

RECYCLING OF CYANIDE WASTEWATER BY OZONE OXIDATION COMBINED WITH UV RADIATION AND ION EXCHANGE

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Introduction

Ozone decomposes cyanides by oxidation¹⁾.

The process of cyanide oxidation by ozone, unlike that by chlorination, does not produce salts or partial oxides that must be removed, because excess ozone decomposes into oxygen.

Ultraviolet (UV) radiation facilitates the oxidation of cyanides by ozone²⁾. Ion exchange resin adsorbs cyanide ion and can be used to make de-ionized water from wastewater. However, if cyanide ion is contacted by a H-type cation resin and acidified in a cation exchanger vessel, it changes into harmful cyanogen gas, and the efficiency of the ion exchange reaction is reduced.

In this paper we describe the results of experiments

regarding the oxidation of cyanide wastewater by use of ozone oxidation combined with UV radiation and ion exchange.

1. Experimental

Cyanide plating is practiced with copper, zinc, gold and silver. Since copper cyanide plating gives good adherence between plating layer and metal surface, it is introduced into the first stage of almost all plating processes. Copper cyanide plating is thus employed generally as a basic process in many plating plants.

Accordingly, a plating plant usually discharges copper cyanide wastewater.

Wastewater from the copper cyanide plating pro-

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Table 1. Composition of raw and treated water

Processing stage	Sample No.	pH	Electrical conductivity ($\mu\text{S}/\text{cm}$)	CN ⁻ CNO ⁻ Cu ²⁺ COD			
				(10 ⁻³ kg/m ³)			
Raw wastewater	1	9.6	610.9	58.5	0.0	31.3	28.8
	2	9.8	669.0	85.8	0.0	40.8	38.5
	3	9.5	585.6	42.9	0.0	25.9	22.8
	4	9.9	780.8	95.2	0.0	48.8	54.4
	5	9.7	690.2	72.8	0.0	39.7	36.1
Solution oxidized by ozone combined with UV radiation for 0.5 hour	1	7.3	640.2	0.0	88.0	0.2	2.5
	2	7.2	700.5	0.1	130.1	0.2	2.9
	3	7.4	610.2	0.0	64.8	0.1	2.0
	4	7.6	819.5	0.1	148.8	0.4	3.9
	5	7.1	722.1	0.0	108.7	0.3	2.8
Effluent of cation column	1	3.3	650.2	0.0	2.7	0.0	2.3
	2	3.0	715.6	0.0	3.7	0.0	2.6
	3	3.4	620.2	0.0	2.6	0.0	1.9
	4	2.9	831.6	0.0	3.9	0.0	3.5
	5	3.2	737.6	0.0	3.3	0.0	2.5
Effluent of anion column	1	8.2	8.0	0.0	0.0	0.0	0.6
	2	8.3	8.8	0.0	0.0	0.0	0.7
	3	8.1	7.8	0.0	0.0	0.0	0.4
	4	8.4	9.8	0.0	0.0	0.0	0.8
	5	8.1	9.2	0.0	0.0	0.0	0.6

cess generally contains alkaline (NaOH, Na₂CO₃), copper cyanide (CuCN) and COD components (thiourea, surface-active agent) arising from the plating chemicals. For example, the components of raw wastewater are shown in Table 1 (samples No. 1 through No. 5).

Figure 1 shows the arrangement of the experimental apparatus. Cyanide wastewater from tank No. 1 (1 × 10⁻³ m³) is sent by a constant-rate pump (0.4 m³/h) to the oxidation reactor. The reactor (4 × 10⁻³ m³) is equipped with a 40 w low-pressure mercury-vapor lamp that emits UV rays (253.7 nm and 184.9 nm). Part of the air sent to cool the lamp (at a rate of 0.12 m³/h) turns into ozone due to UV rays of 184.9 nm wavelength. The ozonized air is distributed through the bottom of the reactor to oxidize the cyanide wastewater.

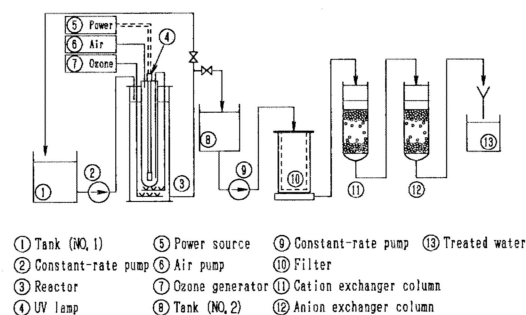
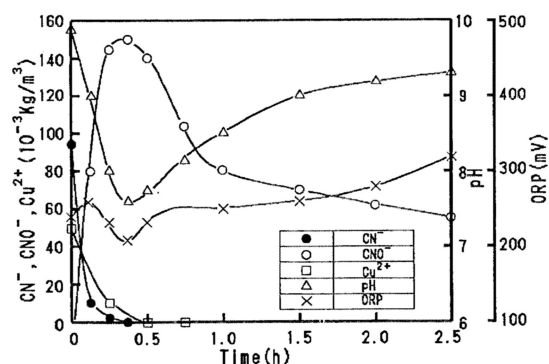
Moreover, ozone from another ozone generator (generated at the rate of 1 × 10⁻³ kg/h) is distributed from the bottom of the reactor at a rate of 0.24 m³/h.

This portable generator produces ozone from the air. It uses the PSA method³⁾ to reduce the by-production of NO_x by letting zeolite adsorb nitrogen in the air so as to bring the oxygen concentration to more than 90 %.

In one experiment, all or a part of the processed water returns to tank No. 1. In another, all the water flows into tank No. 2 (1 × 10⁻³ m³). The processed water from tank No. 2 flows through two kinds of ion-exchanger columns (diameter 25 mm, length 500 mm, volume of resin 0.2 × 10⁻³ m³) at a constant rate of 4 × 10⁻³ m³/h after being filtered through a 3 μm bag-filter to remove metal sludge and other particles.

One of the ion-exchange columns is filled with porous cation resin of the strong-acid type (H-type) and the other is filled with porous anion resin of the strong-alkaline type (OH-type).

The water processed by ozone oxidation is sent

**Fig. 1** Experimental apparatus**Fig. 2** Variation of CN⁻, CNO⁻, Cu²⁺, pH and ORP in ozone oxidation combined with UV radiation

through the cation resin column and then the anion resin column at a rate of 20 × 10⁻³ m³/1 × 10⁻³ m³-resin/h (20 space velocity, SV20 hereafter).

The water is sampled from the drains of the cation and anion resin columns at a constant time interval. The amount of adsorbed components per unit volume of resin (volume of cation resin plus anion resin) is calculated from treated water volume (the water volume of 10⁻³ m³ passed through 1 × 10⁻³ m³ of resin), when the electrical conductivity of the effluent rapidly increases.

Cyanide ion, copper ion, COD, pH, ORP (oxidation reduction potential) and electrical conductivity were measured according to JIS K0101 or JIS K0102. Cyanate ion is analyzed as ammonium ion by the JIS K0102 indophenol-blue method after hydrolysis of cyanate ion into ammonium ion by sulfuric acid⁴⁾.

2. Results and Discussion

Figure 2 shows the result of experiments regarding raw wastewater No. 4 in Table 1.

The raw wastewater was oxidized by ozone combined with UV radiation for 2.5 hours while it was circulated at a rate of 0.4 m³/h from tank No. 1 through the pump and the oxidation reactor to return to tank No. 1.

Treated water was sampled at a constant time interval and measured after being filtered through No. 5C filter paper.

The concentration of cyanate ion began to rise along with the decrease in cyanide ion, copper ion and pH value. After 15 minutes, blue metal sludge emerged

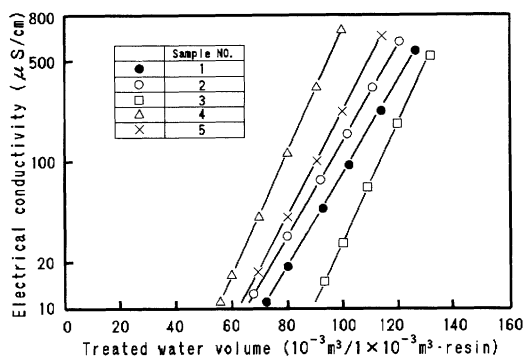
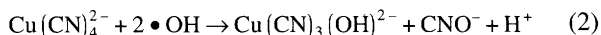
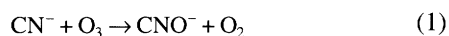


Fig. 3 Electrical conductivity of effluent from anion column passing through cation column

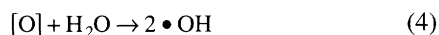
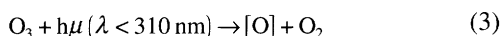
from the processed water.

One-half hour later, cyanide ion and copper ion decreased to an undetectable level.

This is due to cyanate ion produced by the oxidation of cyanide ion by Eqs. (1) and (2).



The reaction was twice as fast as oxidation by ozone alone. This is supposedly due to the hydroxy radical ($\bullet\text{OH}$) generated by the 253.7-nm UV rays and ozone in the water. (184.9-nm UV rays convert oxygen into ozone.)



After 0.5 hour, the concentration of cyanate ion gradually decreased, raising the pH and ORP values. These changes are supposed to be due to the decomposition of cyanate ion as in Eq. (5), which is a slower process than the oxidation of cyanide ion by Eqs. (1) and (2).



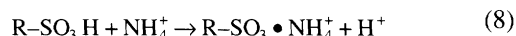
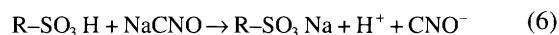
This experiment suggests that the decomposition of cyanides into hydrogen carbonate ion and nitrogen through cyanic acid is still incomplete after more than 2.5 hours.

Since lengthy ozone oxidation with UV radiation is not a practical method, supposedly to give oxidation damage to ion exchange resin we chose brief oxidation times up to 0.5 hour (till cyanide ion is oxidized into cyanate ion).

We also adopted highly cross-linked ion exchange that which can withstand oxidation damage.

We tried to remove cyanate ion by passing the oxidized solution through a cascade of cation and anion exchange resin columns. Table 1 shows the analyses of samples No. 1 through No. 5 as raw wastewater, solution oxidized by ozone combined with UV radiation for 0.5 hour, and initial effluents from cation and anion exchange columns. The cyanate ion at the outlet of the cation column is reduced to less than $5.0 \times 10^{-3} \text{ kg/m}^3$.

This is thought to occur due to the following processes in the cation column. First, neutral sodium cyanate was acidified in the cation column by the H-type cation resin and changed into cyanate ion. Next, the cyanate ion is changed into CO_2 and NH_4^+ by hydrolysis. Ammonium ion was then adsorbed by the cation exchange resin as described by Eq. (6) through (8).



The electrical conductivity of the effluent from the anion exchanger column was less than $10 \mu\text{S/cm}$. No cyanides, cyanate ion or copper ion were detected.

COD was less than $1 \times 10^{-3} \text{ kg/m}^3$. This is due to oxidation of the COD components, such as thiourea, surface-active agents as additive chemicals, or oxidation of cyanide into cyanic acid.

Figure 3 shows the relation between the electrical conductivity of the effluent from the anion exchanger column (after passing through the cation column) and the treated water volume of the samples No. 1 through No. 5 after processing by ozone oxidation with UV radiation for 0.5 hour.

The electrical conductivity began to increase to the level of that of treated water volume between 55 and 90.

Conclusions

Ozone oxidation of cyanide wastewater combined with UV radiation can process cyanide ion into cyanate ion in a short time without addition of chemicals. Moreover, by passing the oxidized wastewater through cation and anion exchanger columns, we can obtain high-purity de-ionized water that can be reused as rinsing water in plating processes.

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