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Review of the Impact on Water Quality and Treatment Options of Cyanide Used in Gold Ore Processing

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Additional information is available at the end of the chapter

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Abstract

Cyanide has been widely used in several industrial applications such as electroplating, photography, metal processing, agriculture, food and the production of organic chemicals, plastics, paints and insecticides. The strong affinity of cyanide for metals such as gold and silver makes it suitable for selective leaching of these metals from ores. Cyanide is highly toxic; hence, there is a need to regulate and limit the amount of cyanide that may be discharged into the environment. Technologies focusing on the use of physical, chemical and biological methods have been developed to reduce the concentration of cyanide and cyanide compounds in wastewaters to permissible limits. This chapter reviews the current and emerging technologies for treatment of cyanide from wastewaters generated in gold mining processes.

Keywords: cyanide, gold, leaching, oxidation, wastewater

1. Introduction

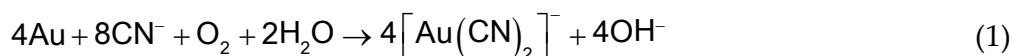
Cyanide is an extremely toxic substance that is produced naturally and artificially. Cyanide has been widely used in several industries applications such as textile, plastics, paints, photography, electroplating, agriculture, metal treatment and mining. The high binding affinity of cyanide for metals such as gold, zinc, copper and silver has enabled it to selectively leach these metals from ores.

Southern Africa is a region rich in minerals such as gold. Countries in the southern Africa boost their economies through vast investments in gold mining. Cyanide leaching has become the dominant gold extraction technology since the 1970s replacing previously used less efficient and more toxic mercury. These gold mines discharge effluent containing toxic cyanides into

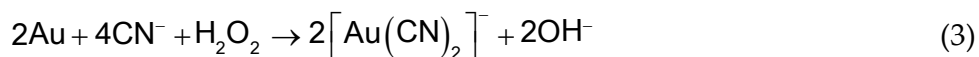
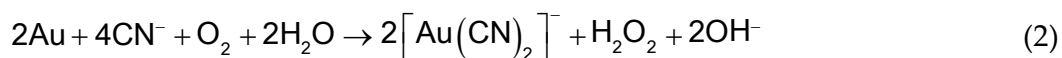
natural water bodies posing the greatest threat to the quality of water intended for human use. Therefore, it is imperative to develop effective strategies for the removal of cyanide from aqueous industrial wastewater streams.

2. Gold extraction process using cyanide

Cyanidation is the predominant gold extraction technique since the late nineteenth century. The dissolution of gold in aqueous cyanide is commonly described using Elsner's equation [1]:



Gold dissolution is an electrochemical process in which oxygen is reduced at the cathodic zone, while gold is oxidised at anodic regions. The precise overall dissolution of gold in alkaline, aerated cyanide solutions taking place at cathodic and anodic regions is represented in Eqs. (2) and (3).



The main merits of cyanidation are the high selectivity of free cyanide for gold dissolution compared to other metals and an extremely high stability constant (2×10^{38}) of the gold cyanide complex [2].

Dilute sodium cyanide solutions within concentration ranges of 0.01–0.05% are used in mines for gold leaching [3]. Gold ore is subjected to physical processes such as milling, grinding and gravity separation prior to the addition of aqueous sodium cyanide to form slurry. The pH of the resulting extracting solution is increased by adding slaked lime or sodium hydroxide to prevent generation of toxic hydrogen cyanide [4]. The slurry pH is maintained at not less than 10.5 during cyanidation to prevent excessive loss of cyanide by hydrolysis through volatilisation of hydrogen cyanide. Oxygen an important component during cyanidation is continuously pumped into the slurry resulting in the formation of dicyanoaurate (I) complex.

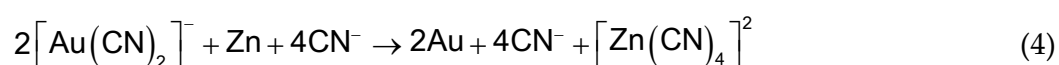
Several methods are employed for cyanide leaching of gold ore [5]. However, agitation leaching is commonly used for most ores due to its commercial viability [6]. Leaching is typically done in steel vessels, and the solids are maintained in suspension by air or mechanical agitation.

The gold complex $\text{NaAu}(\text{CN})_2$ is then extracted from leach solutions by adsorption onto solid adsorbents such as activated carbon or a synthetic ion exchange resin [7–11]. Activated carbon

is the most commonly used adsorbent for gold extraction due to several favourable properties such as high adsorption capacity, good reactivation capabilities, low cost, readily available, high mechanical strength and wear resistance [12].

Gold complexes adsorbed onto activated carbon are eluted to produce concentrated high-grade gold solutions suitable for final gold recovery. Eluents such as sodium hydroxide [13] and organic solvents in aqueous solutions [14] have been used for desorption or stripping of gold from activated carbon.

Gold is extracted from solution into a concentrated solid form by a process termed recovery. Zinc precipitation [15] and electrowinning [16] have been used to treat concentrated gold solutions produced from activated carbon stripping. Eq. (4) represents the electrochemical reduction process for gold.



The gold recovered from crude undergoes refining to produce crude bullion containing between 90 and 99.5% pure gold [17]. Refining involves roasting the crude gold to convert base metals such as iron, lead, copper and zinc to their respective oxides. This process is then followed by smelting, which removes base oxide impurities in form of slag. The bullion produced can be upgraded further to higher purity platinum group metals by processes such as pyrorefining, hydrometallurgy and electrowinning [18, 19]. These extraction processes leave behind toxic cyanide tailings.

3. Occurrence of cyanide in environment

Cyanide and related compounds are produced at low levels from plants such as sorghum, cassava, potato, broccoli, cashews and apricots [20]. Cyanide is found in certain bacteria, fungi and algae [21]. Anthropogenic sources of cyanide release also include smoke from cigarettes, automobile exhaust fumes and the production of acrylonitrile. Bulk occurrence of cyanide in the environment is attributed to the human operations in industries, metallurgical and mining activities. Cyanide is mainly produced industrially in form of hydrogen cyanide gas or solid sodium cyanide or potassium cyanide [22].

4. Forms of cyanide in aqueous solution

Compounds of cyanides present in water can be generally classified into total cyanide, complex cyanide and free cyanide [23–25]. These aqueous cyanide compounds exist as simple and complex cyanides, cyanates and nitriles. The most toxic form of cyanide is free cyanide, which exists either as cyanide anion or as hydrogen cyanide (HCN) depending on solution pH. HCN

is predominant in aqueous systems at pH below 8.5 and can be readily volatilised [26, 27]. At higher pH values, the free cyanide is mainly in form of the cyanide anion. Aqueous cyanides form complexes with metal ions present in industrial wastewaters. These metallo-cyanide complexes exhibit different chemical and biological stabilities. The complexes are classified as weak acid dissociable (WAD) and strong acid dissociable [28, 29] in accordance with the metal-cyanide bond strength. Cadmium, copper, nickel and zinc form weak acid dissociable complexes that readily dissociate under acidic conditions [28]. Complexes of cyanide with cobalt, iron, silver and gold are strong acid dissociable (SAD). Both forms of complexes dissociate and release free cyanide. The stability of these complexes depends on several factors such as pH, light intensity, water temperature and total dissolved solids.

5. Toxicity of cyanide

Cyanide is extremely toxic to humans and aquatic life. Unlike toxic metal ions, the cyanide anion does not accumulate in the body, but instantaneously results in death of aquatic life and human beings in a short time at low dosages through depressing the central nervous system [30]. Cyanide strongly binds cytochromes inhibiting the electron transport chain in mitochondria and energy release in cells [31]. Liquid or gaseous hydrogen cyanide gains entry into the body through inhalation, ingestion or skin absorption. Exposing animals to hydrogen cyanide has several effects such as headaches, dizziness, numbness, tremor and loss of visual sharpness. Other toxic effects of cyanide include an enlarged thyroid gland, cardiovascular and respiratory problems.

6. Acceptable limits for the use of cyanide

There is need for the treatment of wastewater containing cyanide before discharging into the environment to protect water bodies. As a result of this, several countries and environmental bodies have imposed limiting standards for discharging wastewater containing cyanide to main natural water bodies. **Table 1** shows the set acceptable discharge limits of total cyanides by different organisations.

Agent	Cyanide limit	Reference
The U.S. Environmental Protection Agency (USEPA)	50 ppb (aquatic-biota)	[32]
	200 ppb (drinking)	
India Central Pollution Control Board (CPCB)	0.2 mg/L	[25]
Mexico	0.2 mg/L	[33]

Table 1. Permissible cyanide discharge limits in industrial effluents.

In view of the data outlined in **Table 1**, strategies aimed at cyanide recovery and removal need to be adopted to maintain concentrations within regulatory limits.

7. Cyanide removal strategies from wastewaters

Various cyanide attenuation processes have been successfully implemented in the treatment of industrial effluents. Gold mines in southern Africa have adopted various cyanide attenuation techniques aimed at reducing the toxin level in the tailings to internationally acceptable levels. The common methods of treating cyanide are natural, chemical and biological degradations [34].

7.1. Natural degradation of cyanide

Natural attenuation reactions occur in cyanide solutions placed in ponds or tailings resulting in the reduction in the cyanide concentration. The dominant natural degradation mechanism is volatilisation of hydrogen cyanide with subsequent atmospheric transformations to less toxic chemicals [34]. Other reactions such as hydrolysis, photolysis, oxidation, complex formation, oxidation to cyanate, thiocyanate formation and precipitation also take place. This natural process occurs with all cyanide solutions exposed to the atmosphere.

Cyanide forms complexes with metals ions in solution such as zinc, iron and copper. Ferri- and ferrocyanide complexes are extremely stable under most environmental conditions except when exposed to ultraviolet radiation [22]. Zinc and copper cyanide complexes are relatively unstable and can release free cyanide to the environment. Iron cyanide complexes are precipitated by several metals such as Zn, Cu, Ni, Pb, Sn, Cd and Ag over a wide range of pH (2–11). Cyanide and cyanide metal complexes adsorb onto clay, organic matter and oxides of aluminium, manganese and iron. The adsorbed cyanide can be naturally oxidised by oxygen, hydrogen peroxide and ozone into less toxic cyanate. The cyanate is hydrolysed under acidic conditions into ammonium salt and carbon dioxide. Cyanide can be biodegraded to ammonia, which is further oxidised to nitrate [35]. Under anaerobic conditions, HCN is hydrolysed to formic acid or ammonium formate as shown in Eq. (5).



Elemental sulphur and sulphur containing ores such as chalcopyrite react with cyanide to produce less toxic thiocyanate [36].

7.2. Chemical, physical and biological methods

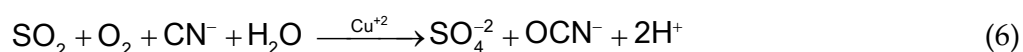
Natural methods of cyanide attenuation have failed to produce effluents of acceptable quality. This has led to the development of numerous biological, physical and chemical treatment methods [37].

Among the methods used in removing cyanide from wastewater include photocatalysis [38], biotreatment [39], copper-catalysed hydrogen peroxide oxidation [40], ozonation [33], electrolytic decomposition, alkaline chlorination [22], reverse osmosis, thermal hydrolysis and adsorption [41]. Most of these methods have limited applications due to the high cost, production of toxic residues and incomplete degradation of all cyanide complexes [42, 43]. However, biodegradation of aqueous cyanide ions is cheaper than chemical and physical methods [30].

7.2.1. Chemical oxidation methods

7.2.1.1. Sulphur dioxide/air (INCO) process

This process was developed by a Canadian company, Inco metal limited, in 1984 [44]. The process makes use of air and sulphur dioxide in the catalytic oxidation of free and complexed cyanide to cyanate [37, 45, 46] as shown in Eq. (6). The process is catalysed by aqueous copper (II) ions under controlled pH of 8–10. The pH is normally maintained by addition of lime.



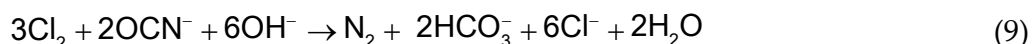
After completion of the oxidation process, previously metal ions complexed with cyanide such as Zn^{+2} , Cu^{+2} and Ni^{+2} are precipitated as metal hydroxides. This process effectively treats cyanide in slurries and solutions.

7.2.1.2. Alkaline chlorination

In this process, cyanide is oxidised by alkaline chlorine. The process converts all acid dissociable cyanide except for iron cyanide complexes and more stable metal-cyanide complexes. The process is a two-stage process. The first stage involves initial oxidation of free cyanide to cyanogens chloride followed by hydrolysis of cyanogens chloride to cyanate (Eqs. (7) and (8)) at pH 11.



During the second stage, cyanate is further oxidised to hydrogen carbonate and nitrogen as shown in Eq. (9). The reaction occurs at pH 8.5.



The alkaline chlorination process is primarily applied in the treatment of cyanide solutions rather than slurries, which consume a lot of chlorine.

7.2.1.3. Hydrogen peroxide oxidation

Oxidation of cyanide tailings by hydrogen peroxide is more suitable for solutions rather than slurries. The oxidation process is maintained at pH of 9–10 to avoid formation of hydrogen cyanide [47]. The oxidation reaction is catalysed by copper (II) sulphate resulting in the production of carbonate and ammonium (Eqs. (10) and (11)).

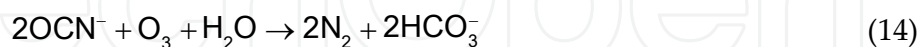


7.2.1.4. Ozonation

Ozone is a superior oxidant to oxygen and has been extensively studied in the oxidation of cyanide [48–51]. Two oxidation mechanisms of cyanide to cyanate by ozone have been proposed, namely simple (Eq. (12)) and catalytic (Eq. (13)).

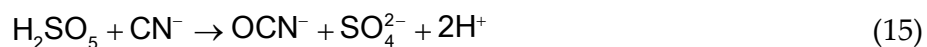


Catalytic ozonation rarely occurs and has only been observed under high acidic conditions. Continued addition of ozone results in the formation of hydrogen carbonate and nitrogen (Eq. (14)).



7.2.1.5. Peroxymonosulphuric acid

Peroxymonosulphuric acid (H_2SO_5) or Caro's acid [52] is used for cyanide treatment in gold tailings. Caro's acid is prepared in situ by the reaction of hydrogen peroxide with sulphuric acid since it easily decomposes. This acid is mostly used in situations where sulphur dioxide/air cannot be used. Caro's acid oxidises cyanide to cyanate as shown in Eq. (15).



7.2.1.6. Precipitation of cyanide

Stable cyanide complexes can be precipitated by the addition of complexing agents such as iron. Iron cyanide complexes can coprecipitate other compounds containing cyanide in solution producing solids of cyanide salts. Finely divided insoluble iron sulphide is used for adsorbing free and complexed cyanide in solutions. The adsorption occurs at optimum pH of approximately 7.5. The iron sulphide is prepared from the reaction of iron (II) sulphate and sodium cyanide [53]. If hydrated ferrous sulphate is used, iron (II) cyanide precipitate is produced. Precipitation of iron cyanide occurs at pH between 5 and 6.

7.2.2. Physical methods

Cyanide tailings can be treated using physical methods such as dilution, membrane and electrowinning.

7.2.2.1. Dilution

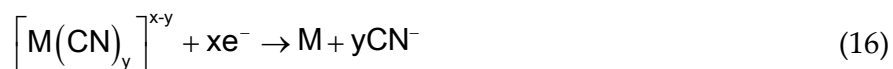
This is a technique that does not destroy toxic cyanide, but dilute it with an eluent that reduces cyanide concentrations below acceptable discharge limits. Dilution is a cheap simple technique, which is often used as a standalone or in conjunction with other methods as a way of ensuring that discharged effluents are within permissible limits [54]. Dilution is normally an unacceptable method since it does not degrade or reduce the quantity of toxic cyanide exposed to the environment.

7.2.2.2. Membrane technology

Reverse osmosis and electrodialysis techniques using membranes have been used in extracting cyanide from wastewater. Both techniques have been effectively applied in the removal of free and complexed cyanide [55–57].

7.2.2.3. Electrowinning

Strong acid dissociable and weak acid dissociable cyanide complexes can be reduced to metals releasing free cyanide (Eq. (16)) by the application of an electric potential across electrodes immersed in complexes solution. The freed cyanide can then be treated by other processes.



Four electrowinning cell designs have been developed for gold processing, namely Zadra, AARL, NIM graphite chip and MINTEK parallel plate cells [54, 58]. Electrowinning performs well in concentrated solutions and has been predominantly utilised for gold processing. This process is termed as Celec or HSA process [59] when it is used for cyanide regeneration.

7.2.2.4. Adsorption

Activated carbon, resins and minerals have been used for cyanide adsorption from solution. Contact vessels such as elutriation columns, agitation cells, packed-bed columns and loops have been used for this purpose. Various separation techniques such as floatation, gravity separation and screening are applied to remove the adsorbed cyanide from solution. The adsorbent is subsequently transferred into another vessel where cyanide is desorbed into low-volume solution, concentrated, reactivated and recycled.

7.2.2.5. Resins

Resins are typically polymeric beads containing a numerous surface functional groups capable of chelating or ion exchanging. Resins that require a substrate are deposited as thin film, while those that do work without a substrate are mostly used in continuous processes. The first column resin for cyanide recover was developed in 1959 [60]. Metal-cyanide complexes have been reported to adsorb more strongly to resins [61, 62]. The extent of adsorption depends on nature of resin used and how the resin and/or solution is pretreated [63]. Resins are cheaper and more effective than activated carbon since they resist organic fouling, have longer life, desorb faster and regenerate more efficiently [63]. Conventional, commercial strong base resins are most suitable for cyanide recovery since most common cyanide species in gold plant tailings are free cyanide anions within 100–500 mg/L range and the tricyano copper complex, both of which can be extracted directly from pulps using anion exchange resins [22].

7.2.2.6. Minerals

Free and metal-complexed cyanides are adsorbed by solid wastes, soils and ores containing minerals such as bauxite [$\text{AlO.OH}/\text{Al}(\text{OH})_3$], ilmenite (FeTiO_3), haematite (Fe_2O_3) and pyrite (FeS_2). Mineral groups such as zeolites, clays and feldspars are also effective adsorbents [64, 65].

7.2.2.7. Activated carbon

Cyanide packed-bed systems can be used to adsorbed cyanide in dilute solutions [30, 66, 67]. Activated carbon has a relatively high affinity for many metal-cyanide complexes, including the soluble cyanide complexes of copper, iron, nickel and zinc [41, 68, 69]. Cyanide is adsorbed at various sites through chelation, ion exchange, solvation and coulombic interactions. This adsorption technique suffers a major drawback of being technically complex and expensive regeneration of activated carbon [70].

7.2.3. Biological oxidation methods

The use of microorganisms in the degradation of cyanide in tailing ponds has often been found to be potentially inexpensive and environmentally friendly compared to conventional chemical and physical processes [23, 71, 72]. Enzymatic activities associated with certain species of bacteria, fungi and algae are known to oxidise cyanide to less toxic cyanate [20, 73, 74]. Aerobic and anaerobic passive biological treatment processes are cost-effective alternatives to conventional cyanide treatment strategies since they do not need external energy, chemicals

and routine maintenance. However, they suffer limitations such as the need for warmer climates ($>10^{\circ}\text{C}$), large space and long retention times. **Figure 1** shows a flowchart for the aerobic and anaerobic oxidation of cyanides and thiocyanides in gold tailing ponds. Common passive biological treatment processes comprise engineered wetlands containing substrate or a mixture of organic and inorganic compounds like manure, straw, saw dust and limestone [22]. In anaerobic wetlands, bacterial oxidation of cyanides and thiocyanides to sulphates, carbonates and ammonia occurs as illustrated in Eqs. (17) and (18).

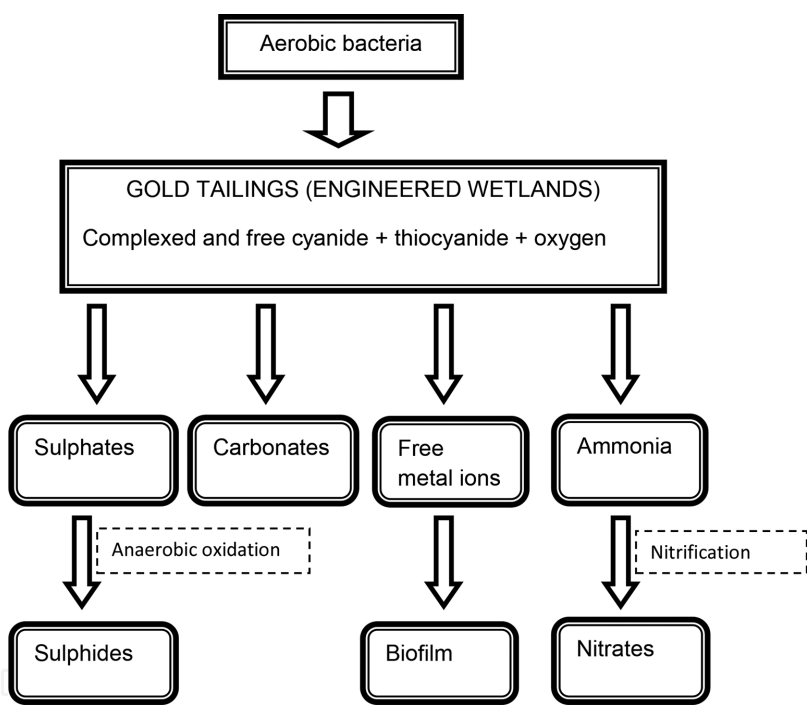
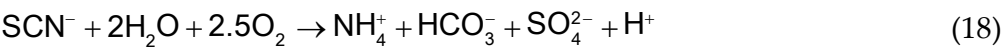
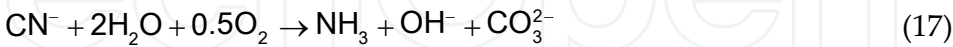
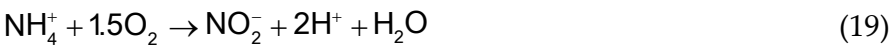


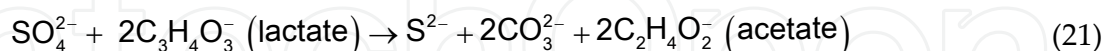
Figure 1. Biological cyanide degradation processes in gold tailings.

The ammonia produced by the aerobic processes provides nutrients for microbial growth and the resultant uptake, sorption, conversion and/or precipitation of cyanides, thiocyanates, sulphates and nitrates by microorganisms [74]. The metals released during the oxidation of cyanide metal complexes are removed from gold tailings by chemical precipitation and/or adsorption on bacterial biofilm. Ammonia also undergoes further oxidation in a two-step nitrification process (Eqs. (19) and (20)).





Sulphates undergo anaerobic reduction to sulphides (Eq. (21)). This process is effected by sulphate-reducing bacteria [75]. The sulphide produced is precipitated by metal ions resulting in its removal from aqueous tailings.



Several factors influence the biodegradation of cyanide in gold tailings. The most important environmental factors influencing biological treatment include pH, temperature, oxygen levels and nutrient availability. Enzymes that degrade cyanide are generally produced by mesophilic microorganisms, often isolated from soil, with optimum operating temperatures of between 20 and 40°C [34, 43, 76–79]. The availability of nutrient carbon has been found as a limiting factor in the biodegradation of metal-cyanide complexes [75].

Highly acidic and basic conditions have adverse effects on cyanide-degrading microorganisms since bacterial and fungal growth is optimal at pH 6–8 and 4–5, respectively [80]. Cyanide-degrading enzymes have optimum operating pH between 6 and 9. Concentrations of cyanide ions in water or slurries have an impact on the survival and growth of microorganisms. For instance, high cyanide concentrations have been reported to be toxic to *Klebsiella oxytoca* by damaging the nitrile-degrading enzyme, nitrile hydratase [81].

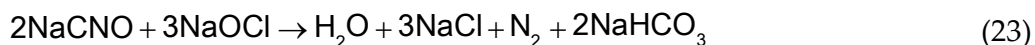
7.3. Emerging technologies on cyanide remediation

Since the 1990s, research has focused on introducing cyanide treatment technologies aimed at reducing costs and producing environmentally friendly products.

Carbon dioxide has been successfully used without a catalyst to replace SO_2 as an inexpensive alternative to the SO_2 /air process [82].

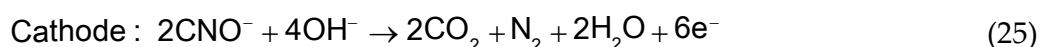
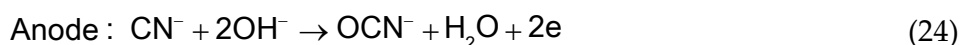
Wastewater containing free and complexed cyanides can be oxidised by ultraviolet radiation in the presence of a semiconductor catalyst such as titanium dioxide [33]. When the catalyst mixed in the wastewater is exposed to the sunlight, it generates a highly reactive hydroxyl radical oxidant. These radicals initially convert cyanide to cyanate. Photocatalysis partially dissociates ferricyanide and ferrocyanide complexes to free cyanide and iron hydroxide. Photocatalytic oxidation is effective in relatively clear solutions. In the presence of ozone, ultraviolet oxidation does not produce undesirable by-products such as ammonia.

Solid or liquid cyanide wastes can be thermally decomposed upon treatment at elevated temperatures and pressure in batch or continuous mode [83]. This process is capable of destroying all cyanide complexes. Cyanide hydrolysis occurs in two steps (Eqs. (22) and (23)) producing ammonia and carbonates.



This cost-effective process was developed in the early 1990s for the treatment of wastes containing high concentrations of cyanide (100,000 mg/L). Thermal reduction reduces cyanide concentration to approximately 25 mg/L, which can be further oxidised by conventional methods such as ozone or hydrogen peroxide to environmentally permissible levels.

Free cyanide and cyanide complexes containing waste can be treated by electrochemical oxidation. This is an economical and environmentally friendly technique of destroying cyanide. The process results in cyanide ions being destroyed at the anode as metals are deposited at the cathode [27, 84]. During electrolysis, cyanide is initially oxidised at the anode producing cyanate ions, which are further decomposed to carbon dioxide and nitrogen gas at the cathode (Eqs. (24) and (25)).



8. Conclusion

There is a growing use of water as the gold mining activities increase. Water losses should be minimised and recycling adopted as much as possible. Cost-effective and environmentally friendly practices for cyanide treatment need to be implemented. The gold mining industry needs to implement the best practices for cyanide management that are aimed at assisting in protecting human health and reducing environmental impacts through discharge of permissible levels of cyanide in effluents into main water bodies. Such practice will ensure maintenance of good quality of water and sustenance of aquatic life.

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