Whole Effluent Toxicity Reduction by Ozone

Brandon R. Ball, Kevin V. Brix, Mary Sue Brancato, Mick P. Allison, Shaundelle M. Vail

Parametrix, Inc., 1231 Fryar Avenue, Sumner, WA 98390

An investigation of the effects of ozone and ozone-induced hydroxyl radical on reducing whole effluent toxicity is discussed relative to the application of ozone for industrial water treatment. Results from operation of an ozone system treating industrial effluent from a lead/zinc mine in Colorado are presented. The mine discharges 1,000 gpm (227 m^3/hr) of wastewater and has historically exceeded Whole Effluent Toxicity (WET) limits. On occasion, it has exceeded numeric limits for copper, ammonia, and cyanide.

Based on test results, an applied ozone to COD ratio of 3:1 by weight and a contact time of 30 minutes was found to be effective for reducing whole effluent toxicity at pH 11 but not at pH 7, indicating oxidation by hydroxyl radical to be the dominant mechanism responsible for toxicity reduction. At an applied ozone to COD ratio of 3:1 and a pH of 11, toxicity was reduced with survival increasing improved from 0 percent survival to 100 percent survival for Ceriodaphnia dubia *and fathead minnow* (Pimephales promelas) *based on 48-hour and 96-hour WET tests, respectively. This application rate of ozone with a 99 percent mass transfer efficiency was also effective in reducing total cyanide from an average of 0.45 mg/L to less than 0.05 mg/L and COD from 28 mg/L to 9 mg/L. The rate of ammonium nitrogen oxidation appeared to follow first-order kinetics; however, the rate of oxidation was decreased significantly by the presence of COD.*

INTRODUCTION

The reactions of ozone (O_3) in wastewater can be divided into two types: direct ozonation reactions and free radical decomposition reactions. In pure aqueous solution, ozone is thought to decompose as follows [1]:

$$O_3 + H_2O \rightarrow HO_3^{\ +} + OH^- \qquad (1)$$

$$HO_3^{\ +} + OH^- \rightarrow 2\,HO_2\cdot \qquad (2)$$

$$O_3 + HO_2^{\cdot} \rightarrow OH\cdot + 2O_2 \qquad (3)$$

$$OH\cdot + HO_2^{\cdot} \rightarrow H_2O + O_2 \qquad (4)$$

The direct reactions of ozone involving molecular O_3 are highly selective and relatively slow compared with reactions involving free hydroxyl radicals ($OH\cdot$). The hydroxyl radical typically reacts a million to a billion times faster than ozone. Hydroxyl radicals have much higher oxidation potential and are also much less selective in their reaction than ozone itself. The free radical produced by decomposition of ozone is considered to be the principal reacting species involved in the destruction of organic toxicants [1, 3, 4].

Advanced oxidation processes (AOPs) involve acceleration of O_3 free radical decomposition, thereby increasing the $OH\cdot$ concentration and promoting oxidation of toxic organics. Several AOPs that work in combination with ozone to promote hydroxyl radical formation include hydrogen peroxide, UV light, and high pH. In addition to accelerating ozone decomposition, high pH ozone (pH 9 and greater) is favorable for ammonia oxidation, cyanide destruction, and precipitation of heavy metals [5].

This paper focuses on using high pH in combination with ozone to remove the compounds of interest as described in the following case study.

CASE STUDY

Background

In November 1994, an ozone treatment system was installed to treat wastewater effluent from an active lead and zinc mine in Colorado. The mine discharges, on average 1,000 gpm (227 m^3/hr) of wastewater into a tributary of the Arkansas River. Ozone was selected for wastewater treatment because of its potential ability to destroy toxic organics, precipitate heavy metals and metal complexes, destroy cyanide, and oxidize ammonia. Thus, potentially all treatment objectives for the site could be satisfied by one simple treatment system. The chemicals of concern and associated numeric discharge requirements are shown in Table 1.

In addition to meeting these numeric standards, the facility is required to meet Whole Effluent Toxicity (WET) test limits. The treatment objective for toxicity is to obtain no statistically significant effects in 100 percent effluent for *Ceriodaphnia dubia* and fathead minnows (*Pimephales promelas*). Based on a Toxicity Identification Evaluation

TABLE 1. Chemicals of Concern and Numeric Standards

Chemical	Effluent Range (mg/L)[1]	Effluent Limit (mg/L)[2]
Ammonia	2–7	4.5
Copper	0.025–0.5	0.05
Cyanide	0.2–0.5	0.1

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[1] Typical effluent range without ozone treatment.
[2] Effluent limit based on 30-day average concentration.

TABLE 2. Mine-Mill Reagents Contributing to Effluent Toxicity

Reagent	LC50 (mg/L)	Estimated Usage (mg/L)	TUs(1)
Sodium Isopropyl Xanthate	0.9	7.1	7.9
Potassium Amyl Xanthate	2.4	2.1	0.88
Sulfhydryl Compounds	15.5	7.5	0.48

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(1)TUs = Toxic Units (the usage rate ÷ the LC50)

(TIE) conducted on the effluent, organic mine-mill reagents were determined to contribute significantly to effluent toxicity. Effluent Toxicity Units (TUs) for the primary reagents of concern are shown in Table 2. A TU value of greater than 1 represents significant toxicity.

In the mill, finely ground ore is concentrated in a froth flotation circuit. Thickener overflow and tailings waste streams containing residual organic reagents and heavy metals are adjusted to pH 10.5 to 11 and discharged to a large settling pond (tailings pond). In the tailings pond, metals are precipitated and settled at high pH. The decant from the pond is routed through sand filters before final discharge.

Description of Treatment System

As shown in Figure 1, the ozone treatment system was installed directly downstream of the existing tailings pond and sand filter, and an additional filter was installed after the ozone system to remove metals oxidized by ozone.

Ozone is generated on-site using pure oxygen stored in a 13,000 gallon (49 m^3) pressurized tank. Each of the two ozone generators (Hankin Ozotec II) is rated at 300 pounds (136 kg) O_3 per day at 4 percent concentration. Filtered wastewater flows by gravity through three stainless steel contactors connected in series. Each contactor has a diameter of 12 feet (3.7 m) and a height of 20 feet (6.1m). Ozone is fed to each contactor through 8-inch (20 cm) stainless steel venturi injectors, and wastewater from the contactors is recirculated through each injector at a rate of 2,000 gpm (454 m^3/hr).

The injection/recirculation contact system provides very high ozone transfer efficiencies, on the order of 99 percent. This compares favorably with other conventional methods of contacting ozone such as mixed tank reactors and fine bubble diffusers, which provide transfer efficiencies on the order of 90 percent [*1*, *2*].

Because the wastewater is weakly buffered, ozonation results in a drop in pH. To maintain pH between 10.5 and 11, sodium hydroxide is automatically added to the contactors. The ozone feed rate may be adjusted manually or automatically based on wastewater flow or ozone off-gas concentrations. Off-gas ozone is routed through an ozone destruction unit prior to atmospheric discharge.

Removal of Toxicity

Figure 2 shows test results for COD and toxicity during ozonation of wastewater at high pH. Ozone was applied at varying doses ranging from 1:1 to 3:1 (mg/L O_3:mg/L initial COD). The initial COD value was 28 mg/L. In this case, because the transfer efficiencies are high (greater than 90 percent), the applied ozone dose is approximately equal to the absorbed ozone dose. As shown in Figure 2, ozone at an applied dose of 84 mg/L (O_3:COD = 3:1), reduced toxicity to meet the treatment objective and reduced COD by greater than 60 percent.

It was found that ozone treatment resulted in a drop in pH from 11 to 9. The observed drop is expected due to consumption of hydroxide ion. Also, it is typical for ozone to form carboxylic acids during the oxidation of organics, leading to pH depression. To control pH at 11, sodium hydroxide solution was added to the contactors.

Effect of pH on Ozone Performance

To observe the effects of pH on ozone treatment, tests were conducted on wastewater at both high pH (11) and

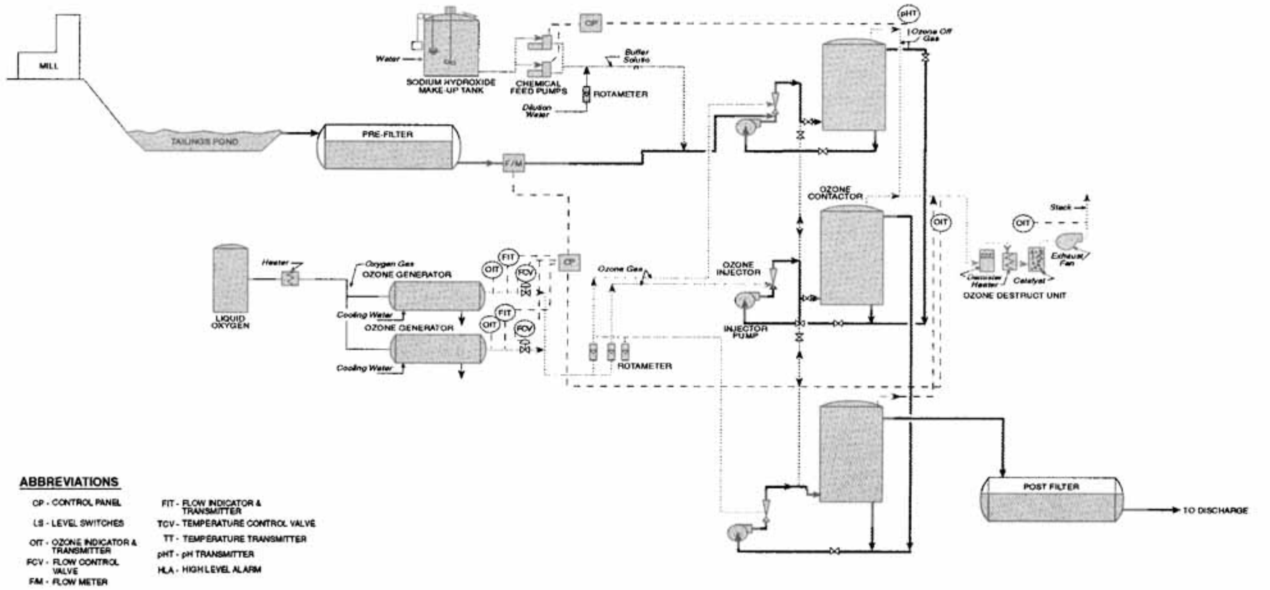

FIGURE 1 Ozone treatment system.

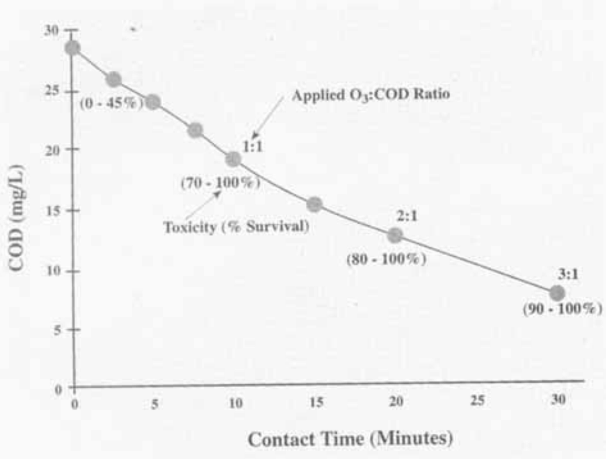

FIGURE 2 Toxicity and COD reduction by ozone at high pH.

neutral pH (7). Both tests involved ozone addition at a 2:1 ratio of O_3 to COD and a long contact time of 100 minutes. Figure 3 shows a direct comparison between treatment performance at high pH versus treatment at neutral pH. As shown, toxicity is completely eliminated by ozone at high pH, but no toxicity reduction is observed at neutral pH. These findings indicate that oxidation by hydroxyl radical is primarily responsible for removal of organic toxicity. Figure 3 also shows that reduction in COD and cyanide is considerably greater at high pH as compared to ozone at neutral pH.

Oxidation of Cyanide

Ozone reacts rapidly with free cyanide ion and many stable metal cyanide complexes [5]. Ozonation of cyanide proceeds rapidly to form cyanate as shown by the following reaction:

$$CN^- + O_3 + H_2O \rightarrow CNO^- + O_2 + H_2O \qquad (5)$$

The oxidative/hydrolytic destruction of cyanate ion proceeds much more slowly upon continued treatment with ozone:

$$CNO^- + OH^- + H_2O \rightarrow CO_3^{-2} + NH_3 \qquad (6)$$

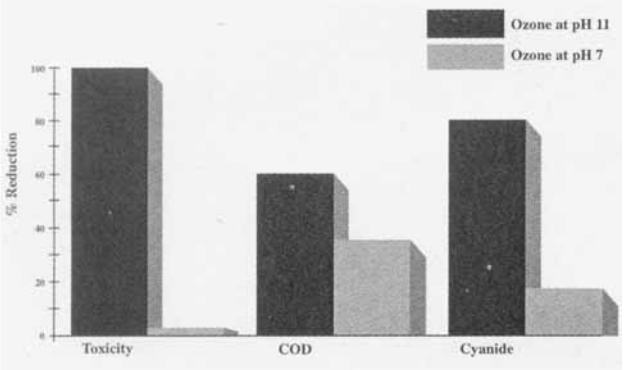

FIGURE 3 Comparison of ozone at high pH vs. low pH.

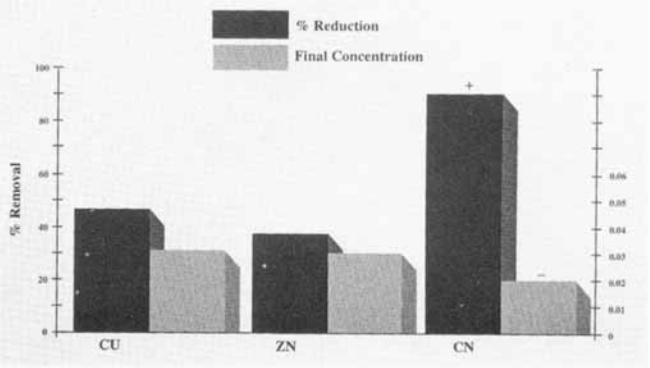

FIGURE 4 Removal of cyanide and heavy metals by ozone.

This study shows that cyanide can be removed to below 0.05 mg/L by an applied ozone dose of 30 mg/L (O_3:COD = 1:1) and a 15-minute contact time. As shown in Figure 4, the percentage reduction in cyanide by ozone is greater than 90 percent. Cyanide removal was only 18 percent at neutral pH, supporting research literature indicating that cyanide reactions are faster at high pH [5].

Reduction of Heavy Metals

All easily oxidized heavy metals can be oxidized by ozone. Specific heavy metals that have been oxidized under wastewater treatment conditions include arsenic, aluminum, lead, nickel, chromium, copper, cobalt, barium, zinc, cadmium, and organic complexes of some of these metals [5]. Netzer and Bowers [6] showed that a large percentage of these metals is removed by lime adjustment to alkaline conditions and that the remaining dissolved metals are precipitated by ozone. Combined treatment with lime followed by ozone resulted in greater than 99.5 percent removal of aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, and zinc [6].

As shown in Figure 1, the treatment system is arranged to provide pre- and post-ozone filtration. The first filter removes precipitated metals and other suspended solids that carry over from the tailings pond. Suspended solids exhibit an appreciable ozone demand, and therefore pre-filtration is necessary to conserve ozone. The second filter in the treatment system is located to remove trace dissolved metals or complexed metals that are oxidized by ozone. Both the pre-filter and post-filter contain the same sand media.

The average removal of copper and zinc by ozone and post-filtration is shown in Figure 4. The results are based on an ozone to COD ratio of 2:1 and a contact time of 100 minutes. Both copper and zinc were removed to near detection limits (0.025 and 0.02 mg/L, respectively) and well below discharge standards. Both metals were already at low levels before treatment, approximately 0.05 mg/L.

Removal of the trace metals may be associated with oxidation or possibly by destruction of metal-cyanide complexes. In either case, ozone is shown to be effective in reducing trace metals remaining after initial high pH precipitation and filtration.

Oxidation of Ammonia

Under the proper conditions, ammonia may be oxidized completely to nitrate by ozone in accordance with the following stoichiometry:

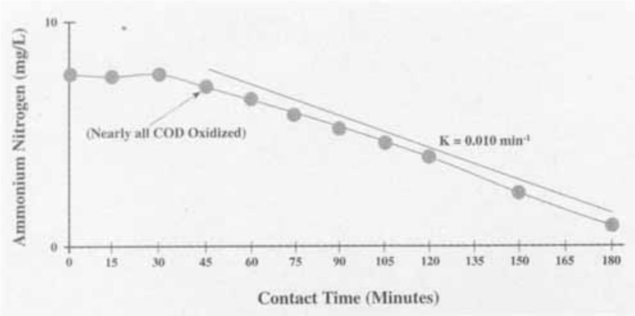

FIGURE 5 Ammonium-nitrogen oxidation.

$$NH_4 + 4O_3 \rightarrow NO_3 + 4O_2 + H_2O + 2H^+ \qquad (7)$$

The oxidation reaction is first order with respect to the concentration of ammonia, and reaction kinetics are greatly accelerated at high pH [7]. For example, the oxidation of ammonia is about 10 to 20 times faster at pH 9 than at pH 7, and the molar ratio of ozone consumed to ammonia oxidized is about 8 times higher at pH 7 than at pH 9 [7]. The fact that ammonia oxidation is faster at high pH indicates that the hydroxyl radical may be driving the reaction.

The ozone contactors were operated in batch mode to evaluate the removal of ammonium nitrogen with respect to time. The contactors were fed with ozone at a continuous rate of 1 mg/L per minute. The results are displayed on a semi-log graph in Figure 5. As shown, the rate of ammonia oxidation accelerates considerably once most of the COD has been removed. In this case, the treatment objective for ammonia of 4.5 mg/L was met at an accumulative ozone dose of 75 mg/L and a contact time of 75 minutes. The rate of oxidation appears to be first order in ammonia, as illustrated by the straight line in Figure 5. The first-order rate constant is calculated to be 0.01 min^{-1}.

SUMMARY

Ozone treatment of high pH wastewater resulted in complete removal of effluent toxicity. Removal of toxicity and COD was considerably higher at pH 11 than at pH 7, indicating that the hydroxyl radical (and not molecular O_3) is chiefly responsible for toxicity removal. Ozone was effective in reducing trace metals remaining after initial high pH precipitation and settling. The removal of ammonia nitrogen appeared to follow first-order kinetics once COD was removed by ozone oxidation.

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