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Laboratory Studies of Methods for the Treatment and Disposal of the Waste Stream from the Silver-Recovery Facility at Oak Ridge National Laboratory

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Chemical Technology Division

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LABORATORY STUDIES OF METHODS FOR THE TREATMENT AND DISPOSAL OF THE WASTE STREAM FROM THE SILVER-RECOVERY FACILITY AT OAK RIDGE NATIONAL LABORATORY

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ABSTRACT

Studies have shown that the waste stream, resulting from the process used to recover silver from spent photographic solutions at the Department of Energy's Oak Ridge National Laboratory (ORNL) and Y-12 Plant facilities can be disposed of via ORNL's sewage treatment plant. The results of laboratory studies of alternative treatment methods are discussed.

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1. INTRODUCTION

A process has been developed at ORNL for recovering silver from spent photographic solutions.[1] This process involves chemical precipitation of the silver using NaOH and sodium hydrosulfite as a reductant.

The waste stream generated from the silver-recovery process is essentially free of silver but contains ~15 g/L sodium hydrosulfite, a variety of undetermined organics (~100 mg/L), and other inorganic components. It is highly toxic, based on 48-h biotoxicity tests with fathead minnow larvae (*Pimepheles promelus*). The components responsible for this toxicity have not been determined. In addition to the toxicity, the direct discharge of the waste would place a high oxygen demand on any receiving stream. For example, a fish kill occurred when a portion of the waste was discharged to White Oak Creek. It is believed that this was the result of a reduction in dissolved oxygen, which was caused primarily by the sodium hydrosulfite. Therefore, the waste stream must be treated before discharge to the environment.

Several options for treating the waste were investigated. The options are:

1. removal of the organics by adsorption on granular activated carbon,
2. biodegradation of the organics by microbial action in the ORNL sewage treatment plant (STP),

3. enhanced removal of the oxygen demand by oxidation (aeration) by the addition of chemicals, and
4. oxidation of the organics using ultraviolet (UV) light and hydrogen peroxide.

The results of these investigations and current plans for the treatment and disposal of the photographic waste are presented in this report.

2. EQUIPMENT AND METHODS

2.1 PHOTOGRAPHIC WASTE SOLUTION

Initially, ~19 L of spent photographic waste solution was obtained from the ORNL silver-recovery facility. This particular batch of solution, which had been processed several months previously, adjusted to pH 7, and then stored in a tank, was used for the carbon adsorption column studies and for the initial bioreactor treatment studies. It was suspected, and subsequently confirmed, that the oxygen demand of this particular batch of waste was diminished because of exposure to air during long-term storage.

A fresh batch of photographic waste was processed in the silver-recovery facility in early November 1986, and a total of ~10 gal was obtained for use in the remainder of these studies. The waste solution was stored in sealed polypropylene jars at ambient temperature in total darkness to prevent deterioration by light. The pH of the new solution was 12.3. As needed, portions were adjusted to pH 7 with concentrated sulfuric acid.

2.2 ANALYTICAL PROCEDURES

Total organic carbon assays and chromatographic studies for toxic organic compounds were carried out in ORNL's Analytical Chemistry Division. Forty-eight-hour acute biotoxicity tests using fathead minnow larvae (*Pimephales promela*) were performed at the Aquatic Toxicology Laboratory, Environmental Sciences Division, ORNL.

Dissolved oxygen (DO) measurements were made with a YSI oxygen probe (Model 5739, Yellow Springs Instruments Company, Yellow Springs, OH).

2.3 CARBON ADSORPTION COLUMNS

Activated carbon was tested to remove the organic compounds in the photowaste by adsorption using neutralized (pH 7), undiluted photographic waste. The waste was passed once through a prefilter (upflow) and then through an activated carbon adsorption unit (downflow). The carbon adsorption unit consisted of a peristaltic pump, a glass wool prefilter, and three 2.54-cm-diam x 61-cm-long glass columns connected in series by 0.64-cm plastic tubing. Each column contained approximately 235 cm^3 of prewetted Calgon Filtrasorb 300 (Calgon Corp.) granular activated carbon. Sample ports were located at the entrance to each column to determine intermediate levels of organic adsorption.

The flow rate was 25 mL/min, providing a residence time of ~3 min/column. Samples were taken hourly from the port at the entrance to each column for total organic carbon (TOC) and toxic organic assays.

2.4 ULTRAVIOLET LIGHT/HYDROGEN PEROXIDE APPARATUS

A UV light apparatus designed for flow-through sterilization of liquids was used to determine whether a combination of UV light and hydrogen peroxide (H_2O_2) would decrease the oxygen demand of the photographic waste and/or reduce the toxicity by oxidizing and degrading the organic components. The apparatus consisted of a 2.54-cm-diam x 27.3-cm-long quartz tube, which was illuminated along its entire length by a high-intensity UV light (Aquafine UV water sterilizer, Cole-Palmer Instrument Co., Chicago, IL). A peristaltic pump was used to circulate the photographic waste between a mixing vessel and the UV unit.

Two separate experiments were run. One experiment consisted of passing 3500 mL of a solution of photographic waste [adjusted to pH 7 with concentrated sulfuric acid (H_2SO_4)] containing 1% w/v H_2O_2 through the UV light apparatus once at a flow rate of 50 mL/min. The dissolved oxygen content of the collected effluent was then measured.

In the second experiment, 1 L of a H_2O_2-supplemented (1%) photographic waste (pH adjusted to 7) solution was recirculated (50 mL/min) between a reservoir and the UV light apparatus. After 1.5 h of recirculation, the pump was stopped and air was bubbled through the

treated waste solution. After 10 min, 1 h 10 min, 1.5 h, 2.5 h, and 3.5 h, the airflow was temporarily stopped and DO readings were recorded for 10 min. A portion of the solution treated for 3.5 h was submitted for a 48-h acute biotoxicity test.

The addition of H_2O_2 to the photowaste resulted in a violent exothermic reaction, and it was necessary to allow the solution to cool before circulating it through the UV light apparatus so as not to break the quartz tube. It had been previously determined (J. M. Begovich, ORNL, Chemical Technology Division, personal communication) that the H_2O_2 was reacting primarily with the organic constituents in the waste and not with the sodium hydrosulfite or other possible inorganic components (i.e., thiosulfates or sulfites).

2.5 CHEMICAL OXIDATION EQUIPMENT

A series of experiments was conducted to determine the capability of several metal ions for enhancing the reduction of the oxygen demand of photographic waste during aeration. The procedure consisted of aerating 200 mL of photographic waste solution containing a known amount of a specific metal ion using a gas dispersion tube. The solution was also stirred at a slow speed with a magnetic stirrer. At varying times up to 24 h, the airflow was stopped and the DO level was determined. The initial DO level of the photographic waste was 0.455 mg/L.

The metal ions investigated, Fe^{3+}, Cu^{2+}, Mn^{2+}, and MnO_4^-, were derived from the dissolution of $FeCl_3$, $CuSO_4$, $MnCl_2$, and $KMnO_4$, respectively. Each metal was tested at a concentration of 0.1%; $FeCl_3$ and $KMnO_4$ were also tested at 0.01%.

2.6 ACTIVATED SLUDGE BIOREACTORS

Two 10-L plexiglass activated sludge units (see Fig. 1) were designed, constructed, and operated to simulate ORNL's STP. One unit was used as a control, while the other was used as a test reactor with the feed amended with photographic waste. Each bioreactor had a vertically movable baffle dividing it into two sections: a mixing/aeration chamber and a sludge-settling chamber. Mixing and aeration were provided by the

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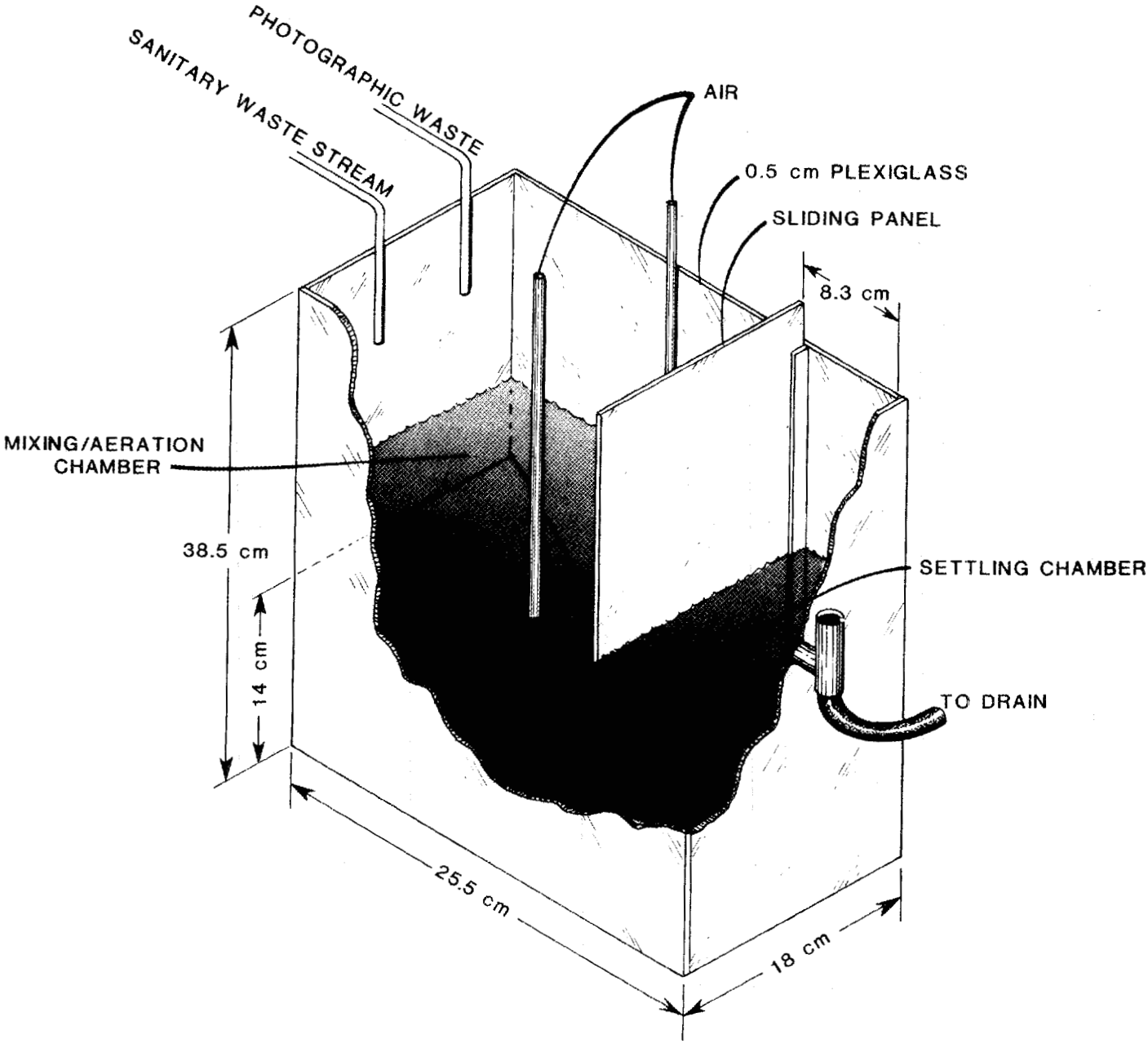

Fig. 1. Activated sludge bioreactor system.

air emanating from two gas dispersion tubes. A constant reactor volume was maintained by discharging the effluent through an overflow port near the top of the sludge-settling chamber. A constant flow of the primary feed (sanitary sewage) was provided to the mixing/aeration chamber of both reactors using a dual-head Masterflex pump (one head/unit; Cole-Palmer Instrument Co. Chicago, IL). The photographic waste solution was introduced to the mixing/aeration chamber of the test unit using a separate single-head pump.

The two activated sludge test reactors were operated in the basement of the STP facility (Bldg. 2521). The primary feed to each unit was withdrawn from the main sanitary sewage stream just prior to the comminuters. The STP receives the same stream after comminution of the solids.

The feed rate of sewage into the bioreactors, 5.5×10^{-3} L/min, was chosen to provide a loading rate and a residence time (30.3 h) similar to that of the STP. [An average flow of 7.57×10^{5} L/d (200,000 gal/d) of sewage through the STP was assumed.] The initial feed rate of photographic waste to the test unit was based on the projected photographic waste production rate of 2.27×10^{3} L (600 gal) per week from the silver-recovery operation, which would be discharged into the sanitary sewage stream at a constant rate (379 L/d) over a 7-d period. For operational purposes, this was determined to be 0.1 mL/min of a 1:45.5 dilution (in water) of photographic waste, giving an overall dilution of 1:2500 of the photographic waste as it enters the treatment unit.

A reduction in TOC between the influent and effluent streams was used as an indicator of biological activity and, hence, the effectiveness and operational stability of the bioreactors.

Initial startup of each reactor was accomplished by filling it with 10 L of sludge from the STP. This sludge was obtained from the STP approximately three-fourths of the way around the tank from the entry point of the raw sewage. Both reactors were filled to the level of the overflow port. Airflow was started immediately to provide aeration and mixing of the sludge. Influent and effluent TOC samples were taken daily for 4 weeks before the addition of photographic waste was begun. This allowed the reactors time to reach a steady-state operating condition.

After 4 weeks, the addition of photographic waste was begun to the test unit. The control unit received no photographic waste. At times during the operation of the bioreactors, the concentration of photographic waste entering the test unit was intentionally increased to two or four times the original level to determine the effect. These changes were made by altering the dilution of the photographic waste solution being added while leaving the flow rate at 0.1 mL/min, that is, 1X = 0.1 mL/min of 45.5:1 photowaste, 2X = 0.1 mL/min of 23:1 photowaste, and 4X = 0.1 mL/min of 11.5:1 photowaste.

3. RESULTS AND DISCUSSION

3.1 CARBON ADSORPTION STUDIES

The use of activated carbon to remove dissolved organic contaminants is an established waste treatment procedure.[2,3] Although this approach is generally used for wastes containing <1% organics, it has also been applicable to higher concentrations of organics. Carbon treatment is partially effective for inorganic compounds as well.

The original batch of photographic waste was used in these experiments. As noted earlier, the oxygen demand of the waste was partially reduced by natural oxidation as a result of exposure to air. The feed had a dark greenish-brown color. The effluent from the carbon columns was initially a clear yellow; however, after a 4-h period, no color difference was evident between the column influent and effluent.

Samples of the treated waste were submitted for TOC and total toxic organics analyses. Analytical Chemistry Division personnel stated that a chromatographic examination of the photographic waste revealed an extremely complex range of organic compounds at low levels (detection limit, 10 g/L). The analyses were complicated by a precipitate that developed during attempted extractions with methanol. No conclusions could be reached. Also, no TOC results could be obtained because of an apparent difficulty in assaying solutions with this high oxygen demand. The oxidizing capacity of the instrument was insufficient to overcome the high concentration of reductant (sodium hydrosulfite). No biotoxicity samples were submitted.

It was concluded that carbon adsorption would not be an effective means of treating the photographic waste unless extensive pretreatment was carried out. Therefore, this process was not investigated further.

3.2 TREATMENT WITH ULTRAVIOLET LIGHT/HYDROGEN PEROXIDE

The use of oxidants to degrade organic contaminants (and reduce toxicity) in wastewater has been found to be effective.[2,3] Oxidants such as ozone and hydrogen peroxide have been used. Degradation is enhanced in the presence of UV light. The use of ozone was considered to be impractical for treating the photographic waste because of the relatively high costs associated with the process. However, the effectiveness of H_2O_2 combined with UV light was briefly investigated. It also was hoped that the high oxygen demand of the waste could be reduced by this treatment.

A single pass through the UV apparatus did not appreciably decrease the oxygen demand. No biotoxicity tests were conducted.

Recirculation of the H_2O_2-amended photographic waste through the UV light for 1.5 h did not decrease the oxygen demand. However, the oxygen demand was reduced by about 50% when the waste solution in the reservoir was aerated for 3.5 h during the UV/hydrogen peroxide treatment. No reduction in the acute biotoxicity of the treated waste was observed as compared with untreated photographic waste (see Table 1).

3.3 CHEMICAL OXIDATION STUDIES

It had previously been determined that aeration of the photographic waste for an extended period (days) reduced its oxygen demand through oxidation of the sodium hydrosulfite. A series of experiments was conducted to determine whether several metal ions could enhance the oxidation of the dithionite during aeration. As shown in Table 2, 0.1% $FeCl_3$ and 0.1% $KMnO_4$ reduced the time required to oxidize the sodium hydrosulfite to <24 h. However, this level of iron would exceed waste discharge limits (0.3 mg/L). Also, this treatment did not decrease the toxicity of the waste (see Table 1).

Table 1. Acute biotoxicity (48 h) of untreated and treated photographic waste to fathead minnow larvae (*Pimephales promelus*)

Sample	Strength tested (%)	Survival of larvae (48 h)	
		Alive	Dead
Control (dechlorinated tap water)	-	6,6,6	0,0,0
Effluent from bioreactor with photographic waste added at 1X feed rate	100	6,6,6	0,0,0
Effluent from control bioreactor (no photographic waste)	100	6,6,6	0,0,0
Sanitary sewage	100	6,5,6	0,1,0
Neutralized (pH 7) photographic waste	0.01	6,6,6	0,0,0
	0.05	6,6,6	0,0,0
	0.1	6,6,6	0,0,0
	0.5	0,0,0	6,6,6
Photographic waste + 0.1% $FeCl_3$, aerated 24 h	0.01	6,6,6	0,0,0
	0.05	6,6,6	0,0,0
	0.1	6,6,6	0,0,0
	0.5	0,0,0	6,6,6
	1.0	0,0,0	6,6,6
Photographic waste treated with 1% H_2O_2 and UV light	0.01	6,6,6	0,0,0
	0.05	6,6,6	0,0,0
	0.1	0,0,0	6,6,6

Table 2. Enhanced removal of oxygen demand by aeration in the presence of metal ions

Metal ion	Concentration (wt %)	Dissolved oxygen[a] (mg/L)
None	---	1.7
$FeCl_3$	0.1	5.2
$FeCl_3$	0.01	2.7
$MnCl_2$	0.1	1.8
$CuSO_4$	0.1	1.3
$KMnO_4$	0.1	4.8
$KMnO_4$	0.01	2.0

[a]Dissolved oxygen values were taken after 24 h of aeration. Aeration was then stopped, and readings were taken for 10 min.

3.4 ACTIVATED SLUDGE TREATMENT

Photographic waste was introduced to the activated sludge test reactor at a rate equivalent to the constant discharge (379 L/d) of 1 week's production from the silver-recovery facility to the STP. It had no discernible effect on biological activity or effluent quality, based on TOC reduction, when compared with the control reactor. No effect was noted when the waste was added at twice this rate. Uniform sampling of the primary feed stream was difficult because of the varying solids content of the sanitary sewage stream. Representative data are shown in Table 3. It is not known if the organic components in the photographic waste were degraded. The amount of organic carbon added to the feed stream was very low compared with that in the primary sanitary waste stream.

The toxicity of the photographic waste to the biological population in the test reactor at a 4X feed rate (and higher concentrations during physical upsets) was indicated by a change in the physical appearance of the sludge. It became a much lighter gray color. There was also a significant reduction in sludge volume, which occurred in a few (1 to 3) days. TOC results were not used as an indicator of reactor activity during these periods because of the excessive amount of sludge in the effluent. Reactor activity was restored by reducing or stopping the flow of photographic waste.

As shown in Table 1, no acute biotoxicity of the effluent from either the control or the photographic waste-amended (1X) reactors was indicated when tested at full strength. In contrast, untreated photographic waste showed acute toxicity at 0.5% strength. According to A. J. Stewart (ORNL, Environmental Sciences Division, personal communication), the untreated photographic waste would be expected to show chronic toxicity at concentrations less than 0.5%. However, subsequent problems with the STP, which were incidental to the operation of the activated sludge test reactors, have precluded chronic toxicity tests on 1X and 2X feed strength effluents. Appropriate comparisons of the chronic toxicity of the STP effluent with those of the test reactors could not be made.

Table 3. Reduction in total organic carbon in photographic waste-amended wastewater treated in a laboratory-scale activated sludge bioreactor

		Total organic carbon (mg/L)			
		Photographic waste-amended reactor		Control reactor (without) photographic waste)	
Date	Strength	Influent	Effluent	Influent	Effluent
10/9/86	None	42	7	42	8
10/11/86		8	7	8	7
10/13/86		7	4	7	4
10/15/86		40	8	40	9
10/21/86		36	7	36	5
10/23/86		26	6	26	5
10/28/86		15	3	15	3
11/3/86		28	4	28	3
11/4/86		34	5	34	4
11/5/86	1X[a]	22	4	24	3
11/6/86		9	4	7	3
11/7/86		9	4	8	3
11/11/86		16	5	18	4
11/12/86		10	5	11	3
11/13/86		14	4	25	4
11/14/86	1X[b]	10	5	12	3
11/17/86		11	3	15	3
11/18/86		16	4	28	5
11/21/86		43	4	67	4
11/26/86		31	4	31	4
12/1/86		17	3	17	3
12/4/86	2X				
12/8/86		18	3	11	3
12/12/86		19	4	17	3
1/12/87	2X				
1/13/87		12	5	8	3
1/16/87		21	9	46	6

[a]Initial batch of photographic waste used in feed.
[b]Second (fresh) batch of photographic waste used in feed.

4. CONCLUSIONS

The use of activated carbon to remove organics from photographic waste solutions does not appear to be an effective treatment option. The inherent characteristics of such solutions prevented a determination of whether there was a significant reduction in the organic content of the waste as a result of the treatment. Carbon adsorption might be effective following some pretreatment of the photographic waste. It should be recognized, however, that carbon adsorption creates another problem, since the spent activated carbon packing itself must be properly disposed of.

Aeration of a chemically amended waste (e.g., with $FeCl_3$) was effective in reducing the time required to remove the oxygen demand of the photowaste. However, the resulting waste solution has an iron content above discharge limits. Also, there was no change in toxicity.

Ultraviolet light-aided oxidation with H_2O_2 was not effective in reducing the toxicity or oxygen demand of photowaste.

The discharge of the photographic waste to ORNL's STP appears to be an effective means of treatment and disposal. At the projected rate of discharge (379 L/d), the waste had no effect on reactor performance as measured by TOC reduction, and there was no indication of acute biotoxicity. Reduction of the oxygen demand before treatment was not necessary, but it was not determined whether neutralization of the waste is required. The rate at which photographic waste is discharged to the STP must be controlled to ensure that its concentration does not reach toxic levels.

Based on the results of these studies, ORNL's Department of Environmental Management and the Operations Division have requested (from the State of Tennessee) a modification of the STP operating permit to allow the discharge of the waste from the silver-recovery facility to the main sanitary sewage stream at a rate not to exceed 379 L/d.

5. REFERENCES

1. C. Krause, "Silver Recovery from ORNL Wastes," ORNL Rev. No. 3, 1-7 (1982).

2. J. M. Thomas, M. D. Lee, P. B. Bedient, R. C. Borden, L. W. Canter, and C. H. Ward, Leaking Underground Storage Tanks: Remediation with Emphasis on In Situ Biorestoration, EPA/600/2-87/008, 1987, p. 144.

3. J. Ehrenfeld and J. Bass, Evaluation of Remedial Action Unit Operations at Hazardous Waste Disposal Sites, Noyes Publications, Park Ridge, N.J., 1984, p. 434.

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