

Use of ozone in the treatment of cyanide containing effluents

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ABSTRACT

The treatment of effluents of the gold and silver cyanidation process is one of the main problems that the precious metals industry faces. These effluents contain variable quantities of free cyanide, weak complexed cyanide, strong complexed cyanide and thiocyanate. Different methods are used for the removal of cyanide but most of the times the consumption of reagents raises the operation cost to unaffordable levels, and there exists as well the possible formation of residual by-products that are also toxic. Ozone is an alternative gas for oxidation of cyanide compounds that presents several advantages; however the lack of information on the reactions of these compounds with ozone has delayed its industrial application in the treatment of cyanidation effluents.

This paper summarizes the research work developed at CINVESTAV between 1996 and 2001 to study the use of ozone to treat cyanidation effluents. Results are presented on the stoichiometry of free cyanide oxidation and copper cyanide complexes. The effects of pH, of temperature and of ozone addition rate on the cyanide oxidation rate are also presented. © 2003 SDU. All rights reserved.

Keywords: Cyanidation; Cyanide oxidation; Thiocyanate; Ozone

1. INTRODUCTION

The effluents of the cyanidation process for gold and silver extraction contain not only free cyanide but also soluble cyanide complexes of different metals, which do not possess the same stability and therefore their toxicity and treatment method in each of the cases are not the same. There are also different substances in the effluent that can affect both the efficiency and the treatment cost (ammonia, thiosulfate, thiocyanate, etc.). On the top of this, the difficulty of analysis of cyanides makes the treatment of cyanidation effluents a very complex process.

The main methods used by the gold milling industry to destroy residual cyanide include: natural degradation, alkaline chlorination, oxidation with air/SO₂ (Inco Process), hydrogen peroxide (Degussa Process), and biodegradation. With these methods it is possible to produce a cyanide free effluent, but frequently the following problems appear: a very expensive treatment caused by the high consumption of reagents or a too long time of treatment.

The possibility of oxidizing cyanide with ozone is being studied at CINVESTAV, Mexico, since 1996. Ozone gas is one of the most powerful oxidizers available. Although ozone can only be produced at a maximum concentration of 10% weight, it is a promising chemical reagent to treat cyanide effluents because it presents many advantages: no need of transportation, storage and handling of chemicals, a very rapid and complete decomposition of cyanides, low maintenance, low labor requirements and simple operation, among others.

The possibility of cyanide oxidation by ozone in synthetic solutions was first studied in 1959 (Khandelwal *et al.*, 1959; Selm, 1959; Zeevalkink *et al.*, 1980; Gurol *et al.*, 1984). In industrial basis, ozone has been used with good results in spent developing baths (Garrison *et al.*, 1973) and in electroplating effluents (Bollyky, 1973; Streebin *et al.*, 1980). In cyanidation effluents, two researchers have published promising results (Mathieu, 1977; Rowley and Otto, 1980), but they do not conclude definitively the convenience of using ozone due to the lack of information, basically on the effect of impurities and of pH on the cyanide oxidation rate and on the stoichiometry of the reaction. These authors nevertheless coincide in affirming that ozone would present advantages with respect to the current methods, namely a faster oxidation rate.

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From 1980 to 1990, no attempts were made on the use of ozone in mining effluents. In 1990-1995, research on this topic was conducted at Laval University (Quebec, Canada), and a patent was issued on the cyanide recovery from cyanidation effluents using the ozone (Jara *et al.*, 1996). In Mexico, at CINVESTAV, some research work has been done with the aim of knowing the effect that some parameters have on the cyanide oxidation rate. This paper summarizes the results obtained.

2. MATERIALS AND METHODS

Tests were performed with synthetic solutions prepared with distilled water and sodium or potassium cyanide (Aldrich, 99.9%), and adjusting the pH with sulfuric acid and NaOH solutions. Five series of tests were made in order to understand the stoichiometry of the reaction, and the effect of the ozone addition rate, the pH, the temperature and the copper presence on the cyanide oxidation rate.

The experiments were conducted in batch mode by filling the column with the synthetic cyanide solution and then bubbling the oxygen/ozone mixture for a given period of time. The solution was continuously circulated counter-currently to the gas, at a flow rate of 1.4L/min by means of a peristaltic pump. A sampling port located at the bottom of the column permitted to sample the solution for chemical analysis.

The experimental setup consisted of a conventional bubble column (0.057m diameter and 2m height) equipped with a stainless steel gas sparger (2 μ m pore size, 0.015m diameter and 0.025m height) located at the bottom of the column. A sampling port is also provided at the bottom of the column, where pH (Ag/AgCl electrode), ORP (gold disc vs. Ag/AgCl) and dissolved ozone (ATI A15/64 monitor) are measured. Solution was circulated through the column, counter-currently to the gas bubbles by means of a peristaltic pump.

Ozone was produced from oxygen with a Pacific Ozone Technology generator (L22), with a maximum capacity of 0.4g O₃/min, was analyzed in the exhaust gas exit with a BMT ozone gas monitor (963) and completely eliminated with an ozone destruction unit (Pacific Ozone Technology D412).

On-line monitoring was performed for solution pH, ORP, dissolved ozone and ozone gas concentration by using a data acquisition board (Keithley D-1601). Cyanide was analyzed both by titration with silver nitrate (Standard Methods 4500-CN-D) and with the help of a cyanide-specific electrode (Standard Methods 4500-CN-F). Metals were analyzed by atomic absorption; thiocyanate was analyzed with the colorimetric technique (Standard Methods 4500-CN-M) and cyanate was determined with the help of an ammonia electrode (Standard Methods 4500-CN-L) (American Public Health Association *et al.*, 1989). Figure 1 shows a diagram of the experimental setup used.

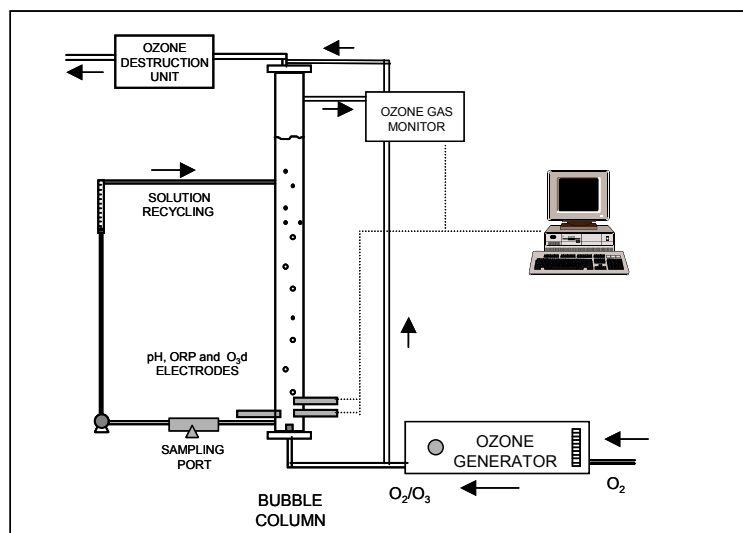


Figure 1. Experimental setup for cyanide oxidation with ozone

3. RESULTS AND DISCUSSION

Different tests were performed in order to establish both the stoichiometry of the cyanide oxidation with ozone, and the effect of pH, temperature and ozone addition rate on the cyanide oxidation rate.

3.1. Stoichiometry of cyanide-ozone reaction

Experiments to determine the stoichiometry of the reaction were carried out with synthetic solutions at alkaline pH (10.5 ± 0.5). The results obtained in a typical test are shown in Figure 2. In this test, 1.5 liters of 240mg CN/l solution were oxidized with 5.19L/min of oxygen containing 10.5g O₃/Nm³ (ozone addition rate 0.04g O₃/min). The test lasted for 20 minutes and the profiles of pH, redox potential (ORP), dissolved ozone (O_{3d}), ozone gas (O_{3g}) and free cyanide are presented in Figure 2.

As shown in the figure, cyanide is completely oxidized by ozone at a constant rate. As long as cyanide is present in solution, pH, ORP, O_{3d} and O_{3g} values remain constant. When cyanide is completely eliminated, the redox potential of the solution, which was negative (reducing), displays a sudden increase, reaching values up to 1000mV, when the time of ozone addition is extended. At the same time, the ozone in gas phase suffers a sudden increase when cyanide is exhausted. During the test, dissolved ozone was not detected in solution. If the ozone addition is maintained longer, it is possible to detect dissolved ozone after the complete oxidation of cyanide has been achieved. The pH of the solution remained constant until the complete oxidation of the cyanide, and after that, it slightly diminishes.

Considering that as long as cyanide is present in solution, no ozone is detected neither in the gas phase nor in the aqueous solution, it may be assumed that all the amount of ozone added is consumed by cyanide oxidation. By computing, the amount of oxidized cyanide and the added ozone, we find an stoichiometric ratio of one mole of cyanide oxidized by one mole of ozone to produce one mole of cyanate, according to Equation (1). Calculations for all tests corroborate this conclusion. If the ozone addition is maintained, cyanate is in turn oxidized according to Equation (2). Table 1 presents results for test in Figure 2.

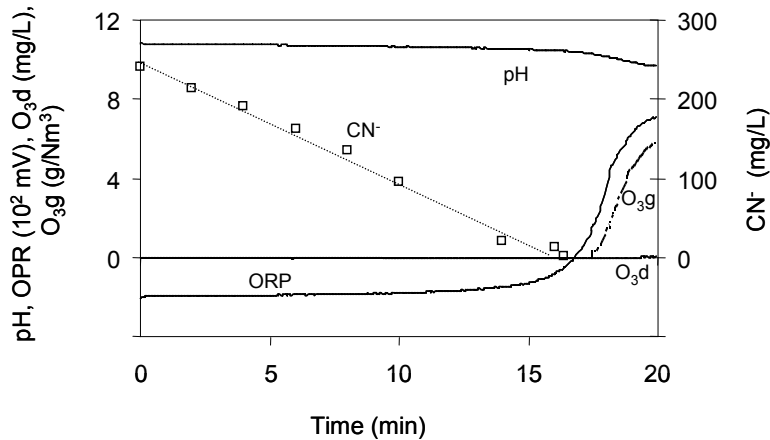


Figure 2. Ozone oxidation of 1.5L of cyanide solution ($T = 25.4^\circ\text{C}$, $\text{pH} = 10.7$, 240mg/l (CN^-), gas flow rate = 5.19L/min oxygen with $0.04\text{g O}_3/\text{min}$)

The linear relationship obtained between $[\text{CN}^-]$ and time for all the cases suggests a reaction of zero order with respect to cyanide, that is to say, that the reaction rate does not depend on the quantity of cyanide present in solution, and it also suggests that the oxidation rate of cyanide is proportional to the quantity of ozone added.

Table 1
 Ozone consumption and cyanide oxidation for Test 39-J

| Time (s) | CN ⁻ (mg/l) | CN ⁻ tot. (mol) | CN ⁻ oxidized (mol) | O ₃ added (g) | O ₃ consumption (mol) | mol O ₃ /mol CN ⁻ |
|----------|------------------------|----------------------------|--------------------------------|--------------------------|----------------------------------|---|
| 0 | 240 | 0.0138 | 0 | 0 | 0 | - |
| 120 | 213 | 0.0122 | 0.001557 | 0.08778 | 0.001827 | 1.17 |
| 240 | 191 | 0.0110 | 0.002826 | 0.1755 | 0.003657 | 1.29 |
| 360 | 162 | 0.00934 | 0.0045 | 0.2633 | 0.005486 | 1.21 |
| 480 | 136 | 0.00784 | 0.006 | 0.3511 | 0.007315 | 1.21 |
| 600 | 95.5 | 0.00550 | 0.00833 | 0.4389 | 0.009143 | 1.09 |
| 840 | 20.7 | 0.00119 | 0.01265 | 0.6144 | 0.012801 | 1.01 |
| 960 | 11.9 | 0.00068 | 0.01315 | 0.7022 | 0.01463 | 1.11 |
| 980 | 1.4 | 0.00008 | 0.0137 | 0.7168 | 0.01493 | 1.08 |

3.2. Effect of the ozone addition rate

A series of tests was performed in order to verify the effect of the initial concentration of cyanide and of the ozone addition rate on the oxidation rate of cyanide. Table 2 shows the experimental conditions for these tests.

Table 2
 Experimental conditions for tests performed to evaluate the effect of the initial cyanide concentration and ozone addition rate

| Test | CN ⁻ ini. (mg/l) | Gas flow rate (l/min) | O ₃ in gas (%) | O ₃ addition (g O ₃ /min) | Temp. (°C) |
|---------|--------------------------------|--------------------------|------------------------------|--|---------------|
| CIAN6-R | 300 | 4 | 2.49 | 0.11 | 27 |
| C20-R | 500 | 4 | 2.49 | 0.11 | 27 |
| CIAN3-R | 300 | 3 | 2.56 | 0.085 | 27 |
| C4-R | 750 | 3 | 2.49 | 0.082 | 27 |

Figure 3 presents the free cyanide profiles for these tests. It may be observed in this figure that, if the ozone addition rate remains constant, the initial concentration of cyanide does not affect the cyanide oxidation rate; it only affects the time needed to oxidize cyanide completely. The cyanide oxidation rate can be described by an equation of zero order with respect to cyanide (cyanide oxidation rate does not depend on the initial cyanide concentration), and it is possible to estimate the apparent rate constant from the slope of the cyanide profile. Rate constant data for different conditions are reported elsewhere (Carrillo-Pedroza, 2000). It is also possible to observe, in Figure 3, that a greater ozone addition rate results in a shorter treatment time. It is necessary to mention that the ozone addition rate is affected by both ozone concentration in the gas phase and gas flow rate. The ozone concentration in the gas depends on the operating parameters of the ozone generator: current intensity, gas flow rate and type of gas used for ozone production.

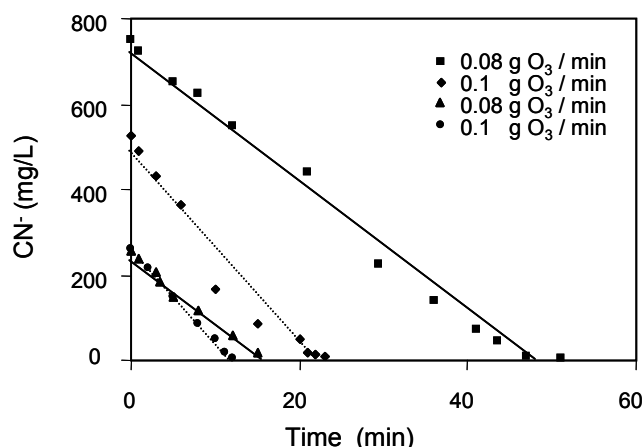


Figure 3. Effect of the initial concentration of cyanide and ozone addition rate on cyanide oxidation rate (Tests C4-R, C20-R, CIAN3-R y CIAN6-R)

3.3. Effect of pH

In order to study the effect of pH on cyanide oxidation rate, several cyanide ozonation tests were conducted at different solution pH. The ozonation conditions were kept constant (gas flow rate = 1.5L/min, ozone addition rate = 0.1g O₃/min, initial cyanide concentration = 500mg/l). Figure 4 shows the cyanide profiles obtained in these tests. In these results, it may be observed that only in the case of alkaline solutions (pH > 9) cyanide can be completely destroyed. If the pH is alkaline (9 - 11.7), the cyanide oxidation rate is similar; nevertheless, as the value of pH becomes more acid, the oxidation rate diminishes, becoming negligible for pH values of 2. This behavior suggests that the hydrocyanic acid formed by cyanide hydrolysis at pH values below 9 is not oxidized by ozone.

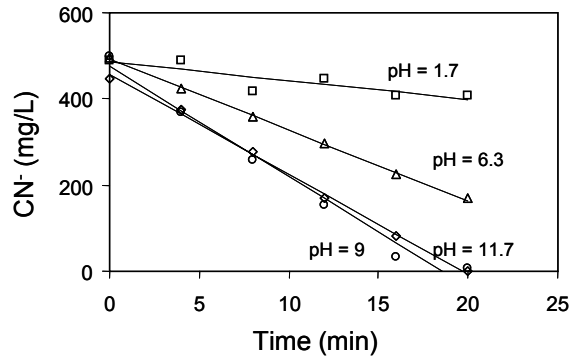


Figure 4. Effect of initial pH of solution on cyanide oxidation with ozone

3.4. Effect of temperature

Due to the fact that cyanidation effluents are exposed to different climatic conditions, in some cases involving extreme weather variations, it is important to consider the effect that temperature may have on the kinetics of the cyanide oxidation with ozone. Three tests were carried out at 15, 25 and 40°C for the same operating conditions: volume of solution = 2 liters, gas flow rate = 1.3L/min, ozone production = 98.4g O₃/Nm³, pH = 11.7 and ozone addition rate = 0.1g O₃/min. Figure 5 presents the cyanide profiles for these tests. It may be observed that cyanide oxidation rate is similar for all the temperatures. To this respect, it is well known that temperature enhances the kinetics of the reaction; however, the ozone solubility decreases by increasing the temperature, and the global effect is negligible. It is important to say that, in the case of the cyanide oxidation by ozone, the process is limited by the amount of ozone that can be introduced to the system (a maximum of 10%w, depending on the generator characteristics). For this reason, the beneficial effect of the temperature on the kinetics of the reaction cannot be appreciated in these cases.

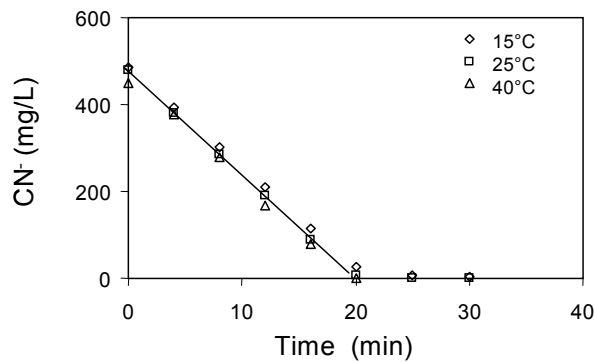


Figure 5. Effect of temperature on cyanide oxidation with ozone

3.5. Effect of the presence of copper and thiocyanate

Cyanide consumption is one of the most important factors that contribute to the total operating cost of a cyanidation plant. The theoretical stoichiometry indicates that to dissolve the gold contained in a typical ore, only 3 to 4 grams of cyanide per ton of mineral should be consumed; nevertheless, typical cyanide consumption ranges from 300 to 2000g/t. It is worth mentioning that the largest loss of cyanide occurs through the formation of thiocyanate and cyanide complexes with copper. Of particular importance is the presence of copper in solution, which may completely modify the chemical behavior of cyanide.

It has been reported that the presence of copper catalyzes the cyanide oxidation (Gurol *et al.*, 1984), diminishing the ozone consumption and the time of reaction. In order to corroborate this finding, a series of tests were performed by oxidizing a 300mg/l cyanide solution with different copper concentrations.

3.5.1. Copper effect

All tests conducted made at the same experimental conditions (gas flow rate = 3L/min, ozone concentration in the gas = 3%, ozone addition rate = 0.1g O₃/min and pH = 11). Copper was added as

cupric sulfate. Figure 6 shows the cyanide profiles obtained in these tests. It is important to mention that in this figure the cyanide analysis reported is total cyanide. Free cyanide analysis would not give a real idea of the oxidation rate of cyanide since copper in solution forms complexes with cyanide and diminishes the free cyanide content. Total cyanide was computed by solving the thermodynamical equilibrium balances of all cyanide-copper species presented in the system and taking into consideration the chemical analysis of free cyanide and copper in solution (Lara-Banda, 1999).

As shown in Figure 6, concentrations of copper below than 80mg/l do not affect the oxidation rate of cyanide, a behavior similar to that obtained when no copper is present. If the copper concentration increases, the cyanide oxidation rate increases as well. The copper presence in cyanide solutions causes the formation of the copper complex $Cu(CN)_4^{3-}$. From mass balance it can be determined that ozone consumption to oxidize the copper-cyanide complexes diminishes as the copper content in solution increases, to a certain level: around 0.63g O_3 per gram of total cyanide.

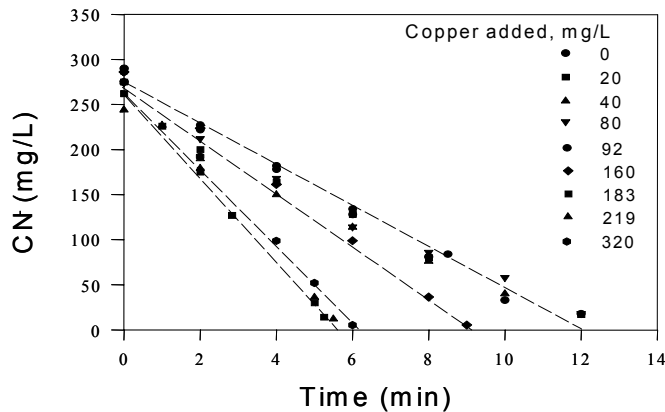


Figure 6. Effect of copper concentration on cyanide oxidation with ozone

3.5.2. Effect of thiocyanate

Thiocyanate (SCN^-) is formed by the chemical reaction of cyanide ions with sulfur species liberated from the ore. Its concentration fluctuates normally between 100 and 400mg/l but sometimes it may reach up to 1500m/l in barren bleeds from Merrill-Crowe operations.

The thiocyanate oxidation with ozone was studied in acid and alkaline solutions at room temperature. Figure 7a shows an example of the oxidation of an alkaline solution containing 460mg/l of thiocyanate. Initially there is no cyanide in the solution. As ozone is fed, thiocyanate disappears forming cyanide, which in turn is oxidized by ozone. During the test, as long as thiocyanate is present in the solution, the redox potential remains constant and dissolved ozone is not detected. Both redox potential and dissolved ozone increase when cyanide oxidation is completed. The ozone consumption for the complete oxidation of thiocyanate is 1.5g O_3 /g SCN^- (2 moles O_3 /mol SCN^-), indicating that one mole of ozone is consumed in the thiocyanate oxidation and one mole is consumed in the cyanide oxidation (Eq. (1)) according to the global reaction:

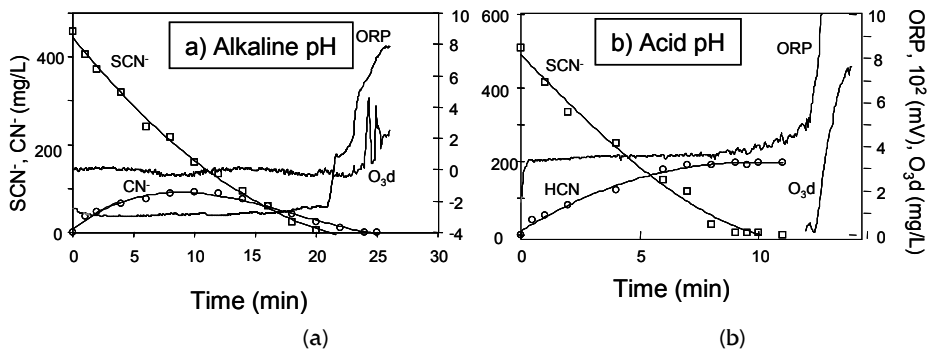
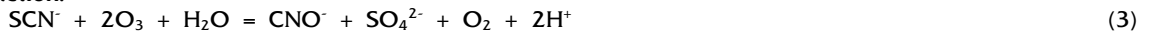


Figure 7. Oxidation of thiocyanate with ozone at different pH values, a) initial pH = 10.5, final pH = 9.1, b) initial pH = 7.2, final pH = 2.6

If the solution is acid, as in the example presented in Figure 7b, the cyanide formed is not oxidized by ozone and remains in solution. This is because, in acid solutions, the cyanide is in the form of hydrocyanic acid which is not oxidized by ozone (as already demonstrated). According to the above, it would be possible to propose a method of recovering the cyanide lost in form of thiocyanate. This process would consist in an acid oxidation of thiocyanate by ozone and a further addition of an alkali in order to convert HCN into CN⁻. That process would be convenient for those effluents in which up to 50% of the cyanide added to the process is lost due to thiocyanate formation (Byerley and Enns, 1984).

4. CONCLUSIONS

Ozonation arises as an interesting option in the treatment of cyanidation effluents. Depending on the composition of the solution, it could be used both to destroy cyanide in order to comply with the environmental regulations and to transform the thiocyanate into cyanide for recycling purposes. Further research work at bigger scale is needed in order to have the data to make a comparative economical study of this proposed method and those currently used (Degussa process and Inco Process).

The principal facts established in this work are:

- In alkaline solutions, cyanide is easily and completely oxidized by ozone at room temperature. The reaction is of zero order with respect to cyanide (regardless of the initial amount of cyanide) and suggests a stoichiometry of one mole of cyanide oxidized by one mole of ozone to produce one mole of cyanate.
- In ozone oxidation of synthetic cyanide solutions, the slope change in the redox potential profile during the test can be used as indicative of the moment at which cyanide has been completely oxidized. This measurement is faster and simpler than any method of cyanide chemical analysis.
- If the solution pH is not very alkaline (pH < 9), cyanide will not be completely oxidized by ozone. When the pH of the solution is below 9, cyanide hydrolyses to hydrocyanic acid, which is not oxidized by ozone.
- The initial cyanide concentration in the solution does not affect the cyanide oxidation rate; it only affects the treatment time. The oxidation rate of cyanide will be proportional to the amount of ozone added, which depends on both gas flow rate and ozone concentration in the gas.
- For the solutions tested, temperature does not have a significant effect on the oxidation rate of cyanide. in the range of 15 – 40°C.
- When copper is present in solution (> 80mg/l), the ozone consumption for cyanide oxidation and the treatment time diminish.
- Thiocyanate is oxidized by ozone in the pH range from 2 to 12 producing cyanide as intermediary product. If the solution pH is alkaline, the cyanide formed is in turn oxidized. If the pH of the solution is acid, the cyanide formed remains in solution in the form of hydrocyanic acid (HCN), which is not oxidized by ozone.

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