

CYANIDE REMEDIATION: CURRENT AND PAST TECHNOLOGIES

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ABSTRACT

Cyanide (CN⁻) is a toxic species that is found predominantly in industrial effluents generated by metallurgical operations. Cyanide's strong affinity for metals makes it favorable as an agent for metal finishing and treatment and as a lixiviant for metal leaching, particularly gold. These technologies are environmentally sound but require safeguards to prevent accidental spills from contaminating soils as well as surface and ground waters. Various methods of cyanide remediation by separation and oxidation are therefore reviewed. Reaction mechanisms are given throughout. The methods are compared in regard to their effectiveness in treating various cyanide species: free cyanide, thiocyanate, weak-acid dissociables and strong-acid dissociables.

KEY WORDS

cyanide, metal-cyanide complex, thiocyanate, oxidation, separation

INTRODUCTION

Waste waters from industrial operations transport many chemicals that have adverse effects on the environment. Various chemicals leach heavy metals which would otherwise remain immobile. The chemicals and heavy metals may be toxic and thus cause aquatic and land biota to sicken or die. Most waste-water processing technologies that are currently available or are being developed emphasize the removal of the chemicals or heavy metals as cations. However, the anions associated with heavy metal cations can be equally as toxic but are largely ignored. In this regard, the remediation of cyanide has been considered paramount [1].

Cyanide is a singly-charged anion containing unimolar amounts of carbon and nitrogen atoms triply-bonded together: C≡N⁻ or CN⁻. It is a strong ligand, capable of complexing at low concentrations with virtually any heavy metal. Because the health and survival of plants and animals are depend-

ent on the transport of these heavy metals through their tissues, cyanide is very toxic. The mean lethal dose to the human adult is between 50 and 200 mg [2]. U.S. EPA standards for drinking and aquatic-biota waters regarding total cyanide are 200 and 50 ppb, respectively, where total cyanide refers to free and metal-complexed cyanides [3]. According to RCRA, all cyanide species are considered to be acute hazardous materials and have therefore been designated as P-Class hazardous wastes when being disposed of. P-Class hazardous wastes are the most regulated waste in regard to amounts accumulated in a given year as compared to the other class designations: F, K and U.

Metal-complexed cyanides are classified according to the strength of the metal-cyanide bond. Free cyanide refers to the most toxic forms of cyanide: cyanide anion and hydrogen cyanide. Weak-acid dissociables (WADs) refer to cyanide complexes with metals such as cadmium, copper, nickel and zinc. Although thiocyanate

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(SCN⁻) is a WAD, it is often considered in its own category. Strong-acid dissociables (SADs) refer to cyanide-complexes with metals such as cobalt, gold, iron and silver. This nonspecific, complexing nature makes cyanide attractive for (1) extracting metals, particularly gold, from ores via various leaching operations; (2) finishing/treating metal products and their surfaces, and (3) preventing certain particles from becoming hydrophobic in the flotation separation of minerals. Cyanide concentrations for leaching and finishing/treating are several orders of magnitude higher than those encountered in flotation whereas cyanide solutions are more voluminous in leaching as compared in finishing/treating. Over a billion tons of gold ore are leached each year with cyanide. Consequently, in order to prevent surface and ground water contamination, procedures for the safe and proper treatment, storage and handling of effluents are of primary concern for cyanide leaching operations [4, 5].

In this study, current and past remediation methods for waste and process waters containing cyanide are reviewed. Emphasis is placed on the oxidation methods which actually destroy the cyanide.

CYANIDE REMEDIATION

Various procedures exist for treating cyanide and are comprised of several physical, adsorption, complexation and/or oxidation methods. These methods predominantly involve separation or destruction processes and may occur naturally. Separation processes include the physical, adsorption and complexation methods that are used to concentrate and thereby recover cyanide for recycling. On the other hand, destruction processes are used to sever the carbon-nitrogen triple bond thereby destroying the cyanide and producing non-toxic or less-toxic species. Because the carbon and/or nitrogen atoms in the cyanide molecule undergo changes in oxidation state, destruction processes are commonly re-

ferred to as oxidation methods. These physical, adsorption, complexation and oxidation methods are described in the ensuing discussions.

Physical methods

Physical methods for cyanide treatment can be accomplished using dilution, membranes, electrowinning and hydrolysis/distillation.

Dilution

Dilution is the only treatment method which does not separate or destroy cyanide. This method involves combining a toxic cyanide waste with an effluent that is low in or free of cyanide to yield a waste water below discharge limits. Consequently, dilution is simple and cheap and is often used as a stand-alone or back-up method to insure that discharge limits are satisfied [3]. Dilution is usually considered to be unacceptable since the total amount of cyanide discharge is not altered and since naturally-occurring processes such as adsorption and precipitation can attenuate and thereby concentrate the cyanide in ground and surface waters.

Membranes

Cyanide can be separated from water using membranes with either electrodialysis or reverse osmosis. In electrodialysis, a potential is applied across two electrodes separated by a membrane permeable to cyanide. The cyanide solution requiring purification is placed in the half-cell containing the cathode or negative electrode. Cyanide, because it is negatively charged, will diffuse through the membrane and concentrate in the half-cell containing the anode or positive electrode. In reverse osmosis, pressure is applied to a cyanide solution needing treatment but, in this case, water is forced through a membrane impermeable to cyanide. Both of these methods have been shown to be applicable to

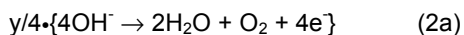
solutions containing free and metal-complexed cyanide [6-11].

Electrowinning

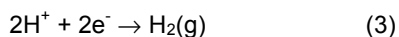
SADs and WADs can be reduced to corresponding metals by applying a potential across two electrodes immersed in the same solution:



Thiocyanate does not respond. Free cyanide is liberated which makes solutions more amenable to other recovery and remediation processes. Because this electrowinning reaction involves the reduction of an anion at the cathode, a negatively-charged electrode, metal recoveries and current efficiencies are low. This is compensated for by using steel wools as high-surface area cathodes, increasing agitation to further increase mass transport, increasing solution temperatures, using appropriate solution pHs and conductivities, increasing metal concentrations if possible, and redesigning the electrowinning cell of which four designs have been developed for gold processing: Zadra, AARL, NIM graphite-chip and MINTEK parallel plate cells [3, 12]. Furthermore, Reaction 1 must be accompanied by a corresponding oxidation reaction, usually oxygen evolution, at the anode with an equivalent number of electrons, e^- , being donated:



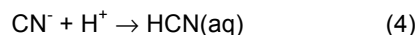
Electrowinning is predominantly used for gold processing; however, it has been used for cyanide regeneration, in which case it is often referred to as the Celec or HSA process [3, 13]. Electrowinning performs well in concentrated solutions; at dilute concentrations, hydrogen evolution predominates, possibly masking Reaction 1 completely:



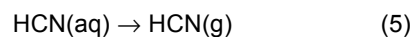
Progress is continuing to make electrowinning technology economically viable to dilute solutions. Direct applications to cyanide remediation may then be possible.

Hydrolysis/distillation

Free cyanide naturally hydrolyzes in water to produce aqueous hydrogen cyanide [HCN(aq)]:



The aqueous hydrogen cyanide can then volatilize as hydrocyanic gas [HCN(g)]:



Because hydrocyanic gas has a vapor pressure of 100 kPa at 26°C, which is above that of water (34 kPa at 26°C), and a boiling point of 79°C, which is below that of water (100°C), cyanide separation can be enhanced at elevated temperatures and/or reduced pressures [14-16]. Distillation rates can also be increased by increasing the agitation rate, the air/solution ratio, and the surface area at the air/solution interface. Hydrocyanic gas can be captured and concentrated for recycling in conventional absorption-scrubbing towers. It can also be vented to the open atmosphere and has been noted to occur naturally in tailings ponds, especially in warm and arid environments [17]. In such cases, it is paramount that environmental regulations be satisfied. Thiocyanate, WADs and SADs are not affected.

Complexation methods

Cyanide treatment can also be done with several complexation methods such as acidification/volatilization, metal addition, flotation and solvent extraction.

Acidification/volatilization

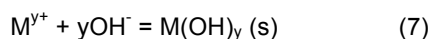
Because Reaction 4 is in equilibrium at pH 9.3, cyanide predominates above this pH value and aqueous hydrogen cyanide predominates below. Consequently, cyanide

will remain in solution at pH values greater than approximately 11, which explains why operations maintain cyanide solutions above this pH. On the other hand, cyanide will volatilize at pH values less than approximately 8; the lower the pH, the higher the rate of volatilization. If the pH is lowered below pH 2, hydrocyanic gas will also be evolved from WADs:

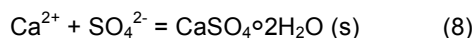


Thiocyanate and SADs react similarly but solutions must typically be adjusted below pH 0 and consequently are only moderately affected [18]. Since this would increase acid consumption beyond reason, typical acidification/volatilization operations use a pH between 1.5 and 2. Volatilization rates can also be increased in the same manner as distillation. In addition, volatilization has been observed naturally due to the dissolution of carbon dioxide and subsequent formation of carbonic acid [15, 16, 19].

After acidification, the solution is predominantly cyanide-free but must be reneutralized so it can be discharged or recycled for further use. Reneutralization causes the metals which were liberated via Reaction 6 to be precipitated as hydroxides:



If lime $[Ca(OH)_2]$ is used for reneutralization and sulfuric acid (H_2SO_4) is used for acidification, gypsum ($CaSO_4 \cdot 2H_2O$) will also be precipitated:

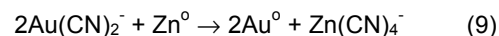


Sludges of gypsum and metal hydroxides are often difficult to separate from water [20], which is a problem that can be minimized by using other acids such as nitric, HNO_3 [21], or other bases such as caustic, $NaOH$ [22]. Nitric and caustic are more expensive but savings can be realized in sludge separation and treatment.

Acidification/volatilization (AV) and reneutralization (R) processes are collectively referred to as the AVR or Mills-Crowe process that was originally developed circa 1930 at the Flin Flon operation in Canada [2, 3, 22]. Different versions were implemented later at the Real del Monte mine in Mexico, the CANMET facility in Canada, and the Golconda CRP venture in Australia [23-25]. A similar technology, the Cyanisorb™ process, has recently been tested at the Golden Cross operation in New Zealand and the De Lamar mine in Idaho and found to be more efficient: (1) acidification was conducted at pH 6 using better designed packed towers, and (2) absorption was conducted using caustic to prevent fouling from gypsum precipitation [26, 27]. It is apparent that the AVR and Cyanisorb™ processes consume tremendous amounts of acids and bases but are preferred over the hydrolysis/distillation process due to reduced energy consumption and increased volatilization rates.

Metal addition

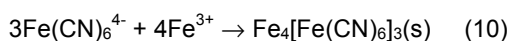
Cyanide can be rendered unreactive by the addition of various metals and metal cations to promote the formation of metal-cyanide complexes or precipitates. For example, in the Merrill-Crowe process developed in 1890 for gold recovery, zinc is added to gold cyanide solutions resulting in the precipitation or cementation of the gold [28]:



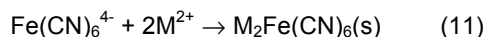
In essence, a gold SAD-complex is exchanged in solution for a zinc WAD-complex thus making the solution more amenable to other remediation methods. Cementation of gold and other metals in cyanide solutions has also been accomplished with aluminum, copper and iron [29-33].

In another process first employed in 1909 [34], ferrous (Fe^{2+}) or ferric (Fe^{3+}) cations

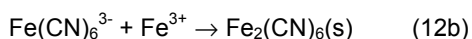
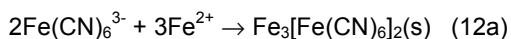
are added to cyanide solutions to form the respective SAD-complexes $\text{Fe}(\text{CN})_6^{4-}$ and $\text{Fe}(\text{CN})_6^{3-}$. These ferrihexacyanide and ferrihexacyanide anions are considered to be essentially nontoxic due to their high stability; however, concerns regarding their photodecomposition (see photolysis methods), and therefore their long term stability, have been raised [2]. Nevertheless, processes have been developed where these anions are precipitated as double salts. For example, ferrihexacyanide anions precipitate as Prussian Blue upon addition of ferric cations [35-37]:



Prussian blue precipitation is commonly observed in process circuits. Ferrihexacyanide anions can also be precipitated as $\text{Cu}_2\text{Fe}(\text{CN})_6$, $\text{Ni}_2\text{Fe}(\text{CN})_6$ and $\text{Zn}_2\text{Fe}(\text{CN})_6$ upon addition of cupric, nickel and zinc cations, respectively [3, 37, 38]:



Similarly, ferrihexacyanide anions can be precipitated as Prussian Brown with ferrous cations or as Prussian Green with ferric cations [39-41]:



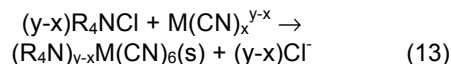
In other precipitation processes, cuprous and argentous cations have been added in excess to form CuCN and AgCN single salts from free cyanide [42-44]. Silver precipitation is used commonly as a titration technique for determining free cyanide concentrations [45].

Each of the cemented metals, SAD-complexes and cyanide precipitates formed by metal addition processes is stable, but it is paramount that the pH be maintained during and after their formation to prevent their decomposition and dissolution. Thiocyanate has limited response to metal ad-

dition but can be removed via substitution for cyanide in the products [46]. Clearly, metal addition is usually not a stand-alone method for cyanide treatment.

Flotation

Flotation was first implemented in 1880 for concentrating minerals from ores [47, 48] and has since been adapted for remediation. In regards to cyanide remediation, ion and conventional flotation practices have been used to separate SAD-complexes and precipitates formed naturally or by metal addition. Flotation is usually conducted quickly to prevent these species from decomposing and redissolving [18, 49-52]. In ion flotation, a heteropolar surfactant, usually a cationic amine such as triacrylmethyl ammonium chloride (R_4NCl), is added to react with the anionic SAD-complex to precipitate as an organic (R) double salt:



Usually, the double salt precipitate will nucleate to form colloids or larger-sized particles. Ion flotation works well for separating SADs but only partially for WADs. The fate of thiocyanate is unknown. By comparison, the same or different surfactant is added in conventional flotation to adsorb at the precipitate surface. In both cases, hydrophobic species are created that can be separated into a froth phase upon injection of air bubbles into the system. Various chemicals such as frothers and modifiers can be added to maximize the flotation response.

Solvent extraction

In solvent extraction (SX), an organic solvent or diluent is used to solubilize at least one of many organic extractants of solvating, chelating or ion-exchange capabilities. The diluent must be immiscible in and less dense than water, the aqueous phase, and the extractant must remain in the diluent and have selectivity for the aqueous spe-

cies being remediated. The diluent and extractant are collectively referred to as the organic phase. When the organic and aqueous phases are mixed, the aqueous species is stripped from the aqueous phase by the extractant in reactions similar to Reaction 13 above. The species has loaded into the organic phase. Various chemicals termed modifiers can be added to the organic and aqueous phases to maximize the extraction. Mixing is ceased at the appropriate time, and the stripped water and loaded organic are allowed to disengage, thus effecting a separation of the species. The process is repeated to transfer the species from the loaded organic to a second aqueous phase of lower volume and appropriate chemistry. As a result, the concentration of the species is increased and the organic phase is stripped and recycled. Recycling is necessary to minimize expenses due to organic loss and is possible because the extraction is reversible.

Solvent extraction technology was originally developed for uranium processing in the mid-1950s [53] and received world-wide attention when the technology was successfully applied to copper processing ten years later [54, 55]. Applications have since been developed for selectively extracting gold cyanide using amine and phosphorous ester solvent extractants [56-58]. Other applications of solvent extraction to cyanide are the analytical detection procedures used in colorimetry [59-61] and, consequently, of industrial interest for possible adaptation to future processing and remediation. In this regard, very little is known about the use of solvent extraction for the remediation of nearly all cyanide species.

Adsorption methods

Minerals, activated carbons and resins adsorb cyanide from solution. Several types of contact vessels can be used for this purpose and include elutriation columns, agitation cells, packed-bed columns and loops, etc. Once the cyanide is adsorbed,

the material is separated from the solution by, for example, screening, gravity separation or flotation. The material is then placed into another vessel where the cyanide is desorbed into a low volume solution and thus concentrated. Finally, the material is separated again and, in most cases, reactivated and recycled for further use.

Minerals

Soils, wastes and ores containing minerals such as ilmenite (FeTiO_3), hematite (Fe_2O_3), bauxite [$\text{AlO}\cdot\text{OH}/\text{Al}(\text{OH})_3$] and pyrite (FeS_2), as well as mineral-groups such as feldspars, zeolites and clays have been shown to effectively adsorb free and metal-complexed cyanides [62-66]. Depending on the mineral, cyanide adsorption is usually a combination of two mechanisms: ion exchange, precipitation or coulombic interaction. Cyanide attenuation by such mineral commodities purifies ground and surface waters but increases cyanide consumption in leaching operations.

Activated carbon

Active or activated carbons are typically prepared by partial thermochemical decomposition of carbonaceous materials—predominantly wood, peat, coal and coconut shells. Adsorption characteristics change with preparation method and material. Because activated carbons have high porosity and high surface area, adsorption capacities and rates are high. Adsorption, however, is not very selective; cations, anions, and neutral species can be adsorbed simultaneously at various sites via ion exchange, solvation, chelation and coulombic interactions. Activated carbons are commonly used in packed-bed systems for treating waste waters and gases. Although the use of activated carbons dates back to ancient Egypt and India, the first commercial application was in gas masks circa 1915 [67]. Applications to cyanide waste waters have been reported with packed-bed systems and shown to be applicable at dilute cyanide concentrations [68, 69] with

increased adsorption of WADs and SADs with copper or silver pretreatment [18, 70, 71].

In gold leaching with cyanide, packed-bed systems are usually avoided and have given rise to the use of continuous operations exemplified by carbon-in-column (CIC), carbon-in-leach (CIL) and carbon-in-pulp (CIP) processes. Although these processes have been designed for gold-cyanide adsorption, it does not preclude applying them for the remediation of free or other metal-cyanide complexes as implied by Muir et al. [15]. High adsorption capacities and rates as well as strong ability for reactivation are important parameters for all activated carbons but, when used in CIC, CIL and CIP processes, they must also have high mechanical strength, high wear resistance, and a consistent particle size.

Resins

Resins are usually polymeric beads containing a variety of surface functional groups with either chelation or ion-exchange capabilities, somewhat similar to solvent extraction processes discussed earlier. They can be selective and have high adsorption capacities depending on whether the chelating or ion-exchange properties are strong or weak. Resins that are deposited on substrates as thin films are predominantly used in packed-bed systems, whereas resins that do not require a substrate are mostly used in continuous processes like those used with activated carbons for gold (i.e., RIC and RIP). Goldblatt [72] developed the first resin column for cyanide recovery. Metal-cyanide complexes have since been found to adsorb more strongly but this adsorption is dependent on which resin is being used and how the solution and/or resin are pretreated [73-77]. Thiocyanate appears to adsorb weakly. In a comparison of resins to activated carbons, Fleming and Cromberge [78] showed that resins can be more cost effective since they resist organic fouling,

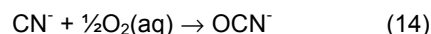
regenerate more efficiently, have longer life, and desorb faster. At present, the only resin being used in industry for cyanide recovery is the chelation resin, Vitrokele V912 [79].

Oxidation methods

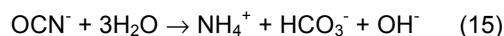
Except for the dilution process, the physical, complexation and adsorption methods yield a high concentration product that still must be treated prior to discharge. The toxic cyanide species remain. Consequently, these methods are used predominantly for separation, recovery and recycling. In order to destroy the cyanide, subsequent oxidation methods are needed. Cyanide oxidation can be conducted using biological, catalytic, electrolytic, chemical and photolytic methods.

Bio-oxidation

Various species of bacteria, fungi, algae, yeasts and plants, along with their associated enzymes and amino acids, are known to oxidize cyanide naturally [80-91]. The predominant mechanism of bio-oxidation is the metabolic conversion of cyanide to cyanate, OCN^- , a species less toxic than cyanide:



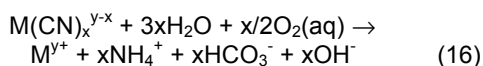
Oxygen is usually considered to be aqueous but may be present as a gas. Several intermediate species are formed during this reaction depending on which biomass is used, what cyanide species are present, and what the solution conditions are regarding cyanide concentration, pH, and temperature. Once the cyanate is produced and released, it will hydrolyze to ammonium and bicarbonate ions:



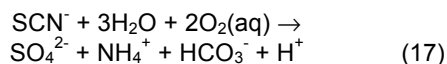
Reaction 15 is favorable under conditions less than approximately pH 7 at room temperatures [92, 93]. Ammonium is also considered toxic and must also be treated prior

to discharge, usually by nitrification or denitrification processes [94].

Of the various biomasses examined, bacteria are perhaps the best known. Bacterial oxidation of cyanide has been developed for effluent treatment at the Homestake gold processing plant in Lead, South Dakota [89, 90]. A biofilm composed primarily of *Pseudomonas paucimobilis* bacteria on rotating biological contactors is used to metabolize cyanide in water from tailings and underground mines. Unlike most other biomasses, this strain of bacteria can treat metal cyanide complexes including the SAD species:



Bacterial accumulation of the metal cations (M^{y+}) occurs by absorption, adsorption or hydroxide precipitation (see Reaction 7). The metal-loaded bacteria continually slough off the contactors and are removed by clarification. In addition, thiocyanate is remediated:



Since Reactions 15 and 16 produce hydroxides, thiocyanate bio-oxidation can help buffer the system. Ammonium produced by Reactions 15-17 is then treated by bacterial nitrification with a biofilm of aerobic, autotrophic bacteria to produce nitrite (NO_2^-) which, in the presence of oxygen, quickly oxidizes to nitrate (NO_3^-). Lime is added to precipitate the sulfate and bicarbonate as gypsum and calcite ($CaCO_3$), respectively (see Reaction 8). The water is clarified and discharged into a stream.

Other bacterial remediation processes are being developed. In one process, alginate-encapsulated *Pseudomonas putida* bacteria is used to treat decommissioned heap leach pads and other sources of ground water contamination [95, 96]. Column tests

on ore from the Summitville Mine, a Superfund SITE in Colorado, proved superior to peroxide rinse tests and, as a result, field tests are underway at the mine site. Furthermore, the technology is being adapted for use in fluidized bed reactors for treating effluents [97]. In other processes, anaerobic bacteria have been used to oxidize cyanide in oxygen-starved conditions [98-100] and could therefore be applied to ground waters and stagnant tailings ponds. In these cases, Reactions 14, 16 and 17 would occur with water and not oxygen.

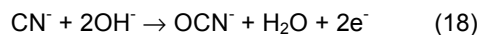
Catalysis

As noted previously, activated carbon is a strong adsorbent for cyanide. However, when adsorption takes place in the presence of oxygen, the activated carbon will catalytically oxidize cyanide to cyanate as shown in Reaction 14 [15, 18, 68, 71, 101-104]. When copper is present either in solution or preadsorbed on the activated carbon, the rate of catalysis increases, a phenomenon attributed to the increased adsorption of cyanide. If the copper co-catalyst is in excess, the cyanate hydrolysis shown as Reaction 15 is enhanced. Gold processing plants therefore minimize oxygen input into their carbon adsorption circuits. Although catalysis by activated carbon is effective for treating free cyanide and WADs as well as some SADs, it has not been developed into a cyanide destruction process. The fate of thiocyanate is unknown. A similar system using a PbO_2 catalyst has been favorably tested [105].

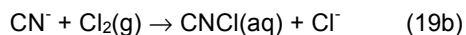
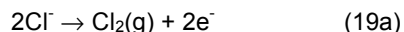
Electrolysis

Principles of electrowinning are applicable to electrolysis and, as a result, operating parameters are basically the same. However, cyanide remediation occurs as an oxidation of free cyanide at the anode rather than a reduction of a metal-cyanide complex at the cathode. Furthermore, because cyanide and the anode are oppositely charged, current efficiencies are much better. Cyanate is usually produced

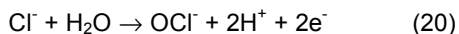
using one of two techniques: electro-oxidation and electro-chlorination. In electro-oxidation, the cyanide reaction occurs directly [13, 18, 106-108]:



whereas, in electro-chlorination, the reaction is the same overall but occurs via a reaction sequence [18, 109]:



Chlorocyanogen (CNCl), or tear gas, is formed as an intermediate and chloride anions are regenerated and therefore serve as a catalyst. The reaction should be carried out between 40°C and 50°C to minimize the formation of chlorate (O_3Cl^-). Under these conditions, hypochlorite (OCl^-) is produced [108]:



which aids in chemical oxidation as discussed in the next section (see alkaline chlorination). Hypochlorite is toxic, especially to fish, and must be controlled prior to discharge. Since hydroxide anions are consumed in both reaction processes, pH control above 11 is necessary to prevent hydrocyanic and chlorocyanic gases from volatilizing. Electro-oxidation does not perform as well as electro-chlorination. Both are effective against thiocyanate and WADs but ineffective against SADs.

Chemical addition

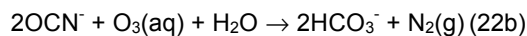
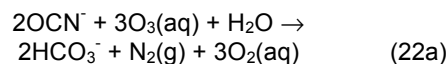
The most popular method for cyanide destruction is by addition of oxidants. Oxidants have high electron affinity and therefore strip cyanide of electrons predominantly yielding cyanate as a reaction product. Oxygen, ozone, hydrogen peroxide, chlorine, hypochlorite and sulfur dioxide are the most common oxidants.

Natural degradation of cyanide can occur via reactions with gaseous and aqueous oxygen (see Reaction 14). The reaction occurs quickly in agitated slurries, slowly in tailings ponds, and is catalyzed in the presence of activated carbon and certain aerobic bacteria as previously noted. It is somewhat effective for thiocyanate and WADs but ineffective for SADs. These reactions are often referred to as atmospheric oxidation reactions [2, 3].

Ozonation for cyanide destruction has been examined extensively because it is a superior oxidant to oxygen [110-116]. Like oxygen, ozone reacts with cyanide to produce cyanate; however two mechanisms have been proposed:



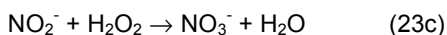
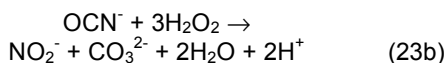
which are referred to as simple and catalytic ozonation, respectively. Simple ozonation yields oxygen which can further oxidize cyanide. On the other hand, catalytic ozonation represents a high reaction efficiency and has been observed at high addition rates, although rarely. Continued addition of ozone will convert cyanate to carbonate and nitrogen gas:



Because continued ozonation prevents cyanate hydrolysis via Reaction 15 and does not oxidize the cyanate to nitrite or nitrate, neither nitrification nor denitrification are needed. Furthermore, ozonation is highly destructive towards thiocyanate and WADs but is not destructive towards SADs. In addition, because hydroxide decomposes ozone, it becomes less efficient at pH values greater than approximately 11. This is a "Catch 22" situation since cyanide solutions should be maintained above pH 11 to prevent hydrocyanic gas volatilization.

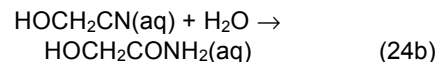
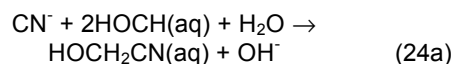
Other disadvantages of ozonation include its high expense for generating ozone.

In the Degussa process, hydrogen peroxide is used to chemically oxidize cyanide [117]. Hydrogen peroxide is an oxidant stronger than oxygen but weaker than ozone. It is often considered better because it is relatively cheap, water soluble, and easy to handle and store. The Degussa process has been examined in several research efforts, especially for comparing to other processes [118-125]. Results of these studies show that hydrogen peroxide reacts with cyanide to produce cyanate and, when added in excess, nitrite and carbonate and, eventually, nitrate form:



Otherwise, the cyanate will hydrolyze according to Reaction 15. The Degussa process is successful at oxidizing most WADs but has little or no effect on thiocyanate and SADs. Even so, it has been incorporated into numerous mining operations in Canada and the U.S. as a primary cyanide destruction process as well as a stand-by process for emergency situations.

Other chemicals can be added to increase reaction rates and efficiencies of hydrogen peroxide: cupric cation, formaldehyde/Kastone reagent and sulfuric acid [1]. Cupric cations act as catalysts for Reactions 23a-c [2, 3] but can be consumed by precipitating ferrihexacyanide anions (see Reaction 11) [2]. Cyanide reacts with formaldehyde (HOCH) in the presence of DuPont's proprietary Kastone reagent to form glycolnitrile (HOCH₂CN) which, in turn, hydrolyses to glycolic acid amide (HOCH₂CONH₂) in the presence of hydrogen peroxide [126-128]:



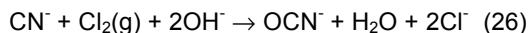
Cyanate and ammonium ions are also obtained as by-products. (3) When sulfuric acid and hydrogen peroxide are mixed, a highly exothermic reaction occurs, forming persulfuric or Caro's acid, H₂SO₅. Caro's acid readily decomposes to oxygen and sulfuric acid and, therefore, must be made on site at the time of use. It reacts with cyanide to produce cyanate [123, 129]:



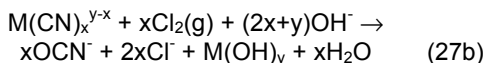
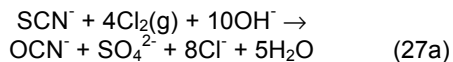
Similar reactions occur for thiocyanate and WADs; however, SADs do not react. Test work has also shown that hydrocyanic gas volatilization is negligible in spite of the fact that an acid is being added and produced. This is attributed to fast reaction rates and the inability of SADs to volatilize since equilibrium pH is established between 6.5 and 8 (see Reaction 6). Reactions similar to Caro's acid were also noted with persulfate, S₂O₈²⁻.

Alkaline chlorination has been practiced ever since cyanide leaching of gold was commercially developed in 1889 and, consequently, has been the most commonly applied technique for cyanide destruction [18, 28, 109, 130-132]. As will be explained, alkaline chlorination removes toxic WAD and free cyanide species completely, quickly and economically. However, it suffers from high reagent costs regarding alkaline pH control and chlorine gas/hypochlorite consumption, high discharge concentrations of chloride and hypochlorite anions of which both are toxic, and inability to remediate SADs.

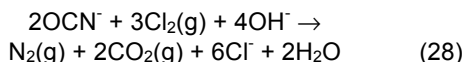
Alkaline chlorination can be accomplished using chlorine gas as discussed earlier for electro-chlorination (see Reactions 19b and 19c):



Chlorine gas also reacts with thiocyanate and metal-complexed cyanides to produce cyanate:

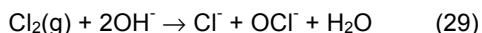


Due to the high pH, sulfate and metal hydroxide precipitates are formed; however, only WADs react according to Reaction 27b. SADs are inert. When in excess, chlorine gas can also react with cyanate to produce nitrogen and carbon dioxide:



In such a case, chlorine and hydroxide consumptions become excessive, only increasing the difficulty in maintaining alkalinity above pH 10 to avoid the volatilization of hydrocyanic and chlorocyanic gases.

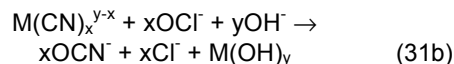
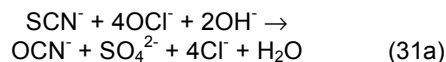
To compensate for this high base consumption, the hypochlorite alkaline chlorination process was adapted due, in principle, to observations that the hypochlorite that was produced by the hydrolysis of chlorine gas also remediated cyanide:



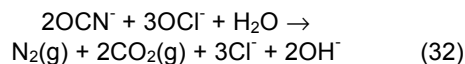
In this regard, hypochlorite reactions are similar to those depicted for chlorine gas (see electro-chlorination). For example, hypochlorite and cyanide react, producing chlorocyanogen which, in turn, hydrolyses to cyanate (see Reaction 19c):



Cyanate is also formed via hypochlorite reactions involving thiocyanate and metal-complexed cyanides:

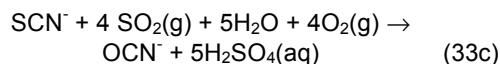
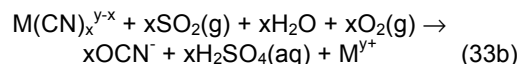
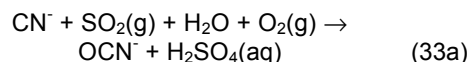


As with chlorine gas reactions, only WADs react in this manner; SADs are inert. Finally, when in excess, hypochlorite can also react with cyanate to produce nitrogen and carbon dioxide:



Clearly, hydroxide consumption is minimal and only becomes high when concentrations of thiocyanate and WADs are high, as indicated by Reactions 31a and 31b. Today, hypochlorite is predominantly added as sodium or calcium salts since these metal cations have natural buffering tendencies.

The INCO process for cyanide destruction involves mixing sulfur dioxide and air with free and metal-complexed cyanide as well as thiocyanate to yield cyanate [133-137]:



Reactions 33a-c can be catalyzed with cupric or nickel cations; however, SADs do not react. Since the reactions generate sulfuric acid and are most efficient near pH 9, lime is added for pH control. This generates sludge due to metal hydroxide and gypsum precipitation which, as noted earlier, can be difficult to clarify (see Reactions 7 and 8). The INCO process has been incorporated into numerous mining operations in Canada and the U.S. since the technology was commissioned in 1983.

Other remediation processes have been considered for cyanide oxidation. These include reacting cyanicides, a term used for species which consume cyanide in leach circuits, with cyanide to produce less-toxic species. For example, solid polysulfide minerals such as elemental sulfur (S₈) and pyrrhotite (Fe_{1-x}S) and aqueous sulfur-oxy anions such as polythionate (S₂O₆²⁻) and thiosulfate (S₂O₃²⁻) are known to react naturally with cyanide to produce thiocyanate [3, 18, 138, 139]. However thiocyanate is difficult to remediate, as already discussed, and is also a good lixivant for gold [43, 140]. Consequently, cyanide remediation via thiocyanate formation is usually not considered viable.

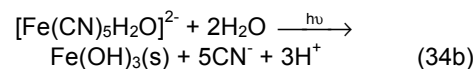
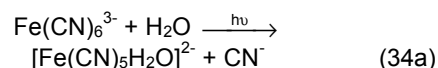
Photolysis

Photolysis can enhance reduction/oxidation (redox) reactions by providing energy from electromagnetic radiation to catalyze electron transfer processes. Electromagnetic radiation is absorbed, causing an electron in the absorbing compound to pass from the ground state to an excited state, possibly separating paired electrons from one another. The electrons become more susceptible to the chemical environment and are therefore more apt to participate in redox reactions. Photoreduction occurs when the absorbing compound donates the excited electron to another species. Photo-oxidation occurs when the absorbing compound accepts an electron from another species in order to fill its electron vacancy. The excited electron will eventually relax to the ground state of the reaction products.

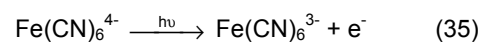
Energy needed to promote electrons from the ground state to the excited state is usually equivalent to that possessed by ultraviolet (UV) radiation. Many redox reactions can be catalyzed upon exposure to artificial sources such as arcs, lamps and lasers or to natural sunlight, which is free but not necessarily available 24 hours a day. Higher energies such as gamma radiation and lower energies such as visible

light can be used but applications are limited [141]. Photolytic reactions can be induced directly if the absorbing compound is the species being remediated or indirectly if the absorbing compound is available for transferring the photon-energy to the species being remediated. Photolysis can, therefore, be conducted in the absence of photosensitizers (direct photolysis) or in their presence as aqueous species (homogeneous photolysis and photocatalysis) or solid semi-conductors (heterogeneous photocatalysis). These photolytic methods are relatively new technologies and are thus referred to as advanced oxidation processes. Recently, they have been reviewed but with primary emphasis on oxidation of organic compounds [142, 143].

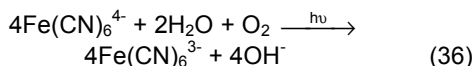
Direct photolysis is not applicable to free cyanides but does occur with some WADs and SADs, particularly the ferric and ferrous hexacyanide complexes [124, 125, 144-146]. Although subject to considerable debate, the following reaction mechanism was proposed for ferrihexacyanide:



These reactions are reversible; however, the ferrihydroxide [Fe(OH)₃] can react further with free cyanide and ferrihexacyanide to form Prussian Blue precipitates, similar to Reaction 10. Reactions 34a and b are referred to as photo-aquation reactions and have also been observed for cobalthexacyanide, Co(CN)₆³⁻, the strongest SAD [146, 147]. Furthermore, ferrihexacyanide can be produced via the direct photolysis of ferrohexacyanide:

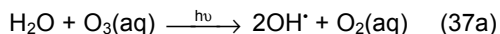


or the homogeneous photolysis of ferrohexacyanide with oxygen [148]:

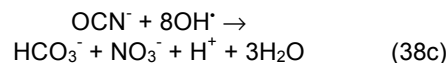
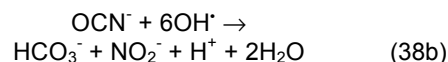
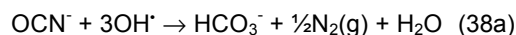


Combinations of Reactions 34a-36 liberate cyanide at UV-wavelengths less than approximately 420 nm, explaining why fish are commonly killed during the day and not the night as well as why adding ferric and ferrous cations to cyanide for detoxification is highly suspect (see metal addition methods) in spite of the fact that UV-radiation does not significantly penetrate water [2]. Clearly, direct photolysis can remediate WADs and SADs but dangerously liberates free cyanide during the reaction.

Homogeneous photolysis has also been used in combination with several of the chemical oxidation methods discussed earlier in order to increase reaction efficiencies, thereby minimizing reagent consumption and making SADs more amenable to destruction. For example, homogeneous photolysis with ozone has been shown to remediate free cyanide, WADs and SADs to concentrations below 0.1 ppm from concentrations ranging between 1 and 100,000 ppm [112, 149-151]. Increases in UV intensities, ozone concentrations (i.e., flowrates), and solution temperatures improve reaction kinetics. Reactions 21a, b and 22 occur but to a much lesser extent due to the production of hydroxyl radicals (OH^\cdot) and their subsequent reaction with cyanide:



Because hydroxyl radicals are devoid of charge and have a high affinity for electrons, they can quickly strip virtually any chemical of electrons including thiocyanate, WADs and SADs, thus causing their oxidation. Resulting cyanate will hydrolyze according to Reaction 15 or will react with continued photolytic ozonation to produce bicarbonate and either nitrogen gas (see Reaction 22a), nitrite or nitrate:



Cyanide destruction by photolytic ozonation requires 1 mole of ozone for every mole of cyanide (i.e., 1:1) to form cyanate but this ratio increases to 5:1 when nitrate is produced. Such high reagent consumptions, when equated with high temperatures and high UV intensities, can make photolytic ozonation costly.

Free cyanide, thiocyanate, WADs and SADs can also be oxidized by the homogeneous photolysis of hydrogen peroxide [122-125, 152, 153]. The photolytic peroxidation reaction also yields hydroxyl radicals:

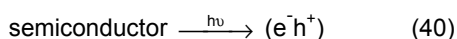


and, as a result, Reactions 15, 37b, and 38a, b and c can be observed depending on the amount of excess hydrogen peroxide that is present. Remediation of free cyanide, thiocyanate, WADs and SADs is near 100%, independent of concentration. Because Reaction 39 occurs quickly, Reactions 23a, b and c do not occur. Like photolytic ozonation, increasing UV intensities, hydrogen peroxide concentrations, and solution temperatures enhance reaction rates. Furthermore, reaction stoichiometries are 1:1 when cyanate forms and 5:1 when nitrate forms. Nevertheless, hydrogen peroxide is more attractive due to its relative inexpense and ease of storage and handling.

Homogeneous photolysis with ozone, hydrogen peroxide, and other aqueous photosensitizers is disadvantageous because the photosensitizers are consumed and often added in excess to ensure complete oxidation occurs. As already noted, photosensitizer consumption and costs are

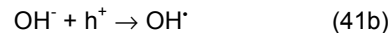
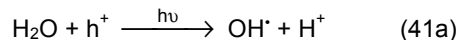
therefore high. In addition, the resulting effluent must be processed to treat the excess photosensitizer. In regards to ozone and hydrogen peroxide, this can be accomplished by giving the hydroxyl radicals time to decompose to water and oxygen in a holding pond; however, such a simple solution is not always available for other photosensitizers. These problems can be alleviated using catalytic photosensitizers that can be recycled. Homogeneous photocatalysis with aqueous photosensitizers and heterogeneous photocatalysis with solid photosensitizers result. Homogeneous photocatalysis, however, is rarely practiced due to the difficulty in separating aqueous species for recycling. On the other hand, heterogeneous photocatalysis is more viable because standard solid-liquid separation processes or fixed-bed systems can be used.

The solid photosensitizers used in heterogeneous photocatalysis are usually cheap, nontoxic and inert semiconductors. UV-absorbance promotes electrons in the valence band across the bandgap and into the conductance band of the semiconductor which creates a hole, h^+ , in the valence band and an excited electron, e^- , in the conductance band:

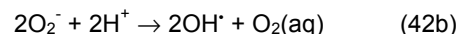
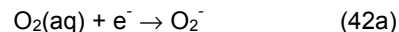


However, the impinging UV radiation must have energy equal to or greater than the bandgap of the semiconductor. The electron-hole (e^-h^+) pair can then induce redox reactions provided that the reacting species are adsorbed at the semiconductor surface and that the reaction products are inert to the reverse reaction and/or desorb quickly.

Heterogeneous photocatalysis has been examined for cyanide oxidation and three mechanisms have been proposed [122-125, 152-161]. The first mechanism produces hydroxyl radicals via the reduction of either adsorbed water or adsorbed hydroxide by holes in the valence band:



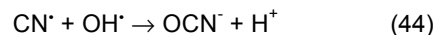
On the other hand, hydroxyl radicals are produced in the second mechanism by reacting dissolved oxygen with excited electrons in the conduction band through a superoxide (O_2^-) intermediate:



Both reaction mechanisms are concluded with cyanide oxidizing to cyanate, nitrogen gas, nitrite and/or nitrate by the hydroxyl radicals (see Reactions 37b and 38a, b, c) and are also effective for remediating thiocyanate, WADs and SADs. Early work had indicated that bicarbonate and ammonia were produced by cyanate hydrolysis according to Reaction 15; however, ammonia is readily oxidized in these systems. The third mechanism involves reducing cyanide by holes in the valence band to produce cyanyl radicals, CN^\cdot :



Hydroxyl radicals produced according to Reactions 41a, b and/or 42a, b then react with the cyanyl radicals:



Resulting cyanate further reacts with hydroxyl radicals as depicted earlier in Reactions 38a, b and c.

Spectroscopic evidence supports these three reaction mechanisms and is believed to be independent of the semiconductor photocatalysts that were tested— TiO_2 , ZnO , FeTiO_3 , SiO_2 , Fe_2O_3 , ZnS and CdS , to name a few. The metal oxides worked best because of their chemical stability; however, anatase, a polymorph of TiO_2 , was preferred due to its high quantum efficiency for photoconversion, its stable formation of

electron-hole pairs, and its large bandgap of 3.2 eV. This band gap equates to a maximum wavelength of approximately 387.5 nm which implies that virtually all portions of the UV spectrum can be used. In addition, electron-hole pairs were also made more stable by depositing metal islands of, for example, platinum and rhodium onto the surfaces of the photocatalysts.

Presently, photolysis is used in at least six remediation systems, aside from those employed for disinfection. These include the perox-pure™ process of Vulcan Peroxidation Systems, Inc. [162], the Rayox® Process of Solarchem Environmental Systems, Inc. [163], the Ultrox™ Process of Ultrox, Inc. [164], the PhotoReDox™ System of ClearFlow, Inc. [165, 166], and the two systems developed at Sandia National Laboratories in Albuquerque, NM [167], and National Renewable Energy Laboratory in Golden, CO [168]. The first three processes use homogeneous photolysis with hydrogen peroxide and have also been adapted for use with ozone and other aqueous photosensitizers. Differences between the systems are in cell design (horizontal versus vertical) and artificial UV-intensity (3 kW versus 60 W). On the other

hand, the other processes use heterogeneous photocatalysis with TiO₂. In these systems, the UV-radiation is artificial or solar and the TiO₂ is either suspended or fixed on one of several supports (glass beads or meshes); however, the supports can decrease photoconversion efficiencies due to reflection and refraction of the incident UV-radiation [169]. Although all six of these systems were principally designed for organic destruction, several have been demonstrated for cyanide oxidation.

CONCLUSIONS

Cyanide remediation can be accomplished using numerous separation and oxidation processes. Separation processes include physical methods with membranes, electrowinning and hydrolysis/distillation; complexation methods with acidification/volatilization, metal addition, flotation and solvent extraction; and adsorption methods with various minerals, activated carbons and resins. These methods are used to purify effluents for discharge by concentrating and recovering the cyanide for recycling. On the other hand, oxidation processes are used to destroy the cyanide and include various biological, catalytic, electrolytic, chemical and photolytic meth-

SEPARATION Remediation Process	Effective for separating						Need Further Treatment?
	Free Cyanide?	Thio-cyanate?	WAD Metal Complex?		SAD Metal Complex?		
			Cd/Zn	Cu/Ni	Fe	others	
Electrodialysis	yes	yes	yes	yes	yes	yes	No but costly
Reverse Osmosis	yes	yes	yes	yes	yes	yes	No but costly
Electrowinning	no	no	some	most	no	most	yes
Hydrolysis/Distillation	yes	no	no	no	no	no	yes
AVR	yes	some	yes	yes	most	some	some
Cementation (est.)	no	no	no	most	some	yes	most
Fe Complexation	yes	little	no	no	no	no	yes
Precipitation Flotation	yes	little	most	most	yes	no	most
Ion Flotation	some	?	some	yes	yes	yes	most
Solvent Extraction (est.)	some	little	yes	yes	yes	yes (Au)	some
Mineral Adsorption (est.)	most	some	most	yes	yes	yes	some
Untreated Activated Carbon	no	some	some	yes	yes	yes	some
Cu-treated Activated Carbon	yes	yes	yes	yes	yes	yes	little
Untreated Resin	no	some	yes	yes	yes	yes	little
Cu-treated Resin	yes	some	yes	yes	yes	yes	little

est. = estimated

Table 1. Effectiveness of separation processes for cyanide remediation as discussed in this paper as modified and updated from Ingles and Scott [18].

ods. Several investigations compared the effectiveness of separation and oxidation processes and found them to be dependent on the cyanide species that were present; free cyanide (CN⁻ and HCN), thiocyanate (SCN⁻), weak-acid dissociables (WADs), and strong-acid dissociables (SADs) may be remediated by one process and not another. The advanced oxidation processes associated with photolytic methods work well for all cyanide species and consequently are the preferred choice for remediation; however, if certain cyanide species are not present, remediation can be accomplished by more appropriate alternatives. This is clearly illustrated in Tables 1 and 2. Consequently, the proper choice for cyanide remediation must be made on a case-by-case basis; then and only then can a real decision be made regarding the need for further cyanide treatment.

ACKNOWLEDGMENT

This work was conducted as part of the Mine Waste Technology Program (MWTP) under an interagency agreement, IAG ID No. DW89935117-01-0, between the U.S. Environmental Protection Agency (EPA) and the U.S. Department of Energy (DOE), Contract No. DE-AC22-88ID12735. This

paper was not subjected to MWTP peer and administrative review and, therefore, may not necessarily reflect the views of the program. No official endorsement should be inferred.

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OXIDATION Remediation Process	Effective for oxidizing						
	Free Cyanide?	Thio-cyanate?	WAD Metal Complex?		SAD Metal Complex?		Need Further Treatment?
			Cd/Zn	Cu/Ni	Fe	others	
Bio-oxidation (Bacteria)	yes	yes	most	most	yes	yes	little
Catalysis	yes	?	yes	yes	no	some	yes
Electro-oxidation	most	yes	most	most	no	no	yes
Electro-chlorination	yes	yes	yes	yes	no	no	yes
Alkaline Chlorination	yes	yes	yes	yes	no	no	yes
Oxygen	yes	some	some	no	no	no	yes
Ozone	yes	yes	yes	yes	no	no	yes
Hydrogen Peroxide	yes	no	yes	some	some	no	yes
Hydrogen Peroxide/Cupric	yes	no	yes	yes	yes	no	some
Hydrogen Peroxide/Kastone	yes	no	yes	yes	yes (ppt)	no	some
Caro's Acid	yes	yes	yes	yes	yes	no	little
Sulfur Dioxide	yes	some	yes	yes	yes (ppt)	most	little
Direct Photolysis	no	no	no	some	yes	some	yes
Photolytic Ozonation	yes	yes	yes	yes	yes	yes	no but costly
Photolytic Peroxidation	yes	yes	yes	yes	yes	yes	no
TiO ₂ Photocatalysis	yes	yes	yes	yes	yes	yes	no

Table 2. Effectiveness of oxidation processes for cyanide remediation as discussed in this paper as modified and updated from Ingles and Scott [18].

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