Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol

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Abstract

Increasingly, there are severe environmental controls in the mining industry. Because of lack of technological advances, waste management practices are severely limited. Most of the wastes in the milling industrial effluents are known to contain cyanides and it is recognized that after extraction and recovery of precious metals, substantial amounts of cyanide are delivered to tailings ponds. The toxicity of cyanide creates serious environmental problems. In this paper we describe several methods for the treatment of cyanide solutions. These include: (1) cyanide destruction by oxidation with chlorine dioxide (ClO_2) in a Gas-Sparged Hydrocyclone (GSH) reactor; (2) destruction of cyanide by ozone (O_3) using a stirred batch reactor, and finally, (3) the photolysis of cyanide with UV light in presence of titania sol. In all cases excellent performance were observed as measured by the extent and of the destruction.
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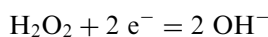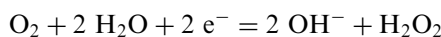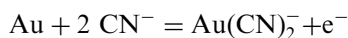
1. Introduction

Although waste reduction and recycling are preferable to the treatment and disposal of wastes, they are not always possible. This is particularly true for many wastes contaminated by cyanide compounds which will, for the foreseeable future, continue to be land disposed. These waste streams arise from different process industries such as those wastes from manufacturing synthetic fiber (acrylonitrile), coal conversion wastes or coking effluents (from the iron and steel industries), electroplating waste, petrochemical wastes, automobile industry waste (from plating shops) and wastes from the processing of precious metals resources by cyanidation. All these wastes have varied characteristics and are, therefore, subject to different processing and treatment strategies that depend upon the concentration of cyanides and the flow rate of the waste stream.

In mining operations, cyanidation is the predominant method by which gold and silver are recovered from their ores. In practice, the dissolution of gold and silver in aqueous cyanide solution is typically carried out using 0.03–0.3% NaCN at pH greater than 10, and aeration to keep the pulp or solution saturated with oxygen (> 7 ppm). The overall reaction for the dissolution of gold and silver in dilute, aerated, alkaline cyanide solutions may be expressed by the classic Elsner equation:

$$4\,Au + 8\,CN^- + O_2 + 2\,H_2O$$
$$= 4\left[Au(CN)_2^-\right] + 4\,OH^-$$
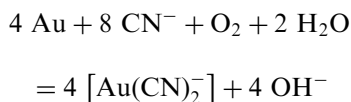
which can be broken into the following half-reactions:

$$Au + 2\,CN^- = Au(CN)_2^- + e^-$$

$$O_2 + 2\,H_2O + 2\,e^- = 2\,OH^- + H_2O_2$$

$$H_2O_2 + 2\,e^- = 2\,OH^-$$

In these reactions cyanide ion is the complexing agent or ligand, and oxygen is the oxidant (Jeffrey and

Ritchie, 2000). The reaction with silver is similar. However, the silver cyanide complex is weaker than the gold cyanide complex and, therefore, more concentrated cyanide solutions and/or longer contact times must be employed for its dissolution. The cyanide solution is recycled after the precious metals have been removed by cementation with zinc powder. A dilution purge is used to minimize heavy metals accumulation.

After extraction and recovery of the precious metals, substantial amounts of cyanide are delivered to tailings ponds, which create environmental problems due to the toxicity of cyanides. Cyanide exists in three forms in wastewater: free cyanide such as hydrogen cyanide; simple cyanide such as sodium cyanide; complex cyanides such as iron cyanide, nickel cyanide, and copper cyanide. Total cyanide is the sum of simple and complex cyanides but excludes the separate chemical compounds such as cyanate and thiocyanate.

Due to the widespread use of cyanide in mining operations the recovery and destruction of cyanide is important both from the environmental aspects of wastewater and effluent treatment, and in some cases, from the economic aspects associated with the high reagent consumption by the process itself. The US Environmental Protection Agency has proposed a limit of 0.2 mg/l cyanide in drinking water. The German and Swiss regulations have set limit of 0.01 mg/l for cyanide for surface water and 0.5 mg/l for sewers (Desai et al., 1998). In México, SEMARNAT has set the limit for cyanide as 0.2 mg/l. In view of these considerations cyanide recovery and/or destruction is a necessary for lowering the concentrations of cyanides to below regulatory limits.

To reduce the cyanide level for disposal of the effluent (<0.2 mg/l), several cyanide treatment systems have been developed. All these methods are based on cyanide recovery by acidification and/or destruction by chemical oxidation (Mosher and Figueroa, 1996). In many cases the process is burdened with high reagent costs and royalty payments (Robbins, 1996). In this regard it was decided to evaluate appropriate treatment options for oxidation of cyanide from the wastewater. The technologies described in this paper use chlorine dioxide, ozone, and titanium dioxide.

1.1. Gas Sparged Hydrocyclone

Application of the Gas Sparged Hydrocyclone (GSH) is considered for the treatment of cyanide wastes by destruction and/or chemical oxidation with the use of chlorine dioxide [$ClO_{2(g)}$]. This approach has not been reported previously. In this part of the work, a study was performed for the destruction of CN^- using the Gas Sparged Hydrocyclone reactor. This reactor allows intimate contact between the cyanide solution and $ClO_{2(g)}$ at a high specific capacity. It offers several

advantages such as ability to deal both with free and complexed cyanide even at high concentration. These advantages derive partly from the fact that $ClO_{2(g)}$ exists in gaseous state and it is a strong oxidizing agent that is effective over a wide pH range (Chang et al., 2000).

1.2. Ozone

Ozone is a powerful oxidizing agent yet it offers the advantage that little or no secondary products are formed upon treatment of the wastewater containing cyanide. Ozone concentrations vary, from 5 to 25 mg/l of air, depending on ozone generator parameters (air flow, generator power, etc.) and concentration can reach 35 mg/l with pure oxygen. Continuous ozone treatment of a cyanide-containing waste stream involves consecutive oxidation reactions, the first of which involves direct oxidation to cyanate. If excess ozone is used, the cyanate can be oxidized to nitrogen and carbonate (or bicarbonate, depending on the pH). The standard oxidation-reduction potential for ozone is high ($+2.07$ V) in acid solutions (Henry, 1996).

1.3. Titanium dioxide photocatalyst

In the last few years, photocatalysis by polycrystalline semiconductors irradiated by near-UV light has been found effective in oxidizing certain organic pollutants to less dangerous species under mild reaction conditions. This method is found to be suitable for the oxidation of both free and complexed cyanides dissolved in wastewater (Mills and Le Hunte, 1997). The process works by subjecting wastewater to the combined forces of sunlight and a semiconductor catalyst. A commonly used catalyst is titanium dioxide (TiO_2). This catalyst may be mixed into the water, creating a slurry, or fixed onto a lattice-type structure through which the water flows or can be used in colloidal form. When exposed to the sunlight, the catalyst absorbs the high-energy photons from the UV portion of the solar spectrum, and reactive chemicals known as hydroxyl radicals are formed. These radicals are powerful oxidizers that break down the cyanide where the first product of photocatalytic oxidation of cyanides in the presence of polycrystalline TiO_2 in aqueous medium is CNO^- (Augugliaro et al., 1999).

2. Cyanide destruction

The leading processes currently being applied for cyanide destruction in effluents involve the oxidation of cyanide which include alkaline chlorination, hydrogen peroxide, INCO/SO_2 air process, ozone, biological treatment and anodic oxidation. All these methods have distinct advantages and disadvantages which are outlined in Table 1 (Botz and Stevenson, 1995; Mosher and

Table 1

Advantages and disadvantages of various cyanide destruction options, from 300 mg/l concentration to 1 mg/l concentration (Botz and Stevenson, 1995; Chang et al., 2000; Desai et al., 1998; Kesting, 1953; Miller and Kinneberg, 1984; Miller et al., 1996)

Detoxification method	Advantages	Disadvantages	Suitability for		kg Reagent	Time (min)
			Low CN⁻	High CN⁻	kg CN⁻	
Alkaline chlorination	•Technology well established •The cyanate is relatively less toxic and further oxidized to carbon dioxide and nitrogen at lower pH •Remove metals through precipitation at elevated pH	•Adds potentially objectionable cations/anions to water •Excess hypochlorite is toxic •Chlorine can react with organics to form chlorinated compounds •Poor process control results in toxic intermediates •Reacts preferentially with thiocyanate •Many of the less expensive hypochlorite sources require special handing	✓	✓	6	120
Hydrogen peroxide	•Excess reagent decomposes to water and oxygen •Relatively simple to operate •Isn't as reactive with thiocyanate	•Reagent cost •If precipitating ferrocyanides with copper, must dispose of precipitate •Requires accurate measurement of chemical dose	X	✓	3.8	60
SO₂/air (INCO) process	•Reagent is very inexpensive •For treating aqueous solutions and gold mine waste sludges •Used over a wide pH range	•At least some of reagent savings are offset by license/royalty payments •Process adds sulfates to treated water •If precipitating ferrocyanides with copper, must dispose of precipitate	✓	X	2.5	30
Biological oxidation	•"Natural approach", received well publicly, and by regulators •Uses heaps as a reactor, reducing total wash volumes, and possibly reach low flow areas of the heap more effectively •Relatively inexpensive •Biomass can be actived by aereation	•Technology is not well established •Requires combination of metallurgy, biology and process engineering •Tends to be very site specific, with each ore type requiring a specific evaluation and study •Viable cell systems may require long adaptation and do not function properly at cyanide concentrations higher than 200 mg/l	✓	X	1.9	10⁵
Ozonation	•Some regeneration of cyanide possible	•Produce ammonia •Reagent cost/equipment	✓	✓	1.9	20
Anodic oxidation	•Treat all cyanide containing baths regardless of concentration	•Requires post treatment by a number of oxidation methods	✓	✓	10 kW-h	5

Figueroa, 1996; Robbins, 1996; Desai et al., 1998; Ogutueren et al., 1999; White et al., 2000).

As can be seen, none of the earlier mentioned chemical processes are fully acceptable for cyanide detoxification. There is no ideal method available for attaining the low levels of cyanide that are permitted in the waste streams. Chemical processes may leave an excess of other objectionable chemicals in the wastewater stream. Biological processes have the problem of the disposal of activated sludge. Even when the problem of disposal of

sludge is overcome, the reaction rates can be very low. The electrochemical methods are not efficient when the cyanide level drops below 100 ppm, which happens because of mass-transfer limitations and low current efficiency.

Because of these limitations, promising alternatives which will help to comply with the EPA regulations for the safe disposal of cyanide wastes are needed. These methods can be found in the detoxification of cyanidation effluents by the use of chlorine dioxide (ClO_2) with the Gas Sparged Hydrocyclone reactor, Ozonation and Titanium dioxide photocatalyst.

3. GSH technology

The GSH technology was originally developed at the University of Utah for the fast and efficient flotation of fine particles from suspension (Miller and Kinneberg, 1984; Miller and Yi, 1989). Recent studies indicate that the fluid flow conditions inside the GSH system can be effectively exploited for air stripping of VOCs from contaminated water (Miller et al., 2000).

The GSH unit, schematically shown in Fig. 1, consists of two concentric right-vertical tubes and a conventional cyclone header at the top. The porous inner tube is constructed of suitable material such as plastic, ceramic, or stainless steel and allows for the sparging of air or any other gas or steam. The outer nonporous tube simply serves as a gas jacket and ensures even distribution of the $ClO_{2(g)}$ throughout the porous tube. The cyanide solution is fed tangentially at the top through the cyclone header to develop a swirl flow adjacent to the inside surface of the porous tube, leaving an empty air core centered on the axis of the GSH unit. The high-velocity swirl flow shears the sparged air to produce a high concentration of small bubbles and intimate interaction between these numerous fine bubbles of $ClO_{2(g)}$ and the cyanide solution. Gaseous products are then transported radially to the center of the cyclone. The major portions of the gas phase move towards the vortex
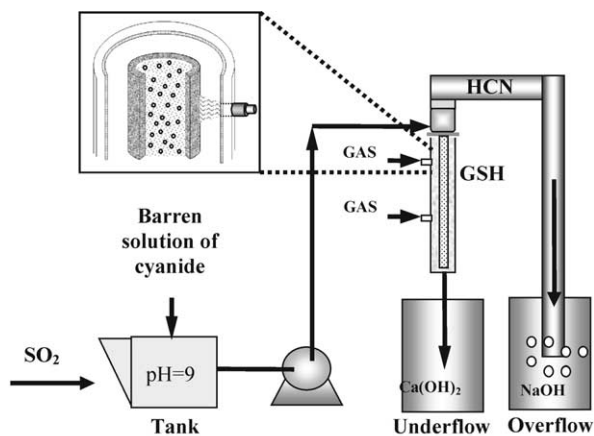

Fig. 1. Schematic drawing of the Gas-Sparged Hydrocyclone reactor.

finder of the cyclone header, and are vented into an appropriate post-treatment device. The specific capacity of the GSH system is at least 300–400 gallons per minute per cubic foot of equipment volume, 100–600 times that of conventional gas-stripping equipment. The GSH equipment requires an operating space significantly less that of a packed tower or other air stripping devices, which result in a significant savings in capital cost.

3.1. Experimental procedure of cyanide oxidation by ClO_2

In order to properly use chlorine dioxide, its properties, like those of chlorine, must be considered both in the gas phase and in the aqueous phase (Perry and Eckenfelder, 1990). Chlorine dioxide has a disagreeable, irritating odor somewhat similar to chlorine. $ClO_{2(g)}$ may be readily decomposed on exposure to UV light. Therefore, it is always stored in the dark. The sensitivity of gaseous and liquid $ClO_{2(g)}$ to temperature and pressure has mitigated against its bulk shipment. It can be handled safely in the gas phase by diluting with air or nitrogen to keep its concentration below about 10%. For potable water and wastewater treatment process, it is only used in aqueous solutions and is generated on site.

Finally, the environmental impacts associated with the use of $ClO_{2(g)}$ as wastewater disinfectant or waste treatment are not well known. It has been reported that the impacts are less adverse than those associated with chlorination (Freeman, 1988). Since it does not react with water, its oxidation potential and strength are pH dependent. Consequently, $ClO_{2(g)}$ is superior to chlorine particularly for wastewater of relatively high pH in which the concentration of hypochlorous acid is low.

Experiments for cyanide oxidation by chlorine dioxide at the Institute Technology of Saltillo pilot plant included preparation of the barren solution with SO_2 gas (pH = 2–11) and stripping with a 2-inch diameter GSH unit. Chemical analysis for cyanide in the effluent streams was accomplished with a reflux distillation method which functioned by lowering the pH with sulfuric acid and collecting the HCN(gas) in NaOH (liquid). The collected cyanide was quantified by titration with silver nitrate for levels above 1 mM and by a cyanide ion specific electrode for lower concentration levels.

During the experiments two streams had to be delivered to the GSH; the cyanide solution and the air. Cyanide solution was provided by a sump pump mounted on a 300-l retention tank. The cyanide solution flow rate was adjusted using a regulated return flow to the tank. Using an air compressor, airflow was evenly distributed between the upper and lower sections of GSH and all parts were sealed with gaskets. Operators were provided with personal HCN gas monitor/alarm units.

The method used for generating on-site $ClO_{2(g)}$ consists of blending a 45% solution of sodium chlorate with

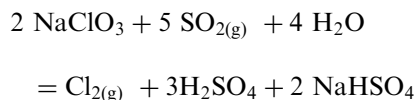$66°$Be sulfuric acid in the top of a reaction vessel. Air containing 10% $SO_{2(g)}$ was blown into a diffuser at the bottom of this vessel and chlorine dioxide plus air was extracted at the top of the vessel (chlorine dioxide content was between 6 and 10%), as described by the so-called Mathieson process (Perry and Eckenfelder, 1990; Kesting, 1953). The basic reactions are:

$$2\ NaClO_3 + H_2SO_4 = 2\ HClO_3 + Na_2SO_4$$

$$2\ HClO_3 + SO_{2(g)} = 2ClO_{2(g)} + H_2SO_4$$
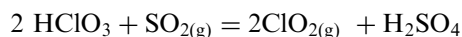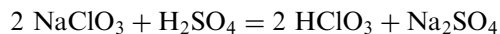
Side reactions also take place, including:

$$2\ NaClO_3 + 5\ SO_{2(g)} + 4\ H_2O$$

$$= Cl_{2(g)} + 3H_2SO_4 + 2\ NaHSO_4$$

Operating conditions are optimized to suppress the latter reaction as much as possible, since this produces only chlorine. The exit gases are reacted with the cyanide solution in the Gas-Sparged Hydrocyclone reactor where the oxidation or destruction of cyanide is expected to occur according to the following reaction:

$$CN^- + 2\ ClO_{2(g)} + 2OH^- = CNO^- + 2\ ClO_2^- + H_2O$$
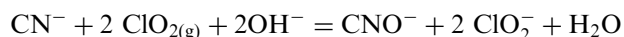
The stoichiometry of the reaction shows that 5.2 kg of chlorine dioxide is needed to destroy 1 kg CN^- in ideal conditions.

3.2. Results and discussion for cyanide destruction with GSH reactor

3.2.1. Effect of pH on cyanide destruction

One of the primary process variables for cyanide destruction with $ClO_{2(g)}$ is the pH of the solution. Table 2, shows the results of a set of experiments for the effect of pH on cyanide destruction. The effluent cyanide concentration (both free and combined cyanide) is plotted

as a function of pH in Fig. 2. It is evident that free cyanide is destroyed at all pH values. The complexed cyanide CN_x is destroyed most effectively at high pH values.

3.2.2. Effect of NaCl in cyanide destruction

The use of NaCl has also been considered for use in cyanide destruction. These experiments were designed to eliminate the use of sulfur dioxide (SO_2) for the chlorine dioxide generation and minimize the danger of explosion. The basic reaction for this process is:

$$2\ NaClO_3 + 2\ NaCl + 2\ H_2SO_4$$

$$= 2\ ClO_{2(g)} + Cl_{2(g)} + 2Na_2SO_4 + 2\ H_2O$$
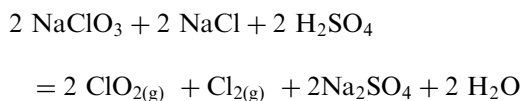
Air is blown into the bottom of the vessel driving off the gas formed, which is diluted by the incoming air. Then the mixture of ClO_2/Cl_2 gas which is extremely volatile is stripped from the aqueous solution by the air and then is circulated through the GSH reactor where in alkaline cyanide solution and the addition of chlorides can react with free cyanide following the reactions:

$$CN^- + Cl_2 = CNCl + Cl^-$$

$$CN^- + ClO^- + H_2O = CNCl + 2\ OH^-$$
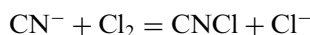
At alkaline pH cyanogen chloride reacts readily, producing cyanate (Szpyrkowicz et al., 2000):

$$CNCl + 2\ OH^- = CNO^- + Cl^- + H_2O$$
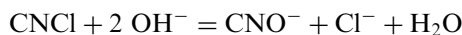
The cyanate is then oxidized to nitrogen and bicarbonate:

$$2\ CNO^- + 3\ OCl^- + H_2O = 2\ HCO_3^- + N_2 + 3\ Cl^-$$
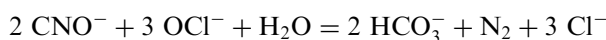
The data are presented in Table 3. The results show 99.9% destruction of free cyanide and the response is similar to that as when sulfur dioxide (SO_2) was used for chlorine dioxide generation.
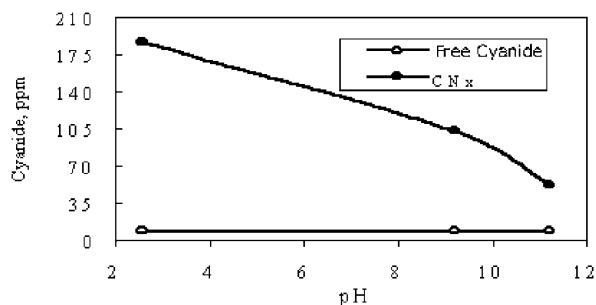
Table 2
Effect of pH on cyanide destruction

Cyanide solution (mg/l)		Final effluent (mg/l)		% Destruction	
pH	Total cyanide	Free cyanide	Complexed cyanide [CN_X]	Free cyanide	Complexed cyanide [CN_X]
11.23	250	0.12	52.54	99.9	78.8
9.20	250	0.19	103.0	99.9	58.8
2.57	250	0.11	187.0	99.9	25.2

Feed solution = 250 mg/l total cyanide; solution flow rate = 40 l/min; Gas (6% ClO_2) flow rate = 100 l/min. CN_X = $Fe(CN)_6^{-4}$, etc.

Fig. 2. Effect of pH in cyanide destruction.

Table 3
Effect of NaCl in cyanide destruction

Barren bleed (mg/l)		Final effluent (mg/l)		% Removal	
NaCl (g/l)	Total cyanide	Free cyanide	Combined cyanide	Free cyanide	Combined cyanide
1.23	250	0.02	52.54	99.9	78.8
0.80	250	0.10	149.0	99.9	40.4
0.40	250	0.09	193.0	99.9	22.8
0	250	0.10	222.0	99.9	11.2

Feed solution = 250 mg/l total cyanide; solution flow rate = 40 l/min; gas (ClO_2/Cl_2) flow rate = 100 l/min; pH = 11.2. $CN_X = CNO^-$, HCNO, $Fe(CN)_6^{-4}$, etc.

4. Cyanide oxidation by ozone technology

4.1. Experimental procedure of cyanide oxidation by ozone

The experimental setup consisted of a stirred batch vessel (Fig. 3) equipped with a gas sparger (2 μm pore size, 0.02 m diameter and 0.027 m height) located at the bottom of the column; and ozone generator (Pacific Ozone L22). On-line monitoring was performed for solution pH (Orion SA520), oxidation-reduction potential (redox potential, Orion 520-A Au vs. Ag/AgCl), dissolved ozone (ATI A15/64) and temperature (Orion 520-A).

Tests were performed by bubbling an oxygen–ozone mixture through 2.7 l of solution for a given period of time. Analytical grade reagents were used to prepare synthetic solutions (NaCN Aldrich 99.99%). Ozone was produced from pure oxygen in the generator. Ozone concentration in the gas phase was analyzed by means of the iodometric method. Continuous ozone treatment of a cyanide in wastewater involves consecutive oxidation reactions, the first of which involve direct oxidation to cyanate:

1.- Vessel (20 x 20 cm)
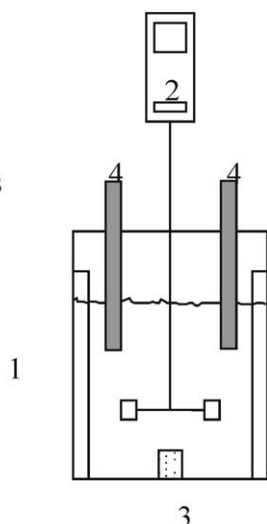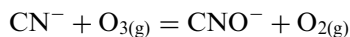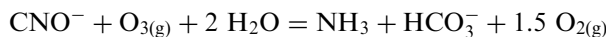2.- Varieble speed stirred
3.- gas sparged
4.- pH and ORP electrodes

Fig. 3. The experimental stirred batch vessel.

$$CN^- + O_{3(g)} = CNO^- + O_{2(g)}$$

If excess ozone is used, the cyanates can be oxidized to nitrogen and carbonate (or bicarbonate, depending on the pH) according to:

$$CNO^- + O_{3(g)} + 2 H_2O = NH_3 + HCO_3^- + 1.5 O_{2(g)}$$

Under basic conditions, the cyanates hydrolyze to yield ammonia, which is then oxidized by the ozone to nitrate (Henry, 1996) in accordance with the following equations:

$$CNO^- + OH^- + H_2O = CO_3^- + NH_3$$

$$NH_3 + 4 O_{3(g)} = NO_3^- + H_2O + 4 O_{2(g)} + H^+$$
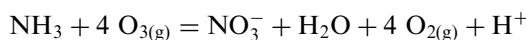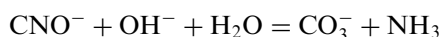
4.2. Results and discussion

The reaction of cyanide with ozone in alkaline solutions is fast, as shown in Table 4. The results indicate that the oxidation of cyanide depends of the addition of ozone. Ozone consumption data obtained in the experiments confirm that one mole of cyanide is oxidized by one mole of ozone to produce one mole of cyanate, according to literature (Henry, 1996). Oxidation of cyanate by ozone is a slow reaction compared with that of cyanide, and therefore, cyanate accumulates while cyanide is almost completely oxidized.

Fig. 4 shows cyanide oxidation is enhanced by increasing the ozone addition rate and does not depend on the initial cyanide concentration in the solution. It is also evident from this figure, that cyanide in solution decreases linearly with time, thus indicating that the oxidation rate is constant and increases proportionally to the increase in ozone addition rate. This behavior identifies a zero order reaction with respect to cyanide concentration in solution.

4.2.1. The cyanide oxidation rate

The model, described by the following equation, fits the experimental data fairly well (correlation coefficient greater 98%). The cyanide oxidation rate constant

Table 4
Cyanide destruction by ozone

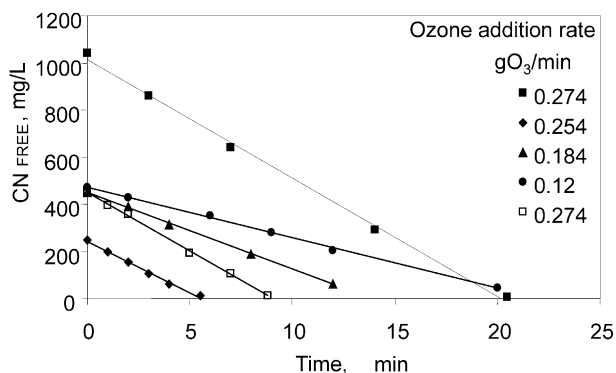| Barren bleed (mg/l) pH = 11.2		Final effluent (mg/l)	% Removal	
Ozone addition g/min	CN_{Free}	CN_{Free}	CN_{Free}	Time (min)
0.12	500	1.00	99.9	20
0.184	500	2.00	99.9	13
0.254	250	1.00	99.9	6
0.274	500	1.00	99.9	8

Fig. 4. Effect of initial cyanide concentration and ozone addition rate on the rate of cyanide oxidation.

obtained is about 10^{-5} mol/l·s, i.e., cyanide disappearance rate is in the range of 15–26 mg/l·min, for the ozone addition rates used in this work.

$$[CN^-]_0 - [CN^-] = k_1 t$$

Assuming, as a first approximation, that the cyanide ozonation reaction is of first order with respect to ozone addition, an engineering rate constant of 0.190.53 l^{-1} is obtained by plotting cyanide oxidation rate vs. ozone addition rate (varied by increasing the O_3/O_2 mixture gas flow). As shown in Fig. 5, the assumption is correct and, therefore, it may be concluded that cyanide ozonation is first order with respect to ozone and zero order with respect to cyanide, being described by the following equation:

Cyanide oxidation rate, mg/l min

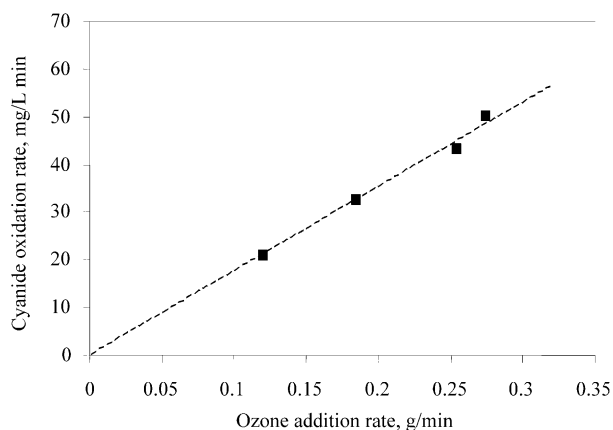$= [190.53 \pm 15]$ [ozone addition rate, g/min]

Fig. 5. Cyanide oxidation with respect to ozone addition rate.

5. Cyanide oxidation by titanium dioxide photocatalyst

5.1. Experimental procedure of cyanide oxidation by titanium dioxide

The photocatalytic oxidation of complexed cyanide ions was carried out in aqueous suspensions containing Titania sol irradiated by UV light. The chemicals $TiCl_4$ solutions, potassium persulfate, sodium nitrite, hydrogen peroxide, were obtained from Fischer Scientific Company, Fair Lawn, N.J. $K_3Fe(CN)_6$ was obtained from J.T. Baker Chemical Co., Phillipsburg, NJ. Polyvinyl alcohol of molecular weights 13,000–23,000 was obtained from Aldrich Chemical Company, Milwaukee, WI. The apparatus was a high-pressure mercury arc UV-lamp that was obtained from CENCO, Central Scientific Company, and 11222 Melrose Avenue, Franklin Park Illinois. A Shimadzu UV-265 Spectrophotometer, Kyoto, Japan, was employed for ultraviolet visible spectrophotometer work.

The experimental procedure was divided into six steps. The first step in the experiments was the preparation of clear titanium dioxide suspension by very slowly adding approximately 3 ml of titanium tetrachloride, $TiCl_4$, to 350 ml water at 0 °C, with continuous stirring. The sol was stabilized by polyvinyl alcohol (PVA). Ten grams of PVA were heated with 150 ml of water to produce a homogenous solution. Two hundred milliliters of TiO_2 solution was added and the mixture was stirred. The pH of the mixture was adjusted with NaOH solution. Solution of potassium ferricyanide in water was made by weighing $K_3Fe(CN)_6$ and dissolving in water.

The presence of CNO^- was determined by using a spot test. A drop of the neutral test solution is mixed with a drop of 2% water solution of hydroxylamine chloride and then one drop of 2% solution of $FeCl_3$ is added. A transient violet color signifies the presence of cyanate ions. The instability of the color is due to the reducing action of the excess hydroxylamine. Qualitative analysis of carbonate was determined by precipitation with calcium chloride. Finally, prior to photochemistry of ferricyanide, solutions were filled in fused silica cuvette and their UV–vis absorption spectra were recorded. They were later irradiated for a known length of time. The UV–vis spectra of the solution were recorded periodically to determine degradation of ferricyanide. The location of the lamp and cuvette containing ferricyanide solution was always fixed. Thus, the intensity of the UV light was the same every time for every solution.

5.2. Results and discussion

In acidic media, cyanides could form hydrocyanic acid. It is, therefore, necessary to investigate its

destruction in alkaline media. Table 5 presents the results of the destruction efficiency as function of pH and time. The destruction appears to be more efficient at pH 10. Therefore, for subsequent studies, a pH of 10 was chosen.

Some experiments were carried out to examine the efficiency of cyanide destruction with solar radiation. Table 6 presents theses results. The solar radiation is seems extremely effective in destruction of iron cyanides. The presence of cyanate ions was detected in the destruction products by the spot test.

In our effort to further enhance the efficiency of destruction, the synergistic effect of several oxidants was examined in a separate study. We considered the use of several oxidants such as sodium hypochlorite, sodium nitrite, potassium persulfate, and sodium perborate hydrate. Summary of these results is presented in Table 7.

It was surprising to find that the additional oxidants did not have any significant effect on the efficiency of destruction. We are investigating the possible causes of this phenomenon. The cause may be that the rate determing step is not the destruction but conversion of ferricyanide to another species. This is supported by Durrant and Durrant, Potassium Ferricyanide first hydrolyzes to $K_2Fe(CN)_5H_2O$ and the free cyanide ion probably oxidized in TiO_2–UV environment (Durrant and Durrant, 1970).

Table 5
Effect of pH and time on the percent destruction of 1 mM iron ferricyanide in the presence of titanium sol exposed to 4 W Hg lamp

Time (h)	pH = 10	pH = 12
0	0	0
3	46	41
6	77	47

Table 6
Percentage destruction of 1 mM iron ferricyanide at pH 10 in the presence of titania sol exposed to solar radiation

Time (h)	Fused silica cell	Corning glass cell
0	0	0
1.5	100	46
3.25		100

Table 7
Percentage destruction of $K_3Fe (CN)_6$ in the presence of colloidal titania and various oxidizing agents at 60 min at pH = 10

Concentrations (mM)	0	1	2
Sodium hypochlorite	38.60	36.70	35.70
Sodium nitrite	38.60	–	32.90
Potassium persulfate	38.60	34.80	35.80
Sodium perborate hydrate	38.60	29.80	35.70

In summary, titanium sol is very efficient in destruction of complexed cyanide, which escape destruction by the traditional chlorination process. The cyanate is found in the products of the destruction. Titania dioxide is chemically and thermally very inert and therefore it does not further deteriorate or pose an environmental problem. Preparation of sol is extremely easy. For destruction of cyanides in tailing ponds, titania sol could be formed in the ponds by using $TiCl_4$ and letting the water body exposed to the sunlight. There is perhaps no other simpler and economical method for destruction of the cyanides.

6. Conclusions

The use of chlorine dioxide in the GSH reactor has been tested in bench and pilot plant scale applications and has been proven effective for the destruction of cyanide in solution and slurries. For the chlorine dioxide the economics of the process are quite attractive because there are additional cost savings due to the short residence time, decreases in operating staff and other chemical utilized (i.e. copper sulphate and NaOH) in the other processes.

It was observed that ozone effectively oxidizes free cyanide; but, according to literature, the oxidation of the stable metal cyanide complexes such as iron cyanide complexes with ozone is difficult (Henry, 1996). To overcome this draw back, ozone process may be combined with photolysis process which uses application of UV light.

Finally, The photocatalytic process may be a viable method for decontamination of wastes containing various cyanide species. The degradation of cyanide wastes is environmentally friendly because the process does not add any toxic pollutant.

References

Augugliaro, V., Blanco, J., Caceres, J., 1999. Photocatalytic oxidation of cyanide in aqueous TiO_2 suspensions irradiated by sunlight in mild and strong oxidant conditions. Catalysis Today (54) 245–253.

Botz, M., Stevenson, J., 1995. Cyanide: recovery and destruction. Eng. & Mining J. (June) 44–47.

Chang, C.Y., Hsieh, Y.H., Hsu, S.S., Hu, P.Y., Wang, K.H., 2000. The formation of disinfection by-products in water treated with chlorine dioxide. J. Hazard. Mater. B79, 89–102.

Desai, J.D., Ramakrishna, C., Patel, P.S., Awasthi, S.K., 1998. Cyanide wastewater treatment and commercial applications. Chemical Engineering World XXXIII (6), 115–121.

Durrant, P.J., Durrant, B., 1970. Introduction to Advanced Inorganic Chemistry. Wiley, New York, NY.

Freeman, H.M., 1988. Standard Handbook of Hazardous Waste Treatment and Disposal. McGraw-Hill, New York.

Henry, R., 1996. Chemical Water Treatment Principles and Practice. VCH Publishers Inc.

Jeffrey, M.I., Ritchie, I.M., 2000. The leaching of gold in cyanide solution in the presence of impurities. I. The effect of lead. J. Electrochem. Soc. 147 (9), 3257–3262.

Kesting, E., 1953. The manufacture and properties of chlorine dioxide. TAPPI 36 (4), 171–176.

Miller, J.D., Kinneberg, J., 1984. Fast flotation with an air-sparged hydrocyclone. In: Proceedings of MINTEK 50, International Conference on Recent Advances in Mineral Science and Technology, Johannesburg, South Africa, pp. 337–338.

Miller, J.D., Ye, Yi., 1989. Froth characteristics in air-sparged hydrocyclone flotation. Mineral Proceeding and Extractive Metallurgy Review 307–309.

Miller, J.D., Lelinski, D., Parga, J.R., 1996. Final Report—CX 823711, Advance Process Technology for the Wastepaper Recycling Plants and Pulp/Paper Plants. Southwest Center for Environmental Research and Policy.

Mills, A., Le Hunte, S., 1997. An overview of semiconductor photocatalysis. Journal of Photochemistry and Photobiology A: Chemistry (108) 1–35.

Mosher, J.B., Figueroa, A., 1996. Biological oxidation of cyanide: a viable treatment option for the mineral processing industry. Mineral Engineering 9 (5), 573–581.

Ogutueren, U.B., Toru, E., Koparal, S., 1999. Removal of cyanide by anodic oxidation for wastewater treatment. Water Research 33 (8), 1851–1856.

Perry, W.L., Eckenfelder, W.W., 1990. Toxicity Reduction in Industrial Effluents. Van Nostrand Reinhold Co, New York.

Robbins, G.H., 1996. Historical development of the INCO SO$_2$/air cyanide destruction process. CIM Bulletin (9) 63–69.

Szpyrkowicz, L., Zilio-Grandi, f., Kaul, S.N., Polcaro, A.M., 2000. Copper electrodeposition and oxidation of complex cyanide from wastewater in an electrochemical reactor with a Ti/Pt anode. Ind. Eng. Chem. Res. (39) 2132–2139.

White, D.M., Pilon, T.A., Woolard, C., 2000. Biological treatment of cyanide containing wastewater. Water Research 34 (7), 2105–2109.