The actual treatment required will depend on the actual components that are in excess the discharge limits to be met.
- Containment on-site with no release to the environment. Effective containment can be achieved by using tailings impoundments, heap leach pads, or solution ponds that are constructed with impermeable barriers between the contained liquid and the surrounding ground. For smaller volumes, steel tanks or concrete sumps can also be used.

The specific issues with treatment of wastewater from gold, base metals, platinum, uranium, and coal ore processing facilities are discussed in the following sections.

### Gold Processing

#### *Effluent Characteristics*

The significant variability of wastewater characteristics from gold mining processes, in terms of heavy metals and cyanide levels, is demonstrated in Table 1. The Yanacocha gold mine in Peru and the David Bell mine in Canada are good examples of technologies applied to reduce cyanide levels in the mine-site wastewater streams (Diaz et al. 1998; Meyer 1992).

#### *Effluent for Recycle*

The need for treatment of recycle streams is driven by the necessity to manage the quality of the process water. As discussed earlier, pH plays a significant role in the efficiency of gold extraction by cyanide. Recycle streams (untreated or treated) that contribute to an increased process water pH are desirable. These could increase alkalinity, or reduce magnesium that acts as a buffer on the cyanide solution.

**Table 1 Chemical composition of barren, decant, and seepage solutions**

| Variable/Parameter | Concentration Range |
|---|---|
| Arsenic, mg/L | <0.020–10.0 |
| Cadmium, mg/L | <0.005–0.02 |
| Chromium, mg/L | <0.02–0.10 |
| Copper, mg/L | 0.1–400 |
| Iron, mg/L | 0.50–40 |
| Lead, mg/L | <0.01–0.1 |
| Manganese, mg/L | 0.1–20 |
| Mercury, mg/L | <0.0001–0.05 |
| Nickel, mg/L | 0.02–10 |
| Selenium, mg/L | <0.02–6 |
| Silver, mg/L | <0.005–2 |
| Zinc, mg/L | 0.05–100 |
| Total cyanide, mg/L | 0.5–1,000 |
| WAD cyanide, mg/L | 0.5–650 |
| Free cyanide, mg/L | <0.01–200 |
| Ammonia-N, mg/L | <0.1–50 |
| Thiocynate, mg/L | <1–2,000 |
| pH | 2.0–11.5 |
| Hardness (as $CaCO_3$), mg/L | 200–1,500 |
| Sulfate, mg/L | 5–200,000 |
| Temperature, °C | 0–35 |

Adapted from Smith and Mudder 1991

In some cases, removal of magnesium by ion exchange or softening may be advantageous. Removal of sulfate ions may assist with reduction of gypsum formation and associated problems with scale deposition. Recycle of cyanide ion could contribute to lower cyanide dosing to maintain cyanide solution concentrations.

### *Effluent for Discharge*

The U.S. Environmental Protection Agency (EPA) sets limits on discharge from sites that utilize processes for the beneficiation of gold ores. The limits shown in Table 2 are based on the degree of effluent reduction attainable by the application of best practical control technology (BPT). These limits are similar to those applied to copper, lead, and zinc processing.

Because cyanide solutions are commonly used for gold extraction, the effluent usually contains free cyanide concentrations that are well in excess of the safe level for release to the environment. There have been several different treatment processes used to treat effluent from gold mining/processing sites, and some of the more commonly used processes are discussed below. These processes have needed to take into account the local conditions such as ore chemistry and site hydrology as well as sludge treatment and disposal costs.

The most critical selection criterion for a certain treatment method is the stability and concentration of a given solution. This is because every facet of the mining operation affects the quantity and quality of wastewater produced. It is within this context that the process, or processes, selected must be reliable and flexible enough to maintain a consistently high-quality effluent throughout the life span of the mine, and even beyond mining.

**Table 2 Guidelines for discharge from gold processing**

| Parameter | EPA* Guidelines for 1 Day | EPA† Guidelines for 30 Days |
|---|---|---|
| Cadmium, mg/L | 0.1 | 0.05 |
| Copper, mg/L | 0.3 | 0.15 |
| Lead, mg/L | 0.6 | 0.3 |
| Mercury, mg/L | 0.002 | 0.001 |
| pH | 6.0–9.0 | 6.0–9.0 |
| Total suspended solids, mg/L | 30 | 20 |
| Zinc, mg/L | 1.5 | 0.75 |

Data from EPA 2018.
*Maximum for any one day.
†Average of daily values for 30 consecutive days.

### *Natural Degradation*

The natural degradation of cyanide is achieved by the combination of the mechanisms of volatilization, UV degradation, the formation of strong complexes, adsorption, and biological oxidation (Rouse and Pyrih 1998). This process occurs primarily because of auto-oxidation. For example, the Homestake Mining site in New Mexico (United States) reported natural cyanide breakdown occurring in the tailings pond as well as in the mine (Halbe et al. 1979).

Research findings in Canada on natural degradation in the tailings ponds showed that natural degradation reduced the $CN^-$ concentration from 68.7 to 0.08 mg/L during the warmer period (Schmidt et al. 1981). Most of the degradation was due to dissociation of cyanide complexes coupled with volatilization of molecular HCN. Oxidation of free $CN^-$ to $CNO^-$ only accounted for about 11% of the conversion, and photo- and biodegradation could not be detected. No degradation was detected during the colder winter months.

Though natural degradation is a simple method that reduces cyanide concentration to acceptable levels, its success depends upon the amount and species of cyanide present as well as the retention time the storage pond can provide. Even where the natural degradation process does not provide a final effluent with the desired level of $CN^-$, the process is useful in decreasing the amount of cyanide that may have to be treated further using chemical means (Ritcey 2005).

Natural degradation can be influenced by variables such as the cyanide species in solution and the relative concentrations, temperature, pH, aeration, sunlight, presence of bacteria, pond size, depth, and turbulence. Evaporation can be used effectively as a means of destroying cyanide in arid regions such as in Western Australia, South Africa, and the western United States. These arid areas are characterized by high evaporation rates, and therefore, the runoff into rivers and lakes is not a problem (Ritcey 2005). The key limitation of natural degradation is that it can take too long to detoxify a heap to meet regulatory limits; consequently, the operation and maintenance costs are higher (Marsden and House 2009).

### *Barren/Freshwater Rinse*

Mosher and Figueroa (1996) described barren/freshwater rinse treatment as the washing of heaps with solution from the barren pond, only using fresh water to make up for the evaporative losses. No reagents were used and cyanide concentrations decreased, possibly due to a combination of native bacterial action, complexation, and volatilization processes. This treatment method suits mostly climate regions where there is a negative water balance as well as relatively cheap sources of water.

The method is characterized by a low requirement for additional capital equipment, no reagent additions, and it incurs no additional engineering costs. However, its shortcomings include high operation and maintenance costs as well as long waiting periods to rinse the heap down to the stipulated closure standards.

#### *Artificial Wetlands*

Greenway and Simpson (1996) presented results indicating that artificial wetlands can be used for treating gold mine leachate that contains cyanide. Their findings showed that the final effluent was of good quality and suitable for reuse purposes such as irrigation. Larsen et al. (2004) showed that cyanide can be removed using woody plants that have a high capacity to eliminate free cyanide.

The selection of suitable plants depends on the conditions at the mine (climate, soil, etc.) and their cyanide removal capacity. For applications in a humid climate zone, the willow hybrids have shown the most promising results so far (Rytter and Hansson 1996). It was found that a maximum of 1,100 kg of free cyanide could be removed by 1 ha of willows for a growth period of 200 days.

#### *Bacterial Oxidation*

Some bacteria species are able to metabolize cyanide and thiocyanate. Different species degrade cyanide into products such as ammonia and formate, based on the results of Raybuck (1992) and others. Free metals are either absorbed within the biofilm or precipitated from solution (Akcil 2003). The ease of degrading the metal cyanide complexes is generally in accordance with their chemical stability, with free cyanide being the most readily degradable and iron cyanide the least.

The first successful large-scale application of the biological oxidation method for the treatment of gold cyanide leaching effluent was carried out by Homestake Mining Company in South Dakota (United States) in 1984 and was operated successfully until the mine closed because of a lack of ore (Whitlock and Mudder 1986). The mechanism of the biological treatment of effluent-containing cyanide has been described in detail by Akcil (2003). The biological process is made up of two main stages:

1. Bacterial oxidation of $CN^-$ and $SCN^-$ to produce $CO_3^{2-}$, $SO_4^{2-}$, and $NH_4^+$, by using indigenous microorganisms that are acclimatized to cyanide and thiocyanate.
2. Nitrification of $NH_3$ into $NO_3^{2-}$ by the Nitrosomonas and Nitrobacter anaerobic species.

Soda ash is added as a source of carbon to assist nitrification. Phosphorus is also required as a trace nutrient.

The bacteria that are attached to the discs in rotating contactors absorb the metals, once released from the cyanide. After the biodegradation and metal removal in the contactors, ferric chloride is added to aid clarification, followed by sand filtration. The key merits of this technique include

- Low reagent and operating costs;
- The potential to treat total cyanides without creating secondary waste streams; and
- The ability to remove thiocyanate, ammonia, and nitrate, unlike the costly chemical-based approaches (Given et al. 1998).

Although the initial investment cost is high, the operational costs are relatively low, so the net present worth is very low for a biological technique (Nelson et al. 1998). Biological processes, which are quite promising in terms of satisfying both the extraction and environmental control requirements, have been proven at large scale in well-understood engineering systems in countries such as the United States and Canada (Mudder et al. 1998).

Biotechnological treatment processes are under various stages of development; however, many proposed processes cannot currently compete with the conventional technologies and are unlikely to do so unless regulatory standards change. Processes that have been applied commercially are

- In-plant cyanide destruction,
- In situ cyanide destruction of spent heap leach piles,
- Metal and sulfate removal using active (in-plant) sulfate reduction, and
- Limited use of passive processes such as wetlands and ecological engineering for metals polishing.

Biotreatment of cyanide and associated species, such as ammonia and thiocyanate, in gold plant effluents can be readily adapted to handle large flows and the cyanide concentrations found in commercial gold operations. Commercial applications involving both in-plant treatment as an alternative to chemical processes and in situ cyanide destruction of spent heap leach piles are being used (Lawrence et al. 1998).

A full-scale combined biological and chemical treatment facility currently operating in Turkey consists of three steps (Akcil 2003):

1. Combined activated sludge treatment for the conversion of thiocyanate ($SCN^-$) to ammonia ($NH_3$) and for the oxidation of the ammonia ($NH_3$) formed to nitrate ($NO_3^{2-}$);
2. Denitrification treatment to reduce $NO_2$ to nitrogen gas ($N_2$); and
3. HDS ferric sulfate treatment to precipitate arsenic and other metals as sulfate ($SO_4^{2-}$).

#### *Trickling Filters*

Trickling filters are the most frequently used fixed-film bioreactors for treating wastewaters containing free cyanide, carbon oxygen demand, thiocyanate, and copper and zinc ions (Evangelho et al. 2001). In these reactors, microorganisms are attached to a solid substratum in which they reach relatively high concentrations. The trickling filter is suitable for treating wastewaters with significant variations in organic and hydraulic loads.

The results indicate that approximately 90% of the free cyanide, thiocyanate, copper, and zinc in the influent are effectively removed. These removal efficiencies were obtained when the pilot bioreactor was operated without recirculation. Using recirculation brought about a decrease in pH and lowered the efficiency of zinc removal. The microbial activity was responsible for thiocyanate degradation and copper removal. The tests carried out in the reactor without biomass showed that the percentage of free cyanide removed by volatilization was low (22.6%) and was even lower when recirculation did not take place (7.7%). This confirms the important role that the biomass plays in the degradation of this pollutant.

Among the key merits of this process are that it is simple and easy to operate and has low energy requirements. It is possible to retain microorganisms with a slow growth rate, such as those responsible for cyanide degradation. However, its weakness lies in the inability to renew the biomass, as the metal accumulation may lead to biological activity inhibition.

#### *Sulfur Dioxide–Inco Process*

The $SO_2$–Inco process involves the oxidation of cyanide to cyanate ($CNO^-$) in the presence of Cu(II) ions as a catalyst, according to the following equation:

$$CN^- + SO_2 + H_2O + O_2 \rightarrow CNO^- + H_2SO_4 \qquad \textbf{(EQ 3)}$$

The oxidation reaction appears specific to cyanide and cyanide–metal complexes. Hexacyanoferrates are not oxidized but are removed in the final treatment stage by precipitation. If present, some thiocyanate is degraded. If nickel is used as the catalyst, oxidation of thiocyanate proceeds at a slower rate.

The process has the added advantage of using a relatively inexpensive reagent. Also, the cyanate produced may be significantly less toxic than cyanide to receptor organisms such as fish, animals, and humans. However, the chemical-handling systems are rather more complex than for a hydrogen peroxide system, resulting in higher capital costs.

#### *Ozonation*

The oxidation reaction of ozone with cyanide is rapid. The rate of decomposition of complex cyanides with ozone varies with the stability of the metal complex. Nickel, zinc, and copper complexes are readily oxidized, whereas iron cyanides decompose with difficulty, unless performed at elevated temperatures or with UV light.

Reaction rates can be improved by metal ions such as $Cu^{2+}$, where the presence of 20 mg/L of copper doubles the rate of oxidation (Rowly and Otto 1980). The rate of decomposition is also increased by 50% at pH 12–13 compared to pH 9–11. A combination of both pH and copper addition can enhance the decomposition threefold.

#### *Acidification, Volatilization, and Reneutralization*

The AVR process (also known as the Merrill–Crowe process) exploits the fact that hydrogen cyanide is volatile at 26°C and 100 kPa. Early applications were aimed at reducing the cyanide consumption, as opposed to effluent control. In this process, the solution containing the cyanide is acidified using sulfuric acid ($H_2SO_4$), and the HCN gas is swept by air to an absorber tower and contacts lime slurry. The alkaline cyanide is returned to the process circuit. Ferrocyanide or thiocyanate are not destroyed by the treatment process, but they are precipitated completely by copper or zinc double-complex formation.

The unique processing steps in the AVR process result in the following benefits:

- Production of a metal salt by-product for recycling to the treatment process, if required.
- Availability of the metal salt by-product for recycling to a novel “polishing” step, which can reduce the metal cyanide content of the final effluent to ~0.1 mg/L.
- Rejection and stabilization of the iron content of the barren bleed for disposal to tailings.
- Cyanide is recoverable for reuse in the leaching process with a recovery potential better than 90%.
- Process efficiency is not sensitive to fluctuations in feed contaminant levels of $CN^-$ or heavy metals concentrations.

However, the AVR process has several limitations:

- The hydrocyanic acid vapor is a hazard. Acidification and volatilization systems must be tightly sealed, and the plant area designated for this part of the operation must be well vented as precautionary safe practice. This increases the costs of operations.
- The process is more energy-intensive than other methods, such as ion exchange or chemical oxidation.
- It may not be suitable for applications where the effluent is discharged directly into any environmentally sensitive receiving watercourse without the utilization of on-property ponding or a polishing step.
- For very dilute barren bleed ($CN^- < 100$ mg/L), the capital equipment outlay is relatively high.

More recently, considerable research has been directed toward improving the AVR process because of the high cost of cyanide destruction. With various specific modifications, the AVR process has now been installed in several gold cyanidation plants throughout the world. It has also been successfully used in the application to silver cyanide leaching circuits for the recovery of cyanide for reuse (Botz and Mudder 1998). Prior to the mine closing in 1998, Kinross Gold Corporation’s DeLamar mine in Idaho (United States), was able to achieve approximately 95% of the cyanide it recovered, leaving a residual of about 20 mg/L to be discharged to tailings and natural degradation. As an alternative to the AVR process, the SART (sulfidization, acidification, recycling, and thickening) process has been used in other mines, as detailed in McGrath et al. (2015).

Because the cyanide is usually complexed with base metals, there has been considerable work directed toward the breakdown of the complexes for the recovery of cyanide. With the modifications applied to liquors, similar processes have resulted in the presence of solids such as the AFR (acidification–filtration–reneutralization) process (Fleming and Trang 1998). In that process, as applied to tailings, it is necessary to achieve lower final-pH values to achieve optimum precipitation of Cu, Fe, $CN^-$, and $SCN^-$. The recovery of cyanide was reported to be in the order of 80%. Because most of the metal and cyanide contents can be recovered, the final waste solids contain no nonferrous base metals, and the precipitated metals can be returned to a mobile state in the tailings pond.

#### *Alkaline Chlorination*

Alkaline chlorination is a chemical process involving the oxidation and destruction of free and WAD forms of cyanide under alkaline conditions (pH range of 10.5 to 11.5). It is among the oldest and most widely recognized cyanide destruction technologies based on operational experience and engineering expertise (Smith and Mudder 1991). Cyanide is oxidized by the hypochlorite ion, which can originate from either chlorine gas or a hypochlorite salt (sodium or calcium). The hypochlorite ion oxidizes cyanide to cyanate according to the following simplified reaction:

$$OCl^- + CN^- \rightarrow CNO^- + Cl^- \qquad \textbf{(EQ 4)}$$

WAD cyanide is also oxidized to cyanate, but hexacyanoferrates are not removed. Ferrocyanide complexes can be partially oxidized to ferric cyanides but are not removed with copper precipitation. Additionally, thiocyanate is oxidized preferentially to cyanide, increasing reagent consumption to meet a given WAD cyanide discharge limit.

This method has recently fallen out of favor because of the environmental implications of the process itself. Chemicals used in the process, whether sodium hypochlorite or chlorine gas, involve complex handling issues. Depending on the receiving water, it may also be unacceptable to add sodium. Notably, the excessive unreacted hypochlorite is toxic to fish. Finally, poor process control can cause the evolution of other toxics. These compounds, together with residual chlorine issues, have necessitated the development of alternatives of non-chlorine methods for the elimination of cyanides.

#### *Hydrogen Peroxide*

Hydrogen peroxide has replaced alkaline chlorination for many cyanide destruction applications, and it is often the method of choice for clear liquor detoxification, including heap leach decommissioning. Although relatively higher in cost, hydrogen peroxide presents some significant advantages over other chemical methods:

- Is a very strong oxidizing agent
- Does not introduce any other contaminants
- Simple process operating over a wide pH range
- Typically reduces cyanide levels down to below discharge limits
- Excess hydrogen peroxide decomposes to water and oxygen

Recent work by Kitis et al. (2005) has attempted to examine the effectiveness and kinetics of destroying cyanide using hydrogen peroxide in the tailings slurry from gold mines that are characterized by low sulfide and heavy metal content. The hydrogen peroxide oxidizes cyanide according to the following reaction:

$$CN^- + H_2O_2 \rightarrow CNO^- + H_2O \qquad \textbf{(EQ 5)}$$

In the event that hydrogen peroxide is added in excess, nitrite and carbonate are formed, and eventually nitrate forms (Monteagudo et al. 2004). Also, copper or proprietary reagents may be used as catalysts. Hydrogen peroxide does not directly oxidize ferrocyanides, but these compounds can be removed by precipitation as copper ferrocyanide.

The primary drawback of hydrogen peroxide is its relatively high unit cost. Recently, the Degussa mine (part of Sandfire Resources) has carried out work with mixtures of hydrogen peroxide and Caro's acid, a promising approach that may reduce the overall reagent cost. The process is typically applied to achieve effluent cyanide levels suitable for discharge. This is a relatively simple process that is capable of operating over wide pH ranges without increasing total dissolved solids, as opposed to other chemical processes.

### Base Metals Processing

#### *Effluent Characteristics*

The main streams contributing to the combined effluent from sites processing base metals (copper, zinc, and lead) usually originate from cyclone underflows, thickener overflows, and tailings dams. These sources contain varying amounts of anions, cations, dissolved heavy metals, suspended solids, and dissolved salts. Return of cyclone underflow from primary grind and regrind operations can introduce high levels of dissolved species from soluble mineral phases such as pyrrhotite, siderite, brucite, and other metal hydroxides, sulfates, and carbonates.

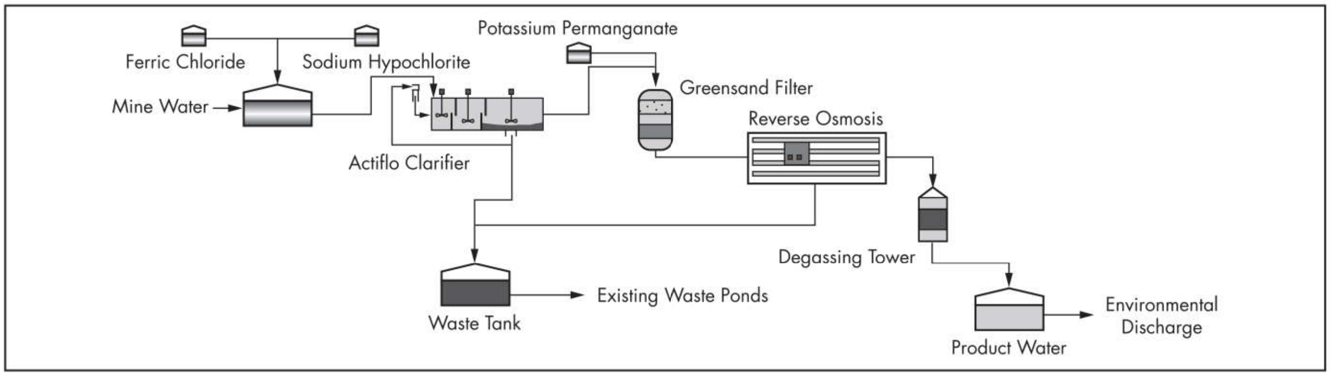
#### *Effluent for Recycle*

The opportunity for treatment of this effluent, either from the individual sources within the mine site or processing area, or as a combined stream, is driven by the need to maintain suitable quality of the water streams. For some of the individual effluents, their quality may be suitable for direct reuse for specific site uses such as dust control (with little or no treatment). In other cases, some treatment may be required before internal recycle to specific end uses. An example of mine-site water treatment is provided in Figure 7.

#### *Effluent for Discharge*

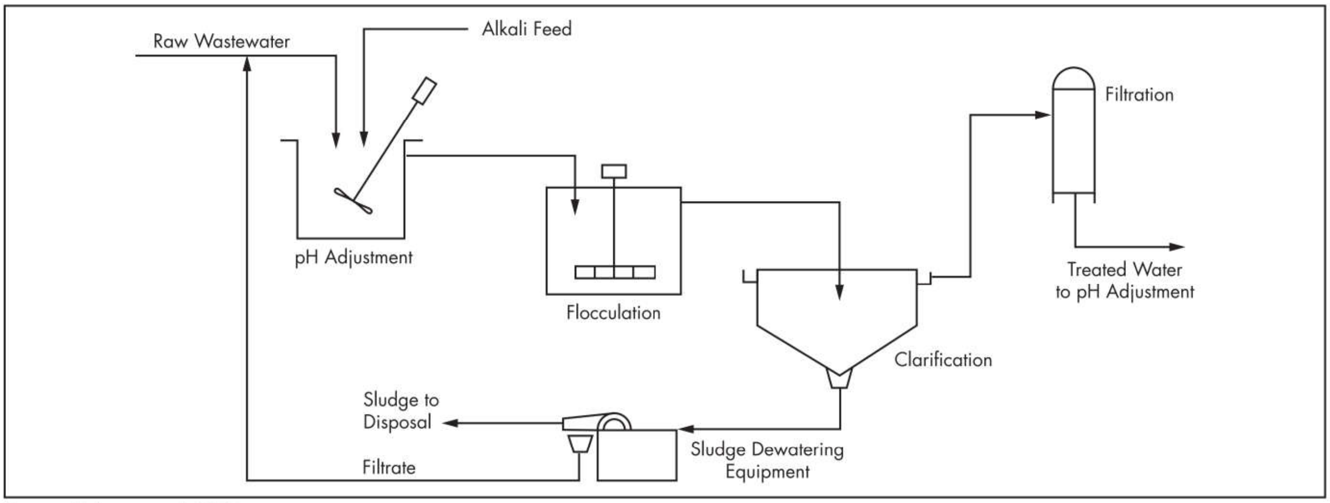
The EPA sets limits on discharge from sites that use froth flotation processes (alone, or in conjunction with other processes) for the beneficiation of copper ores, lead ores, and zinc ores. The limits shown in Table 2 for gold processing also apply to base metals processing and are based on the degree of effluent reduction attainable by the application of BPT. The limits shown in Table 2 are similar to those applied to discharges from silver ore processing (EPA 2018).

The effluent that is surplus to site requirements for recycling may need to be collected on-site before it can be disposed of by evaporation or discharged to a suitable water environment. Where one or more of the contaminants in the effluent exceeds the discharge guidelines, additional treatment over



Source: Madin 2007

**Figure 7 The Bendigo Mining contaminated mine water treatment process**



Source: Coleman et al. 1980

**Figure 8 Hydroxide precipitation process**

that necessary for internal recycle is likely to be necessary. Because effluents from these sites usually contain most of the metals listed, several stages of treatment may be required to address all of the limit exceedances.

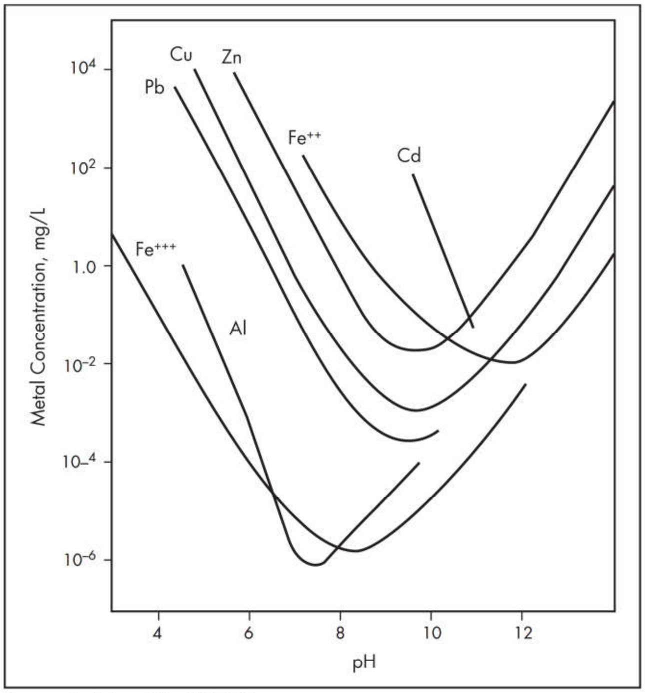
### *Hydroxide Precipitation*

Precipitation of metal hydroxides by adjustment of pH is commonly used for heavy metal removal. This process involves dosing an alkali to adjust pH before flocculation to promote the formation of hydroxide floc (Figure 8). This is followed by settling to separate the solids for dewatering and/or disposal. The alkali used is usually quicklime, hydrate lime, or caustic. The parameters affecting chemical dose rate include inlet pH, temperature, alkalinity, hardness, metals concentration, and the desired final pH. The actual determination of the required chemical dosage is best carried out using laboratory jar tests on samples of the actual wastewater to be treated.

Figure 9 shows the solubility curves for some heavy metals. Most of these exhibit inverted curves as pH increases and have different minimum concentrations. Selection of the desired pH to operate the hydroxide precipitation process will depend on the contaminant levels that are present and their relativity to the guideline limits for these contaminants. For example, copper, lead, and zinc have minimum solubilities within a relatively narrow pH range from 8.9 (copper) to 9.3 (lead). Selecting a pH control range of, say, 9.0 to 9.2 may be suitable for minimizing the concentrations of these three metals. However, the presence of one or more other heavy metals (e.g., nickel) at levels above the guideline limits may necessitate a two-stage pH-adjustment approach.

The theoretical minimum concentrations that can be reached for each heavy metal differ significantly. In the case of copper (0.001 mg/L) and zinc (0.1 mg/L), the minimum theoretical concentrations are well below the guideline limits. However, lead is more soluble and its minimum concentration of about 8 mg/L is well above its guideline limit.

In practice, however, the hydroxide precipitation process (Coleman et al. 1980) seems to yield residual concentrations that are different to the theoretical concentrations. For example, lead residual has been reported as being reduced to about 0.1 mg/L, which is much lower than the theoretical concentration. Several physical phenomena (ionic strength, co-precipitation, and adsorption) are believed to influence the effectiveness of precipitation, especially in solutions containing multiple metal ion species. Therefore, it is very important to carry out jar tests on the specific wastewater to determine likely residual concentrations under different pH conditions. In some wastewaters, hydroxide precipitation may not satisfy the treatment objectives for all the dissolved heavy metals, and further treatment may be required.

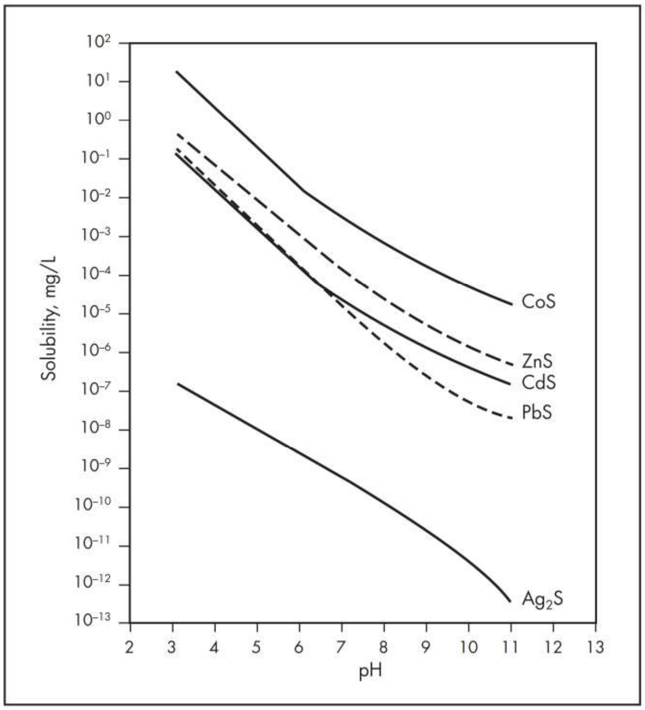


Source: Aubé and Zinck 2003

**Figure 9 Solubilities of heavy metals as a function of pH**

### *Sulfide Precipitation*

In a similar process to hydroxide precipitation, dissolved metals can be removed by chemical formation of their sulfides that



Source: Coleman et al. 1980

**Figure 10 Solubilities of metal sulfides**

are very insoluble. In general, sulfide solubilities are much lower than hydroxide solubilities and continue to decrease as pH increases, as shown in Figure 10. This has the advantage of not requiring adjustment of effluent pH levels to meet guideline limits. However, for a successful outcome, sulfide precipitation requires the following:

- Sufficient available sulfide to drive the precipitation reaction to completion.
- An efficient removal of the sulfide solids from the treated water. This usually requires a final filtration process to remove any unsettled solids from the effluent.

The most commonly used chemicals are the soluble sulfides, including sodium sulfide, sodium bisulfide, calcium sulfide, and barium sulfide. Excess sulfide must be avoided because of the potential formation of hydrogen sulfide gas. Therefore, it is very important that sulfide dosing be accurately controlled. One control method uses oxidation–reduction potential (ORP) measurement to monitor the electrical potential of the reaction solution. When the precipitation reactions are complete, there is a sharp decrease in the solution ORP.

Although the sulfide precipitation process usually produces less sludge than with hydroxide precipitation, sludge disposal is more problematic. If metal sulfide sludges are placed in a typical landfill, exposure to air can oxidize the sulfide and eventually create an acid environment. As the pH decreases, the heavy metals present can redissolve and be leached from the site via surface runoff or percolation into groundwater. Where a metal smelter is also on-site, the sulfide sludges can be recycled back to the smelter for metal recovery.

### Ion Exchange

In general, ion exchange with strong acid cation resin works better at removing heavy metals when the wastewaters are in the pH range of 4 to 8, and when there are low suspended solids, iron, and aluminum concentrations. This process may be better suited to treatment of selected wastewater streams using prefiltration or as a polishing process. The more complex the mixture of contaminants, the more difficult it is to achieve the desired outcome. This is because of the following order of selection for strong acid cation resins to remove ions:

$$\begin{aligned} &Pb^{2+} > Ca^{2+} > Ni^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} \\ &\quad > Mg^{2+} > K^{+} > NH_4^{+} > Na^{2+} > H^{+} \end{aligned}$$

This means that the capability of the resin to remove ions that are lower down in the sequence (e.g., $Zn^{2+}$) can be retarded if there is significant presence of other dissolved metals that are higher in the selection sequence (e.g., $Pb^{2+}$)

Ion exchange has an advantage over the chemical precipitation processes in that it produces much less waste for disposal. The disadvantages of ion exchange are that (1) it cannot handle concentrated metal solutions, particularly containing iron and aluminum, which foul the resin; and (2) ion exchange is nonselective and highly sensitive to the pH of the solution.

### Adsorption

Recently, Barakat (2011) reported that adsorption has become one of the possible alternatives for treatment of wastewater laden with heavy metals. Basically, adsorption is a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by the physical and/or chemical interactions.

Various low-cost adsorbents, derived from agricultural waste, industrial by-product, natural material, or modified biopolymers, have recently been developed and applied for the removal of heavy metals from metal-contaminated wastewater. Technical applicability and cost-effectiveness are the key factors that play major roles in the selection of the most suitable adsorbent to treat these wastewaters.

## Platinum Processing

### Effluent Characteristics

Different platinum ores have different gangue materials, and different grain sizes of precious metals and sulfides, and thus are processed in different concentrators under different conditions. In platinum processing plants, there are two main sources of effluent streams that can potentially be used for recycling on-site:

1. Thickener overflows, dewatering, and filtration units directly connected to the concentrator (called short recycle or internal recycle waters). These streams usually contain higher levels of suspended solids.
2. Tailings dams and clarification ponds (referred to as long recycle water). Typical contaminants are sulfate, chloride, fluoride, magnesium, calcium, sodium, potassium, sulfides, heavy metals, silicates, iron hydroxide, and natural organic matter. Other contaminant residuals that are present from the processing include frothers, collectors, activators, and depressants. TDS levels also tend to be higher than the raw water, as a consequence of evaporation from the open surfaces.

### Treatment for Recycle

The main factors that influence the quality of the water that is available for recycle (Smith and Hertzog 1985) are

- Quality of available makeup water,
- Dissolution of contaminants from the gangue or mineral species,
- Flotation reagents and their degradation products,
- Tailings dam reactions,
- The extent to which recycle water is used and where it is used (this is specific to each metallurgical plant), and
- Biological processes.

In the case of short-recycle waters, the flotation reagents used have not usually had sufficient time in the water circuits to decompose. However, the suspended solids levels tend to be higher, and this can have a consequent negative impact on flotation (Rey and Raffinot 1985).

For long-recycle waters, time effects can become important, due to the delay in the water being returned to the plant (Forssberg and Hallin 1989). Tailings return water tends to have low redox potentials and low oxygen contents due to the oxidation processes taking place in the pond. Most problems connected to the use of recycled water tend to be caused by the process chemical residues and different types of oils that may accumulate in tailings return dams (Forssberg and Hallin 1989).

Because water recycling can cause an increase in total dissolved salts as well as an increase in the specific gravity, this can affect the process slurries. If the specific gravity of the slurry is required to be kept constant, this can result in lower solids percentage and throughput within a plant. Slurry viscosity may also escalate with increasing electrolyte concentrations because of particle aggregation, which can affect mineral floatability as well as classification and pumping.

When recycling water within a process, monitoring the composition of the process water is a necessity. This is needed to identify substances having a negative effect on the process and also to serve as a tool in acquiring information about the process. According to Forssberg and Hallin (1989), chemical consumption decreased when water from the process was reused. However, these recycled waters can cause very stable froths to form’ consequently, measures need to be taken to ensure that recycled water causing stable froth formation is not used.

Generally, a flotation plant producing a single concentrate appears to be more amenable to recycling than one in which two or more concentrates are produced (Johnson 2003). Typically, if more than one concentrate is produced, it is essential that the recycle stream(s) be treated, or be matched to the concentrate, to ensure that deleterious reagents are not introduced into the other concentrate’s water supply.

If treated sewage effluent is to be used as recycle water, it may need to be treated with activated carbon, or ion exchange, before it can be used in metallurgical processes. Different sources of activated carbon need to be tested to find the one that is most suitable for site-specific TOC removal. For example, sugar-based activated carbon was most suitable for the removal of organic sulfur and organic halides (Ng’andu 2001).

Interestingly, in one set of tests on molybdenite flotation using sewage effluent as a water source, the removal of anions with ion exchange was more beneficial than removal of TOC with activated carbon (Schnitzler et al. 1983). This finding was also observed for platinum flotation when treating process water with an anion exchange resin (Slatter 2001).

**Table 3 Guidelines for discharge from platinum processing**

| Parameter | EPA* Guidelines for 1 Day | EPA† Guidelines for 30 Days |
|---|---|---|
| Cadmium, mg/L | 0.1 | 0.05 |
| Copper, mg/L | 0.3 | 0.15 |
| Lead, mg/L | 0.6 | 0.3 |
| Mercury, mg/L | 0.002 | 0.001 |
| Zinc, mg/L | 1.0 | 0.5 |

Data from EPA 2018

*Maximum for any one day.

†Average of daily values for 30 consecutive days.

### *Treatment for Discharge*

The EPA sets guidelines for discharges from mills using the froth flotation process alone, or in conjunction with other processes, for the beneficiation of platinum ores. The limits shown in Table 3 represent the degree of effluent reduction achievable by application of the BPT that is currently available (EPA 2018).

Effluent water that is excess to the site requirements for recycle will usually contain quantities of heavy metals, dissolved salts, and suspended solids. Some of these parameters will likely exceed the limits for discharge directly to the environment. Therefore, before discharge, site effluents usually require treatment to neutralize any chemicals and precipitate any dissolved metals.

## Uranium Processing

### *Effluent Characteristics*

Liquid effluents from uranium mining/processing sites typically contain both radioactive contaminants (uranium and radium) and nonradioactive contaminants (including nickel, arsenic, manganese, magnesium, molybdenum, selenium, fluorides, and sulfates). The characteristics of uranium liquid effluents depend on composition of the ore and the type of mining and processing used to extract the uranium. Local climate can also play a role in treatment and control of effluents.

### *Treatment for Recycle*

Because of the diversity of operating environments and potential contaminating elements and compounds, a single treatment technology may not work for all potential contaminants. Therefore, different combinations of treatment strategies may be required, depending on the chemical composition of the effluents.

Water management within a mining project should start with the characterization of all potential water sources, possible usage, and possible contamination issues. This includes a site water balance analysis that assesses water flows and water quality as well as identifies water recycle options. This water balance analysis would account for seasonal variations and consider the use of cut-off berms, stormwater ponds, and possible evaporation ponds, all based on a probable-maximum-precipitation analysis with a suitable safety margin.

Excess water from mining operations and effluents from mineral processing can be internally recycled to minimize water usage and conserve process chemicals. Typical plant water usage will be on the order of 0.5–2.0 m$^3$ of water per ton of ore.

Table 4 Guidelines for discharges from uranium processing

| Parameter | EPA* Guidelines for 1 Day | EPA† Guidelines for 30 Days |
|---|---|---|
| Arsenic, mg/L | 1.0 | 0.5 |
| Carbon oxygen demand, mg/L | — | 500 |
| $NH_3$, mg/L | — | 100 |
| pH | 6.0–9.0 | 6.0–9.0 |
| Ra-226 (dissolved), pCi/L | 10 | 3 |
| Ra-226 (total), pCi/L | 30 | 10 |
| Total suspended solids, mg/L | 30 | 20 |
| Zinc, mg/L | 1.0 | 0.5 |

Data from EPA 2018

*Maximum for any one day.

†Average of daily values for 30 consecutive days.

### *Treatment for Discharge*

The EPA sets guidelines for discharges from mills processing uranium by using acid leach, alkaline leach, or a combined acid leach and alkaline leach process, including sites where in situ leaching is used. The limits shown in Table 4 represent the degree of effluent reduction achievable by application of the BPT that is currently available (EPA 2018).

Effluent water that is in excess of the site requirements for recycle will usually contain quantities of heavy metals or suspended solids that will exceed the limits for discharge directly to the environment. Before discharge, site effluents usually require treatment to neutralize any chemicals, precipitate any dissolved metals, and to precipitate radium. A multistep process (Figure 11) is usually applied:

1. Heavy metals are removed by coagulation and sedimentation.
2. Ph is adjusted.
3. Radium is precipitated with barium chloride.

The selected treatment processes depend on the plant process, type of ore treated, and chemicals employed. After treatment, the water is discharged into holding ponds, where it is analyzed to ensure that the treated effluents meet environmental objectives before release.

### *Neutralization*

Most conventional uranium mills use acid leach systems. Neutralization of the acidic slurries and liquors with lime before discharge is the preferred method for initial effluent treatment. With the exception of radium-226, the removal of heavy metals and radionuclides is typically greater than 99%. However, the resulting sludge contains concentrations of heavy metals, radionuclides, and dissolved salts that well exceed regulatory standards.

The sludge produced retains moisture and requires large storage volumes that limit the quantity of water that is available for recycle. It is generally known in Australia that recycling of the sludge and blending it with lime slurry can result in higher-density sludge with 50%–65% volume reduction. Recovery of up to 16% more neutralized water for reuse was also realized.

### *Radium Removal*

Radium (as Ra-226) is usually still present in the effluent that overflows from the neutralization process, so this requires further specific treatment. Most operations dose barium chloride to remove the radium by precipitation. Also, special resins have now been developed that can efficiently remove radium from dilute streams such as pond water.

In the case of barium chloride dosing, the resulting sludge has high water content and needs large storage cells. In China, research has been conducted suggesting that recycling the sludge from barium chloride treatment reduces reagent consumption and improves settling properties so that less water is retained, reducing storage requirements and improving availability of water for recycling (Zhang et al. 2004a–d). Aerating the sludge produced during neutralization can also lead to formation of manganese hydroxide that absorbs radium, potentially eliminating the barium chloride step and saving on reagent costs (Zhang et al. 2004a–d). In effect, waste treatment is accomplished by using modified waste from the leaching process.

### *Biological Treatment*

In Australia, two operating uranium mines have used wetlands to treat ore stockpile runoff and water from the open pit for 10 years. The principal solutes of concern are $UO_2$, Mn, $NO_3$, and $SO_4$ and, with the exception of sulfates, all are effectively removed in the wetland environment. Carbon limitation of bacterial activity has been identified as the cause of poor sulfate removal efficacy. Addition of biomass from a specific species of green algae has proven effective in promoting sulfate removal (Ring et al. 2004).

### *Other Treatments*

Not all effluents require lime neutralization. For example, uranium extraction using alkaline leaching produces an effluent that mainly contains sodium sulfate and sodium bicarbonate. Physical treatment methods such as evaporation, electrodialysis, and reverse osmosis (RO) can be used. Some waste streams from acid leaching sites such as mine water, drainage from waste dumps, and contaminated surface waters may also be treated with physical methods without neutralization.

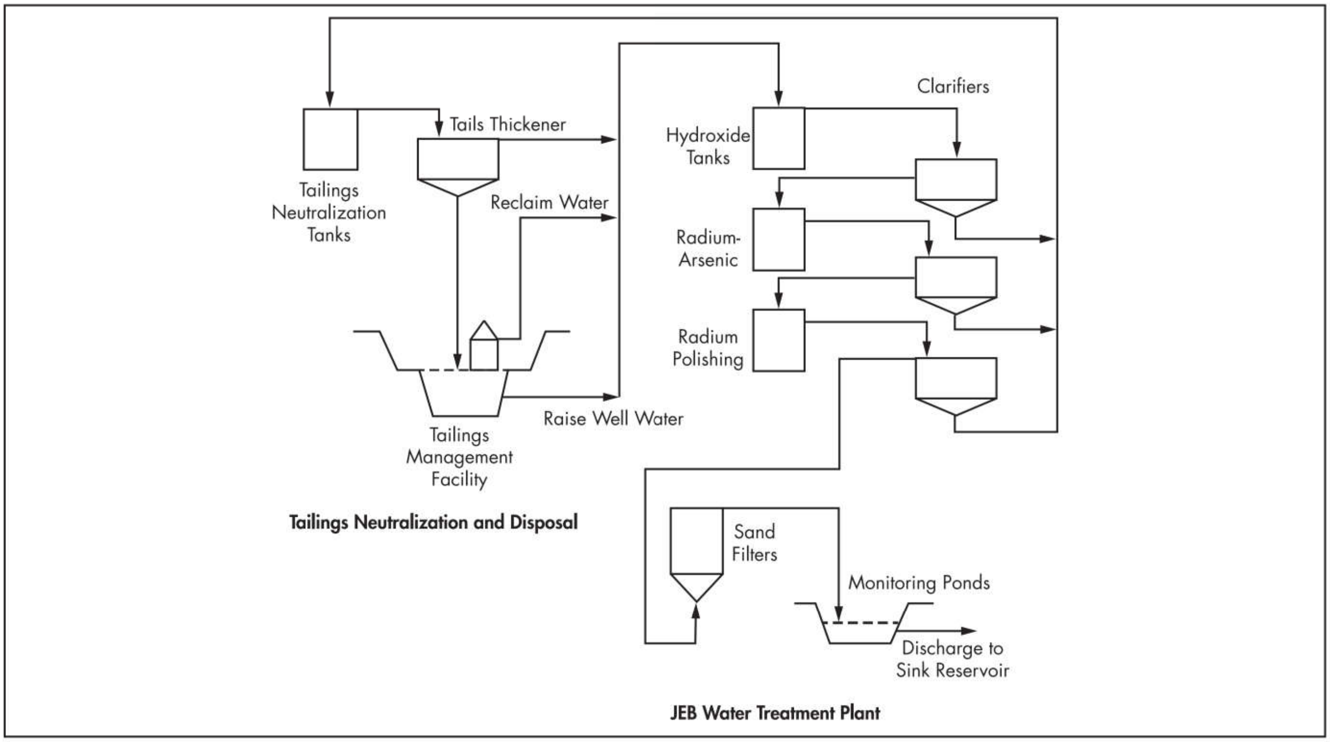
In Australia, nanofiltration is effective in removing ions from contaminated water. Nanofiltration is more cost effective than RO, where the removal of multivalent rather than monovalent ions is important. Research has been conducted in China on the use of macropore resins to remove uranium from mine water (Zhang et al. 2004a–d). The macropore resins have better adsorption properties than strong base ion exchange resins that are currently used in most mine water treatment systems.

## Coal Processing

### *Effluent Characteristics*

One of the main sources of effluent from coal processing is the coal preparation plant, where the run-of-mine coal undergoes a series of treatments, including washing, wet screening, sedimentation, and dewatering. This part of the site requires the circulation of large volumes of water from which large volumes of wastewater containing a variety of solid particles are generated.

Effluent from coal preparation plants can contain high percentages of ultrafine particles and inorganic impurities, which are composed of clay minerals such as kaolinite, illite, muscovite, quartz, and coal particles. Suspended solids levels in the effluent can range from 5,000 mg/L to as high as 30,000 mg/L. Wastewater can also be generated from other coal site sources such as



Source: Schnell and Thiry 2007

**Figure 11 Typical uranium plant effluent treatment**

- Groundwater produced during coal extraction,
- Water used by operators for equipment cooling and dust control,
- Precipitation entering mines, and
- Contaminated stormwater at coal storage facilities.

The combined effluent produced from these sources can be quite variable in quality. Some of these sources can be low pH, with high levels of dissolved salts and heavy metals. Other sources can produce near-neutral wastewater with low concentrations of heavy metals but with high hardness and silica levels.

#### *Treatment for Recycle*

Typical water treatment processes for coal-impacted water would include the following stages of treatment:

1. Removal of fine coal and suspended solids using media filtration or membrane filtration.
2. Removal of heavy metals, silica, phosphate, and hardness by using a chemical precipitation process.
3. Clarification followed by pH adjustment, ultrafiltration, and RO.

#### *Treatment for Discharge*

The EPA sets the guideline limits shown in Table 5 for the discharge of wastewater from coal preparation plant water circuits and coal storage, refuse storage, and ancillary areas related to the cleaning or beneficiation of coal of any rank including, but not limited to, bituminous, lignite, and anthracite (EPA 2018).

There are growing concerns that residual processing chemicals used in coal processing may be harmful to the environment. The vast amount of coal is upgraded without being in contact with any chemical additives using density-based separation processes. However, fine coal particles (typically <0.2 mm) are processed using froth flotation circuits, which require small dosages of reagents known as collectors and frothers. Collectors consist of oily hydrocarbons, such as diesel fuel, kerosene, and fuel oil, which are insoluble in water and coat fine coal particles. If required, dosages are typically in the range of 0.1 to 1.0 kg of collector per ton of fine coal processed. Likewise, frothers are added to all flotation systems to promote the formation of small air bubbles and to create a stable froth. Frothers are typically various types of alcohol and polyglycol surfactants.

**Table 5 Guidelines for discharge from coal preparation**

| Parameter | EPA* Guidelines for 1 Day | EPA† Guidelines for 30 Days |
|---|---|---|
| Iron (total), mg/L | 7.0 | 3.5 |
| Manganese (total), mg/L | 4.0 | 2.0 |
| pH | 6.0–9.0 | 6.0–9.0 |
| Total suspended solids, mg/L | 70 | 35 |

Data from EPA 2018

*Maximum for any one day.

†Average of daily values for 30 consecutive days.

#### *Flocculation and Sedimentation*

The treatment of tailings from the coal preparation plant requires special consideration of the nature of the ultrafine particles and inorganic impurities present. The natural sedimentation rate of these particles in their colloidal and finely divided suspended forms is very slow.

Flocculation technology is applied by using inorganic salts, polymeric flocculants, or both, depending on the chemical and physical characteristics of the pollutants that are present in suspended and dissolved states. Synthetic or natural polymeric reagents are generally used as flocculating agents. To achieve faster settling rates and water clarity, the optimization of process parameters such as suspension pH, polymer type, and dosage are very important. Various flocculent combinations such as cationic, anionic, and non-ionic have been used to achieve the highest settling rate with lowest turbidity.

Das et al. (2006) reported on an investigation into the use of magnetic carrier technology, which is an innovative way of selectively manipulating fine particles in suspension by coating them with a magnetic species. The addition of fine magnetite particles to the flocculation process achieved a significant reduction in final suspended solids after settling.

### *Reverse Osmosis*

The potential for reuse of an effluent can often be limited by the presence of dissolved salts that arise from contact of the process water with the coal within the preparation processes. More recently, several coal mining operations in Australia have installed RO facilities to remove as much dissolved salts as possible, before recycling the treated water back into the site water balance.

Several stages of prefiltration are likely to be needed before RO can be used. Even after a good flocculation and sedimentation process performance, the treated water will still contain some colloidal suspended particles and have concentrations of TSS that are well in excess of that suitable for feeding direct to RO membranes.

Additional stages of filtration will be necessary:

- **Screen filtration.** Screen filters should hold screens with apertures of ≤150 µm and be of the automatic backwashable type to ensure good solids removal performance.
- **Membrane filtration such as ultrafiltration.** Hollow-fiber ultrafiltration membranes can accept particle sizes up to 150 µm and feed TSS levels up to 100 mg/L maximum. These membranes will produce a filtrate with a silt density index of <5 that is suitable for RO membrane feed.

## ACID MINE DRAINAGE

AMD wastes are commonly formed in coal mines, both in aboveground and underground mines. The following reactions can occur under oxidizing conditions:

$$FeS_2 + 7/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \textbf{(EQ 6)}$$

$$Fe^{2+} + ¼O_2 + H^+ = Fe^{3+} + ½H_2O \qquad \textbf{(EQ 7)}$$

$$Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+ \qquad \textbf{(EQ 8)}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad \textbf{(EQ 9)}$$

The rate of pyrite ($FeS_2$) oxidation depends on several variables, such as reactive surface area of pyrite, form of pyritic sulfur, oxygen concentrations, solution pH, catalytic agents, and flushing frequencies. Reaction 6 produces hydrogen ions, which significantly reduce the pH levels in the waste. The oxidation reaction (7) is usually the rate-limiting step. This is due to the conversion of ferrous iron to ferric iron being relatively slow at the low pH (<5) levels that are commonly found in these wastes. Iron-oxidizing bacteria (principally *Thiobacillus*) can greatly accelerate this oxidation reaction, so the activities of bacteria are crucial for the generation of AMD.

If there is low porosity and permeability in the strata (e.g., soft shale), the availability of oxygen may be the rate-limiting step. In this case, oxidation will be limited to the upper few meters of the strata. In contrast, for porous and permeable strata (e.g., coarse sandstone), air convection driven by the heat generated from pyrite oxidation may provide high amounts of oxygen deep into the spoil.

The amount of acidity formed can be estimated empirically by using Equation 6:

$$\begin{aligned}\text{acidity (mg/L as } CaCO_3) = 50 \times [&(3 \times Al/27) \\ &+ (2 \times Mn/55) + (3 \times Fe/56) \\ &+ 1{,}000 \times 10 \text{ (power of } -pH)] \qquad \textbf{(EQ 10)}\end{aligned}$$

where Al, Mn, and Fe represent the concentrations of aluminum, manganese, and iron, respectively (in milligrams per liter).

The metals content of mine wastewater varies significantly depending on the following factors:

- Geology and geochemistry of the mine environment
- Specific ore being mined
- pH and ORP of the mine water, which governs the solubility of metals
- Climatic conditions

Many metals have an amphoteric property, with decreasing solubility up to a threshold pH, above which the metal solubility increases again because of the formation of soluble complexes. Dissolved metal levels in many sources of mine wastewater often exceed the limits for discharge to the environment. Although elevated sulfate levels have a lower toxicity impact than acidity or metals, sulfate in effluents is increasingly coming under the scrutiny of regulatory authorities.

### Lime Neutralization Processes

Although there are many different biological and chemical technologies used for treatment of AMD, lime neutralization remains, by far, the most widely applied treatment method. This is largely due to the high efficiency in removal of dissolved heavy metals and because lime costs are low in comparison to alternatives.

Lime treatment involves bringing the pH of the drainage water to a point where the metals of concern are insoluble and precipitate out in the form of minuscule particles. Figure 9 shows the solubility of metal hydroxides as a function of pH. By controlling pH at 9.5, some of the metals such as iron, aluminum, and copper can be precipitated out to relatively low levels (<0.01 mg/L). However, some other metals may require a higher pH (10.5–11) to effectively precipitate out the hydroxides. Depending on the metal concentrations in the AMD, this may require two or more stages of treatment at different pH levels to achieve the overall limits in the treated water.

A separation process is then required to remove the precipitates and produce a clear effluent that meets regional discharge criteria. It is the method of separation of the precipitates that differs between some of the more recent and complex variations to this AMD treatment method. The older methods use lime less efficiently and do not allow for good control of the treatment system. The more recent processes require a greater capital investment but are considerably more efficient for lime usage and waste production.

The sludge formed depends on the applied process and can contain 1%–30% solids by weight. This sludge must be disposed of in an environmentally acceptable manner. Given that sludge disposal costs can be important, the most advanced processes minimize the volumes by creating an HDS. The sludge disposal and lime costs over the long term usually justify a more important capital investment due to significant savings in operating costs.

A common by-product of lime neutralization is gypsum. Gypsum precipitation occurs because the AMD is often rich is sulfate and the calcium added from lime will bring the solubility product well above saturation. This reaction is often responsible for scaling in treatment processes as well as increasing sludge production at sites where the feed sulfate concentrations can surpass 2,500 mg/L. This scale formation is particularly troublesome for plants where lime is added directly to water that contains significant concentrations of sulfate.

The advantages and disadvantages of several of the different methods of using lime neutralization are discussed in the following sections (Aubé 2004).

### *Pond Treatment*

Pond treatment involves adding lime in a stream or mixing system and allowing the precipitates to settle out within a pond. The pond is often divided into primary and secondary sections. The primary pond serves to accumulate the precipitated sludge and can quickly be filled with solids. These ponds often require yearly dredging of sludge, which then requires a storage area. The secondary pond is usually larger and requires a longer retention time, with laminar flow conditions to allow for "polishing" of the effluent.

Pond treatment systems are often chosen for their simplicity and low capital costs when land is available. They can be used to treat very high flow rates and even important concentrations of metals but require a very large surface area when doing so. The greatest disadvantage of pond treatment systems is their low lime efficiency. A system that uses in-stream addition without any mechanical mixing may have less than 50% efficiency in lime dissolution. By using an agitator and pH control system, the lime usage efficiency can be increased significantly.

To ensure proper treatment in a pond system, the pH set point is often brought up much higher than is necessary for the targeted metals. For example, some pond systems for treating dissolved Zn often control the pH to more than 10.5, rather than the optimum of 9.3. This may necessitate the addition of carbon dioxide or sulfuric acid to reduce the final discharge pH level.

### *Sludge Recycle Process*

In the sludge recycling process, the AMD is neutralized in a reactor tank with the controlled addition of lime to attain a desired pH set point. The slurry is then contacted to a flocculant and fed to a clarifier for solid–liquid separation. Sludge is collected from the bottom of the clarifier and some is recycled back to the reactor tank. The solids in the recycled sludge serve to increase the final sludge density due to precipitation on the surfaces of the existing particles.

The surplus sludge can either be pumped to a storage area or pressure filtered to increase its density prior to transport. The clarifier overflow can normally be released directly, but often a sand filtration system or polishing pond is used to reduce residual suspended solids.

### *High-Density Sludge Process*

The HDS process is commonly used for AMD treatment. Instead of contacting the lime directly with the incoming AMD stream, this system contacts the recycled sludge with the lime slurry for neutralization. To do this, the sludge from the clarifier bottom is pumped to a lime/sludge mix tank, where sufficient lime is added to raise the pH to the desired pH set point. This step forces contact between the solids and promotes coagulation of lime particles onto the recycled precipitates.

The neutralized slurry feeds to the lime reactor where the precipitation reactions are completed. Aeration is often added to this reactor to oxidize ferrous iron to ferric. The slurry then overflows to a floc tank to contact the particles to a flocculant, properly agglomerate all precipitates, and promote efficient settling in the clarifier. The clarifier overflow can either be discharged or polished prior to discharge.

The key to this process lies in the mixing of lime and sludge prior to neutralization of the AMD. Precipitation reactions occur mostly on the surface of existing particles, thereby increasing their size and density. This process is capable of producing sludge of up to 20% solids concentration.

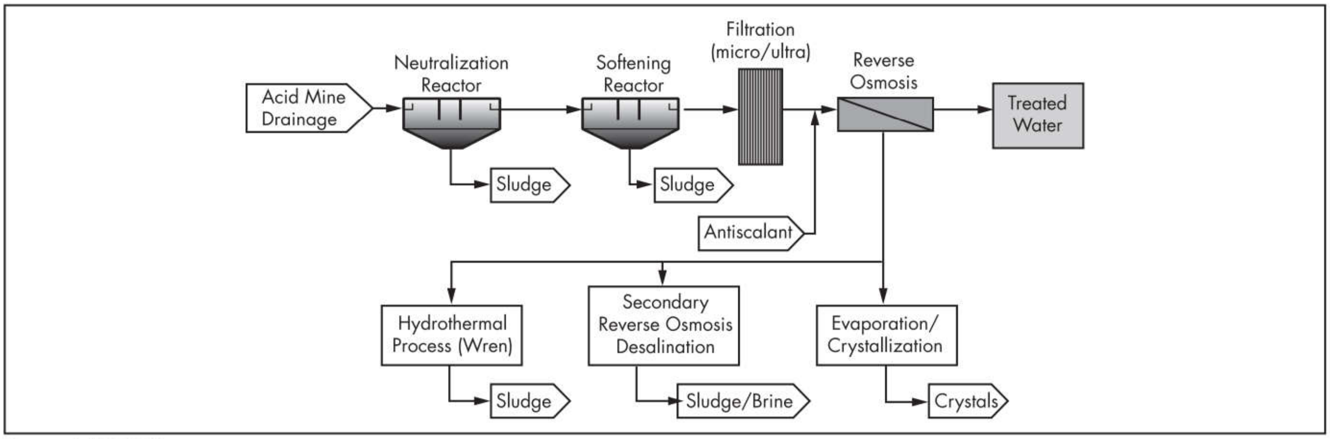
The HDS process minimizes scaling in reactors because the gypsum has other surfaces on which to precipitate. Gypsum is a crystal that preferentially forms on existing gypsum. When sludge is recycled, there are plenty of gypsum needles available in the slurry and these serve as preferred gypsum formation sites. If a plant operates without recycle and significant sulfate is present, some precipitation will occur on the reactor wall surfaces. Once these surfaces are coated, gypsum precipitation is facilitated and the rate of precipitation increases. HDS processes are therefore preferred for high-sulfate effluents, as they will minimize scaling in the reactors.

### *AMD with Arsenic*

Treating AMD that contains arsenic with lime requires a very high pH level and tends to form an unstable sludge due to calcium arsenate. A more acceptable treatment is co-precipitation of arsenic with ferric and/or base metals such as copper and zinc. In all cases, pre-oxidation of As(III) to As(V) may be required, both for improved treatment efficiency and the production of a stable sludge. Many oxidants can be used with varying effectiveness and cost.

When treating with ferric iron, it is preferable to have a two-step process that precipitates most of the arsenic at a slightly acidic pH (4–6). This will form a more stable precipitate (ferric arsenate). In the second step, any other heavy metals present are precipitated and the remaining arsenic is essentially removed from solution.

Sludge recycle can be used to increase treatment efficiency. This can result in significant savings in reagent addition but can also cause the arsenic to be mostly adsorbed as opposed to co-precipitated. Adsorbed arsenic is slightly less stable than when it is co-precipitated as a ferric arsenate. The recycle will also help improve lime efficiency. An excess of iron can be applied with any process to improve sludge stability. The final sludge disposal system can weigh into the decision as to whether a recycle is applied and what ratio of iron to arsenic is used.



Source: INAP 2009

**Figure 12 Typical flow sheet for treating AMD streams**

### *AMD with Molybdenum*

Molybdenum does not precipitate with lime addition as do the typical heavy metals. The most widely applied treatment process for AMD containing molybdenum is ferric coprecipitation. An example is given by Aubé and Stroiazzo (2000), where ferric sulfate is added to the alkaline AMD (about 3 mg/L of Mo) in the first step, and the pH is controlled to 4.5 in the second step. A flocculant is added to improve solid–liquid separation in the clarifier. To achieve a very low molybdenum level in the discharge (0.03 mg/L), a sand filter is also used to remove all residual molybdenum from the effluent.

### *AMD Treatment by Reverse Osmosis*

RO is widely used in South America for treating AMD waters (Chesters et al. 2016). A typical flow sheet for treating AMD water is shown in Figure 12. Chesters et al. undertook a survey of 67 membrane plants worldwide and a summary of the information is provided in Tables 6 and 7. At the time, 25 plants were in Latin America, principally in Peru and Chile. The number of plants in Chile was boosted by 12 seawater RO units. Gold and copper account for 69% of the mines that have invested in RO plants. The largest application of RO plants is for AMD treatment. Only 15 of the RO plants were specifically designed for enhanced metal recovery.

**Table 6 Membrane plans by geography and mine type**

| Location | Number of Plants | Type of Mine | Number of Plants |
|---|---|---|---|
| Latin America | 25 | Gold | 30 |
| Africa | 18 | Copper | 16 |
| North America | 15 | Coal | 6 |
| Australasia | 7 | Diamonds | 3 |
| Europe | 1 | Iron | 3 |
| Asia | 1 | Others | 6 |

Source: Chesters et al. 2016

**Table 7 Treatment by feed water type**

| Treated Water | Number of Plants |
|---|---|
| AMD cleanup | 22 |
| Seawater reverse osmosis | 17 |
| Metal recovery | 15 |
| Drinking water | 8 |
| Leachate | 5 |

Source: Chesters et al. 2016

### *Sludge Disposal*

The choice of method for sludge disposal depends on many factors, including regulatory considerations, sludge stability, sludge production rate, space availability, budget, and aesthetic considerations. Disposal in mine workings is often the least-expensive option but this choice requires more public and regulatory approval.

Other options for sludge disposal include disposal with tailings in engineered ponds, on waste rock piles, under a water cover, or in natural land depressions. Disposal with tailings can be done for operating mines. Another option is to dispose of sludge by placing it on the top of a closed tailings pile. Covering tailings with sludge may help reduce oxidation by providing a wet barrier, similar to that of engineered soil covers. Unfortunately, these options have not yet been sufficiently researched to confirm that this sludge would not eventually redissolve if tailings oxidation continues.

Engineered pond disposal is more expensive at first, but eventually results in the lowest volume of sludge generated. This is because these ponds can be designed to both drain water from the bottom and allow for evaporation from the top. Most sludges will densify further up to two or three times their original solid content. Therefore, some sites allow their sludge to densify in an engineered pond for a year or two before transporting it to a different location (on tailings or in mine workings).

## Innovative Technologies

In recent years, several innovative technologies for treatment of AMD have been put into operation, such as permeable reactive barriers (PRBs), bioreactors, and constructed aerobic wetland technologies. Case studies on these innovative technologies are detailed by Costello (2003). The majority are in situ applications that manipulate natural processes to treat acidic and/or metals-contaminated water. The differences lie in their construction and their water source. Both bioreactors and wetlands almost always include collection and piping systems, whereas PRBs are simply placed in the flow path.

### *Permeable Reactive Barriers*

PRBs have a subsurface reactive section through which groundwater flows as it follows its natural course. In some cases, there are impermeable walls to direct the flow of the water to the reactive section. The reactive media is usually compost that hosts sulfate-reducing bacteria, although there are a few other types of media used.

### *Bioreactors*

In the case of bioreactor systems, the water (ground or surface) to be treated flows through a media bed, and natural biological reactions work to remove dissolved metals. Whether subsurface or exposed to the atmosphere, bioreactors are generally lined, filled with composted materials and/or alkaline agents, and, in some situations, include vegetation.

### *Aerobic Wetlands*

Constructed aerobic wetlands are shallow (10–30 cm deep) and lined ponds that are filled with organic matter and/or alkaline agents and sometimes vegetation. Aerobic wetlands are most often used to treat alkaline waters that are high in dissolved iron and have low capacity to neutralize the acidity.

Oxygen infiltration is encouraged because it flows slowly through vegetation. Iron and other metals precipitate as oxyhydroxides, hydroxides, and carbonates by the mechanisms of absorption and adsorption. Aerobic wetlands can also remove manganese, but oxidation of manganese only starts when oxidation of iron is completed. To remove manganese, it is necessary to have a big pond area, which allows complete iron oxidation, or to add another wetland cell (Zipper et al. 2011).

## REFERENCES

Akcil, A. 2003. Destruction of cyanide in gold mill effluents: biological versus chemical treatments. *Biotechnol. Adv.* 21:501–511.

Arnold, B.J., and Aplan, F.F. 1986. The effect of clay slimes on coal flotation, part II: The role of water quality. *Int. J. Miner. Process.* 17(3-4):243–260.

Aubé. B. 2004. The Science of Treating Acid Mine Drainage and Smelter Effluents. EnvirAube.

Aubé, B.C., and Stroiazzo, J. 2000. Molybdenum treatment at Brenda Mines. In *ICARD 2000: Proceedings of the 5th International Conference on Acid Rock Drainage*. Littleton, CO: SME.

Aubé, B., and Zinck, J. 2003. Comparison of AMD treatment processes and their impact on sludge characteristics. In *Proceedings of Sudbury '99: Mining and the Environment II.* Sudbury: ON: Laurentian University.

Barakat, M.A. 2011. New trends in removing heavy metals from industrial wastewater. *Arabian J. Chem.* 4:361–377.

Bickert, G. 2013. *Seal, Spray and Wash Water Filtration in Coal Preparation Plants.* Brisbane, Queensland: Australian Coal Industry Research Program.

Botz, M.M., and Mudder, T.I. 1998. Cyanide recovery for silver leaching operations; application of CCD-AVR circuits. In *Proceedings of the Randol Gold and Silver Forum*. Golden, CO: Randol International. pp. 295–297.

Botz, M.M., and Mudder, T.I. 2000. Modeling of natural cyanide attenuation in tailings impoundments. *Miner. Metall. Process.* 17(4).

Chesters, S.P., Morton, P., and Fazel, M. 2016. Membranes and minewater—Waste or revenue stream. In *Proceedings of IMWA 2016: Mining Meets Water—Conflicts and Solutions.* Freiberg: Technische Universität Bergakademie. pp. 1310–1322.

Coetzer, G., du Preez, H.S., and Bredenhann, R. 2003. Influence of water resources and metal ions on galena flotation of Rosh Pinah ore. *J. SAIMM* (April).

Coleman, R.T., Colley, J.D., Klausmeier, R.F., Meserole, N.P., Micheletti, W.C., and Schwitzgebel, K. 1980. *Sources and Treatment of Wastewater in the Nonferrous Metals Industry.* EPA-600/2-80-074. Cincinnati, OH: U.S. Environmental Protection Agency, Industrial Environmental Research Laboratory, Office of Research and Development.

Costello, C. 2003. *Acid Mine Drainage: Innovative Treatment Technologies.* Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response.

Das, B., Prakash, S., Biswal, S.K., and Reddy, P.S.R. 2006. Settling characteristics of coal washery tailings using synthetic polyelectrolytes. *J. SAIMM* 106(October).

Diaz, M., Cavero, A., and Yataco, D. 1998. Water management at Minera Yanacocha. In *Latin American Perspectives: Exploration, Mining, and Processing.* Littleton, CO: SME. pp. 329–340.

Dunstan, A. 1999. The effects of water quality on mineral processing. In *Proceedings of WAMMO '99*, August 24–25. pp. 236–242.

EPA (U.S. Environmental Protection Agency). 2018. International cooperation. https://www.epa.gov/international-cooperation. Accessed July 2018.

Evangelho, M.R., Gonçalves, M.M.M., Sant'Anna Jr. G.L., and Villas Bôas, R.C. 2001. A trickling filter application for the treatment of a gold milling effluent. *Int. J. Miner. Process.* 62(1-4):279–292.

Fleming, C.A., and Trang, C.V. 1998. R eview of options for cyanide recovery at gold and silver mines. In *Proceedings of the Randol Gold and Silver Forum*. Golden, CO: Randol International. pp. 313–318.

Forssberg, K.S.E., and Hallin, M.I. 1989. Process Water Recirculation in a Lead-Zinc Plant and other sulphide flotation plants. In *Challenges in Mineral Processing.* Edited by K.V.S. Sastry and M.C. Fuerstenau. Littleton, CO: SME.

Given, B., Dixon, B., Douglas, G., Mihoc, R., and Mudder, T. 1998. Combined aerobic and anaerobic biological treatment of tailings solution at the Nickel Plate mine. In *The Cyanide Monograph.* London: Mining Journal Books.

Greenway, M., and Simpson, J.S. 1996. Artificial wetlands for wastewater treatment, water reuse and wildlife in Queensland, Australia. *Water Sci. Technol.* 33(10-11):221–229.

Halbe, D., Trautman, L., Neville, R.G., Hart, L., and Omnen, R. 1979. Destruction of cyanide in Homestake gold mill effluent—A status report. Presented at AIME Fall Meeting, October.

Hoover, M.R. 1980. Water chemistry effects in the flotation of sulphide ores—A review and discussion for molybdenite. In *Complex Sulphide Ores Conference.* Edited by M.J. Jones. London: Institution of Mining and Metallurgy. pp. 100–112.

INAP (International Network for Acid Prevention). 2009. *Global Acid Rock Drainage Guide*. Rev. 1. www.gardguide.com.

Johnson, N.W. 2003. Issues in maximisation of recycling of water in a mineral processing plant. In *Proceedings of Water in Mining 2003*. Melbourne, Victoria: Australasian Institute of Mining and Metallurgy. pp. 239–245.

Kirjavainen, V., Schreithofer, N., and Heiskanen, K. 2002. The effect of calcium and thiosulphate ions on flotation selectivity of nickel-copper ores. *Miner. Eng.* 15:1–5.

Kitis, M., Akcil, A., Karakaya, E., and Yigit, N.O. 2005. Destruction of cyanide by hydrogen dioxide in tailings slurries from low bearing sulphidic gold ores. *Miner. Eng.* 18(3):353–362.

Larsen, M., Trapp, S., and Pirandello, A. 2004. Removal of cyanide by woody plants. *Chemosphere* 54:325–333.

Lawrence, R.W., Poulin, R., Kalin, M., and Bechard, G. 1998. The potential of biotechnology in the mining industry. *Min. Process Extr. Metall. Rev.* 19:5–23.

Lorenzen, L. 2015. International trends on effluent treatment and management in the Gold Mining Industry. University of Pretoria, Republic of South Africa, November.

Lotter, N. 2005. Cyanide volatilisation from gold leaching operations and tailing storage facilities. University of Pretoria, Republic of South Africa, November.

Madin, C. 2007. Innovative treatment of gold mine water for sustainable benefit—Processes and case studies. In *World Gold 2013.* Melbourne, Victoria: Australasian Institute of Mining and Metallurgy.

Malysiak, V., Shackleton, N.J., and de Vaux, D. 2003. Effect of water quality on pentlandite-pyroxene floatability with an emphasis on calcium ions. In *Proceedings of the 22nd International Mineral Processing Congress.* Marshalltown, South Africa: Southern African Institute of Mining and Metallurgy.

Marsden, J.O., and House, C.I. 2009. *The Chemistry of Gold Extraction.* Littleton, CO: SME.

McGrath, T., Simons, A., Dunne, R., and Staunton, W.P. 2015. Cyanide recovery using SART—Current status. In *World Gold 2015.* Johannesburg: Southern African Institute of Mining and Metallurgy.

Meyer, K. 1992. The David Bell mine water quality management strategy. *CIM Bull.* (September):27–30.

Monteagudo, J.M., Rodriguez, L., and Villasenor, J. 2004. Advanced oxidation processes for destruction of cyanide from thermoelectric power station waste waters. *J. Chem. Technol. Biotechnol*. 79:117–125.

Mosher, J.B., and Figueroa, L. 1996. Biological oxidation of cyanide: A viable treatment option for the minerals processing industry? *Miner. Eng*. 9(5):573–581.

Mudder, T., Fox, F., Whitlock, J., Fero, T., Smith, G., Waterland, R., et al. 1998. The Homestake wastewater treatment process, part 2: Operation and performance. In *The Cyanide Monograph.* London: Mining Journal Books. pp. 365–388.

Mudder, T., Botz, M., and Smith, A. 2001. *The Cyanide Compendium* (CD-ROM). London: Mining Journal Books.

Muzenda, E. 2010. An investigation into the effect of water quality on flotation performance. *Int. J. Chem. Mol. Nucl. Mater. Metall. Eng.* 4(9).

Nelson, M.G., Kroeger, E.B., and Arps, P.J. 1998. Chemical and biological destruction of cyanide: comparative costs in a cold climate. *Min. Process Extr. Metall. Rev.* 19:217–26.

Ng'andu, D.E. 2001. The effect of underground mine water on the performance of the Mufulira flotation process. *J. SAIMM* (October).

NRC (National Research Council). 2012. *Uranium Mining in Virginia: Scientific, Technical, Environmental, Human Health and Safety, and Regulatory Aspects of Uranium Mining in Virginia.* Washington, DC: National Academies Press.

Ofori, P., Firth, B., McNally, C., and Nguyen, A. 2009. *Working Effectively with Saline Water in Coal Preparation—Report and Handbook.* Brisbane, Queensland: Australian Coal Industry Research Program.

Pourbaix, M. 1974. *Atlas of Electrochemical Equilibria in Aqueous Solutions*, 2nd English ed. Houston, TX: National Association of Corrosion Engineers.

Raybuck, S.A. 1992. Microbes and microbial enzymes for cyanide degradation. *Biodegradation* 3:3–18.

Rey, M., and Raffinot, P. 1985. Flotation of ores in seawater. In *Water Management and Treatment for Mining and Metallurgical Operations.* Vol. 6. Edited by H. von Michaelis. Golden, CO: Randol International. pp. 3167–3174.

Ring, R.J., Holden, P., McCulloch, J.K., Tapsell, G.J., Collier, D.E., Russell, R., MacNaughton, S., Marshall, K., and Stimson, D. 2004. Treatment of liquid effluent from uranium mines and mills during and after operation. In *Treatment of Liquid Effluent from Uranium Mines and Mills: Report of a Co-Ordinated Research Project 1996–2000.* IAEA-Tecdoc-1419. Vienna, Austria: International Atomic Energy Agency.

Ritcey, G.M. 2004. Prediction of weathering and contaminant migration in mine/mill tailings. In *Proceedings of the VI International Conference on Metallurgy, Refractories and Environment*. Edited by P. Palfy, M. Solc, and E. Vircikova. Slovakia: Kosice.

Ritcey, G.M. 2005. Tailings management in gold plants. *Hydrometallurgy* 78:3–30.

Rouse, J., and Pyrih, R. 1998. Natural geochemical attenuation of trace elements in migrating precious-metal process solutions. In *Proceedings of the Randol Perth International Gold Conference.* Golden, CO: Randol International.

Rowly, W.J., and Otto, F.D. 1980. Ozonation of cyanide with emphasis on gold mill waste waters. *Can. J. Chem. Eng.* 58(5):646–653.

Rytter, R.-M., and Hansson, A.-C. 1996. Seasonal amount, growth and depth distribution of fine roots in an irrigated and fertilized *Salix viminalis* L. plantation. *Biomass Bioenergy* 11:129–137.

Schmidt, J.W., Simovic, L., and Shannon, E. 1981. Natural degradation of cyanides in gold milling effluents. Seminar on Cyanide and Gold Mining Industry, Environment Canada, Ottawa, ON.

Schnell, H., and Thiry, J. 2007. Processing of high grade uranium ore. Presented at 2007 SME Annual Meeting, February 26, Denver, CO.

Schnitzler, M., Lévay, G., Kühn, W., and Sontheimer, H. 1983. Determination of organic halogen and sulphur compounds in water by group parameters. *Vom Wasser* 61:263–276.

Shackleton, N.J., Malysiak, V., and Slatter, K.A. 2001. Effect of water quality and surface passivation on flotation behaviour. Anglo American Metallurgical Symposium, November 1, Session 4, Paper 2.

Slatter, K.A. 2001. *Flotation of Waterval Mill Feed with Filtered Process Water and Process Water Treated by Ion Exchange.* Internal Report MP/09/01.

Slatter K.A., et.al. 2009. Water management in Anglo Platinum process operations: Effects of water quality on process operations. In *Proceedings of the International Mine Water Conference*, Pretoria, South Africa, October 19.

Smart, R.St.C., Skinner, W.M., and Levay, G. 1999. Process water quality and treatment: issues and methodology. In *Proceedings of WAMMO '99.* pp. 226–235.

Smith, A., and Mudder, T. 1991. *Chemistry and Treatment of Cyanidation Wastes.* London: Mining Journal Books.

Smith, M., and Hertzog, L.D. 1985. Seawater in flotation. In *Water Management and Treatment for Mining and Metallurgical Operations.* Vol. 6. Edited by H. von Michaelis. Golden, CO: Randol International. pp. 3163–3164.

Whitlock, J.L., and Mudder, T.I. 1986. The Homestake wastewater treatment process: biological removal of toxic parameters from cyanidation wastewaters and biossay effluent evaluation. In *Fundamental and Applied Biohydrometallurgy.* Edited by R.W. Lawrence, R.M.R. Branion, and H.G. Ebner. Amsterdam: Elsevier. pp. 327–339.

Zhang, J., Chen, S., Rao, S., and Qi, J. 2004a. Analysis and evaluation of water coming from several uranium processing areas. In *Treatment of Liquid Effluent from Uranium Mines and Mills: Report of a Co-Ordinated Research Project 1996–2000.* IAEA-Tecdoc-1419. Vienna, Austria: International Atomic Energy Agency.

Zhang, J., Chen, S., Rao, S., and Qi, J. 2004b. Barium chloride precipitation-sludge recycle to treat acidic uranium industrial effluent. In *Treatment of Liquid Effluent from Uranium Mines and Mills: Report of a Co-Ordinated Research Project 1996–2000.* IAEA-Tecdoc-1419. Vienna, Austria: International Atomic Energy Agency.

Zhang, J., Chen, S., and Qi, J. 2004c. Research on the removal of radium from uranium effluent by air-aeration hydrated manganese hydroxide adsorption. In *Treatment of Liquid Effluent from Uranium Mines and Mills: Report of a Co-Ordinated Research Project 1996–2000.* IAEA-Tecdoc-1419. Vienna, Austria: International Atomic Energy Agency.

Zhang, J., Chen, S., Qi, J., and Rao, S. 2004d. Study on the technology for the development of macro-porous resin adsorption for high purification of uranium effluent. In *Treatment of Liquid Effluent from Uranium Mines and Mills: Report of a Co-Ordinated Research Project 1996–2000.* IAEA-Tecdoc-1419. Vienna, Austria: International Atomic Energy Agency.

Zipper, C., Skousen, J., and Jage, C. 2011. Passive treatment of acid mine drainage. In *Powell River Project: Reclamation Guidelines for Surface Mined Land*. Virginia Cooperative Extension Publication 460-133. Blacksburg, VA: Virginia Tech.