190
ANL/ES-23
7-17-73

221
ANL/ES-23

22, 24/2

**CHLORINATION EXPERIMENTS AT THE
JOHN E. AMOS PLANT OF THE
APPALACHIAN POWER COMPANY:
APRIL 9-10, 1973**

J. E. Draley

U of C-AUA-USAEC

ARGONNE NATIONAL LABORATORY, ARGONNE, ILLINOIS

**Prepared for the U.S. ATOMIC ENERGY COMMISSION
under Contract W-31-109-Eng-38**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

The facilities of Argonne National Laboratory are owned by the United States Government. Under the terms of a contract (W-31-109-Eng-38) between the U. S. Atomic Energy Commission, Argonne Universities Association and The University of Chicago, the University employs the staff and operates the Laboratory in accordance with policies and programs formulated, approved and reviewed by the Association.

MEMBERS OF ARGONNE UNIVERSITIES ASSOCIATION

The University of Arizona	Kansas State University	The Ohio State University
Carnegie-Mellon University	The University of Kansas	Ohio University
Case Western Reserve University	Loyola University	The Pennsylvania State University
The University of Chicago	Marquette University	Purdue University
University of Cincinnati	Michigan State University	Saint Louis University
Illinois Institute of Technology	The University of Michigan	Southern Illinois University
University of Illinois	University of Minnesota	The University of Texas at Austin
Indiana University	University of Missouri	Washington University
Iowa State University	Northwestern University	Wayne State University
The University of Iowa	University of Notre Dame	The University of Wisconsin

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

Printed in the United States of America
Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151
Price: Printed Copy \$4.00; Microfiche \$0.95

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

CHLORINATION EXPERIMENTS AT THE
JOHN E. AMOS PLANT OF THE
APPALACHIAN POWER COMPANY:
APRIL 9-10, 1973

by

J. E. Draley

Environmental Statement Project

June 1973

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

[Signature]

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
1. INTRODUCTION	6
2. EXPERIMENTAL PROCEDURES	10
2.1 Sampling	10
2.2 Analyses	12
2.3 Operational Procedure	12
3. RESULTS	14
4. APPLICATION OF CALCULATIONAL MODELS	20
ACKNOWLEDGMENTS	26
REFERENCES	26

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Cooling Tower, Showing Sampling Location	11
2.	Chlorination Run No. 1: April 9, 1973	17
3.	Chlorination Run No. 2: April 10, 1973	17

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Analyses of Water of Kanawha River near Amos Plant	8
2.	Analytical Results for Chlorine: Run No. 1	15
3.	Analytical Results for Chlorine: Run No. 2	16
4.	Values for Parameters in Equations 1 and 3	24

CHLORINATION EXPERIMENTS AT THE
JOHN E. AMOS PLANT OF THE
APPALACHIAN POWER COMPANY:
APRIL 9-10, 1973

by

J. E. Draley

ABSTRACT

In two special runs, free and total residual chlorine were measured in the circulating-water system of the cooling tower for the Amos Plant Unit 1. For a typical chlorination period, in which the concentration of free chlorine at the condenser was about 0.1 ppm, the total residual-chlorine concentration reached maxima of 0.63 ppm at the condenser discharge and 0.32 ppm in the discharge from the cooling-tower basin. These residual-chlorine levels declined after the addition of chlorine was stopped, but more than 2 hr elapsed before the residual chlorine could no longer be detected by the amperometric-titration method (sensitivity perhaps 0.01 or 0.02 ppm).

The data for the buildup of residual chlorine at the condenser were fitted with a kinetic expression in which some reduction of chlorine to chloride and some formation of chloramines are assumed. Good fits, with reasonable values of the constants, suggest that the model is correct.

The data for gradual decay of combined chlorine were fitted with an equation based on a model in which the chlorine is assumed to be lost in the blowdown and by processes within the system. Again, good fits, with reasonable parameters, gave credence to the model. The calculated fraction of the chloramines lost per pass through the circulating-water system was 0.4.

1. INTRODUCTION

Maintenance of the quality of our environment requires, among other things, that the release of chemicals be kept to the minimum commensurate with effective operation of power- or product-producing plants. In the preparation of Environmental Impact Statements for construction or operation of nuclear plants to ensure control of such releases, the Atomic Energy Commission, together with its contractors, often must estimate the amounts of substances (such as chlorine) released to the environment without having factual information that will ensure accuracy of the estimation.

In many respects, chlorine is an ideal defouling agent because its high toxicity to fouling organisms is accompanied by its inherent instability in water.^{1,2} The instability is of two types: (a) Free chlorine (i.e., hypochlorous acid) decomposes in water to liberate oxygen and produce chloride ion; this reaction is markedly accelerated by ultraviolet light so that the chlorine is in this way dissipated rapidly in the presence of sunlight. (Rates of this type of reaction for combined chlorine are unknown.) (b) Chlorine reacts with constituents of natural waters that will reduce it to the innocuous chloride ion. These solutes include inorganic reducing agents and organic substances. In addition, biological slimes on the walls of the parts of the cooling-water system at power plants will reduce chlorine.

Ideally, the chlorine should be added at a level and location that will allow maintenance of effective concentrations at the point needed and still allow the chlorine to decay to innocuous levels before discharge to the environment. Unfortunately, rates of decay for actual cases

cannot be predicted, because many of the specific reaction rates are unknown and because rates of reaction vary with the organic material from system to system and perhaps from season to season.

Partly because of this variability, predicting decay rates and developing optimum chlorination plans purely on the basis of empirical relationships are not likely. Instead, it is felt necessary to develop a method of calculating effects for new plants that is solidly based on data from existing plants. The measurements given in this report were therefore taken so that useful calculational models could be developed for predicting the release of chlorine in the blowdown water from recirculating-cooling-water systems using cooling towers and for developing chlorination management procedures.

The John E. Amos Plant of the Appalachian Power Company at St. Albans, West Virginia, which burns coal, has two 800-MWe net units operating. (Unit 2 was down on the days of the measurements.) Each plant has its own circulating-water system, and each has its own natural-draft cooling tower. Some useful parameters for Unit 1 are as follows: The total volume of the circulating-water system is 5.5 million gal; the circulating-water flow rate is 248,000 gpm; the makeup rate varies, with a maximum of about 7000 gpm. The water in the blowdown (4000 gpm for 1-1/2 hours per day) is used to transport ashes from the furnaces to ash-drainage pits, from which the overflow picks up fly ash and carries that to a pond in which the ash settles; the overflow from this pond then is released to the Kanawha River. Some information on the chemistry of the Kanawha River water used for makeup is shown in Table 1. The pH of the circulating water is adjusted by automatic

TABLE 1. Analyses of Water of Kanawha River
near Amos Plant

March 1973 (8 analyses):

M. O. alkalinity, ppm CaCO_3	38-63
Total hardness, ppm CaCO_3	51-68
Chloride, ppm	7-15
Sulfate, ppm	20-40
pH	7.32-7.90
Turbidity	<25-92
Total solids, ppm	100-508 (second highest TS = 264)

*September 10-October 27, 1972
(range and mean of 5 analyses):*

pH	6.71-7.30 (6.96)
Spec. conductance, $\text{ohm}^{-1} \text{ cm}^{-1}$	201-463 (268)
Aluminum, ppb	5-42 (21)
Antimony, ppb	1-23 (8)
Hardness, ppm CaCO_3	65-122 (83)
Barium, ppb	2-29 (24)
Boron, ppm	0.02-0.05 (0.03)
Bromine, ppm	<0.04
Calcium, ppm	18-37 (24)
Copper, ppb	5-17 (11)
Iron, ppb	15-300 (103)
Lead, ppb	0-2 (1)
Magnesium, ppm	4.5-7.0 (5.6)
Manganese, ppm	4-59 (29)
Nickel, ppb	2-4 (3)
Nitrate, ppm	2.6-5.6 (4.3)
Phosphorus, ppm	<0.1-0.2
Potassium, ppm	1.9-4.2 (2.5)
Sodium, ppm	10.5-39.0 (20.3)
Tin, ppb	0-3 (1)
Zinc, ppb	10-340 (150)

addition of sulfuric acid to maintain a level at which calcium carbonate will not precipitate in the system. The normal pH of operation is usually fairly close to 7.5. Since water is taken from the circulating-water system as blowdown only for about 90 minutes a day, the dissolved-solids content of the recirculating water is much higher than that in the river. (The concentration factor is calculated to be about 28, as an average, for the operating parameters given above.)

2. EXPERIMENTAL PROCEDURES

2.1. Sampling

Samples were taken from two locations--immediately following the left condenser, and the outlet of the cooling-tower basin (see Fig. 1). The condenser-exit sample passed through about 260 ft of 3/4-in-diameter copper pipe at about 7.6 gpm before reaching the open cup from which it was dipped out. About 3/4 min was therefore required for the sample to pass from the point of sampling at the condenser to the point of removal for analysis. An estimated additional one minute was required for passage of the water from the point of chlorine injection to the condensers.

The cooling-tower-basin sample was removed from the sluice that passes cold water from the basin (about 6 ft deep) to the point of chlorine injection and to the pumps (there about 13 ft deep), by use of a long-handled (about 8 ft long) polyethylene dipper. For all samples after the first few of the first run, the dipper was inserted in the water as deeply as conveniently possible (about 4-1/2 ft) and quickly withdrawn. The sample, undoubtedly, was partly mixed with water at levels higher than the 4-1/2-ft level during the withdrawal, but the procedure seemed the best readily available. Samples near the surface of the water flowing in the sluice, such as were taken for the first few times, evidently were poorly representative of the water from the cooling-tower basin. The surface water probably is largely composed of the water falling from the cooling-tower periphery close to the opening to the sluice. In addition, the wind-driven surface currents, highly variable, led to variable times of

COOLING TOWER
ELEVATION

PARTIAL PLAN VIEW

Fig. 1. Cooling Tower, Showing Sampling Location

passage from the near point of the cooling-tower discharge to the point of sampling.

2.2 Analyses

After removal from the open source (at either location), amperometric titration for free or combined chlorine, or both, was made with portable Wallace and Tiernan equipment. The titrations for cooling-tower-basin samples were carried out outdoors because excessive losses of chlorine might occur in the time required to transport the samples indoors. Shielding the samples from the sunlight was necessary during transportation to the nearby titration equipment and during titration. On the day of the first run (April 9), this shielding was done crudely by holding a jacket above the sample or the equipment. For the second run (April 10), all titrations were done inside a station wagon, with windows blacked out by covering with opaque plastic sheeting.

2.3 Operational Procedure

The chlorine was injected as an aqueous solution at a constant rate. The flow was started and stopped manually; the injection period for both runs was 30 min. Chlorine injection rates were 2.71 and 3.33 lb/min for Runs 1 and 2, respectively; calculated chlorine concentrations at the point of injection were thus 1.31 and 1.61 ppm for Runs 1 and 2.

During Run 1, blowdown was being taken from the circulating-water system at a rate that was not measured; presumably it was the standard 4000 gpm. During Run 2, there was no blowdown.

Titration for free chlorine in the condenser samples of Run 1 were difficult because of the slowness with which the electrode current (shown by the needle of the measuring microammeter) changed on addition of the standard reducing agent. On this basis, it was decided that the use of a pH 7 buffer would be beneficial for Run 2. However, the chemistry of the circulating water was such that the pH 4 buffer used during the determination of combined chlorine did not overcome the buffering action of the solution plus that of the pH 7 buffer. Accordingly, for Run 2, samples were titrated for free chlorine or total chlorine, rather than for determining both free and combined chlorine on each sample (as had been done for Run 1).

3. RESULTS

Analytical results are shown for the two runs in Tables 2 and 3 and in Figs. 2 and 3.

In Run 1, the free chlorine at the condenser exit rose quickly to nearly 0.1 ppm and then increased only slightly to the end of the addition period. During the same period, the combined chlorine increased more gradually to a maximum measured value of 0.53 ppm. No free chlorine was detected in the sluice samples. The combined chlorine reached a maximum concentration of 0.31 ppm and then started to decline (about 12 minutes after the concentration of combined chlorine at the condenser exit started to decline). If the free chlorine at the condenser was reduced to chloride ion before reaching the sluice, the combined-chlorine level declined about 40% between condenser and sluice. On the other hand, if most of the free chlorine at the condenser was converted to combined chlorine, about 50% of this combined chlorine was lost in the cooling tower. This topic is analyzed further in the next section.

The period of gradual decline of the combined-chlorine level has two notable features for Run 1. First, at its start, the residual-chlorine concentration was higher by a factor of three than had been hoped could be achieved in a cooling-tower-circuit blowdown, even though the excess free chlorine at the condenser exit was only 0.1 ppm. Second, the decay of residual combined chlorine was gradual. After chlorine addition was stopped, the residual chlorine in the sluice soon reached a maximum and then declined to 0.1 ppm at about 50 minutes. An additional 90 minutes was required for the

TABLE 2. Analytical Results for Chlorine: Run No. 1

Condenser Exit			Cooling-tower Sluice		
Time, ^a min	Free, ppm	Total, ppm	Time, ^a min	Free, ppm	Total, ppm
3	0.00	0.00	12.0 ^b	0.00	0.07
7	0.07	0.30	16.0 ^b	0.00	0.12
12	0.08	0.34	20.0 ^b	0.00	0.15
15	0.09	0.43	24.0 ^b	0.00	0.17
19	0.09	0.49	27.0 ^b	0.00	0.25
23	0.09	0.56	29.3	0.00	0.27
27	0.09	0.60	33.0	0.00	0.30
30	0.10	0.63	35.8	0.00	0.31
33	0.06	0.62	39.0	0.00	0.32
38	0.00	0.31	43.0	0.00	0.30
40	0.00	0.27	47.0	0.00	0.30
43	0.04	0.23	50.0	-	0.25
46	0.00	0.19	52.0	-	0.22
49	0.00	0.15	55.0	-	0.20
52	0.00	0.14	58.7	0.00	0.17
57	0.00	0.12	62.8	0.00	0.14
61	0.00	0.10	66.5	0.00	0.14
64	0.00	0.09	72.5	0.00	0.12
68	0.00	0.08	77.8	0.00	0.10
72	0.00	0.07	85.0	0.00	0.10
76	0.00	0.07	91.0	-	0.08
80	0.00	0.07	97.0	-	0.07
82	0.00	0.06	103.0	-	0.07
85	0.00	0.06	112.0	-	0.07
88	0.00	0.06	124.0	-	0.05
91	0.00	0.05	136.5	-	0.05
93	0.00	0.05	150.0	-	0.03
96	0.00	0.05	165.0	-	0.00
103	0.00	0.04			
115	0.00	0.03			
125	0.00	0.03			
136	0.00	0.02			
148	0.00	0.02			
166	0.00	0.01			
174	0.00	0.00			

^aAfter turning on chlorine feed.

^bThese samples taken from near surface, about 3 feet from wall. All other samples taken at a depth of about 4-1/2 feet (with some mixing during withdrawal), about 2 feet from wall.

TABLE 3. Analytical Results for Chlorine: Run No. 2

Condenser Exit			Cooling-tower Sluice		
Time, ^a min	Free, ppm	Total, ppm	Time, ^a min	Free, ppm	Total, ppm
1	-	0.00	20.0	-	0.00
3	-	0.00	22.5	-	0.10
5	-	0.19	25.0	0.14	-
7	0.09	-	28.2	-	0.39
9	0.00	-	32.0	0.00	-
11	-	0.49	35.0	-	0.42
13	0.16	-	38.2	0.00	-
15	-	0.65	40.4	-	0.51
18	0.00	-	44.7	0.09	-
19	-	0.73	48.0	-	0.44
21	0.05	0	52.0	0.05	-
23	-	0.80	56.0	-	0.35
25	0.25	-	60.0	0.00	-
27	0.00	-	62.7	-	0.31
29	-	0.90	66.3	0.00	-
30	0.26	-	69.3	-	0.25
32	0.09	-	74.3	0.00	-
34	0.06	-	78.0	-	0.23
36	-	0.55	81.0	0.00	-
38	0.00	-	87.0	-	0.19
40	-	0.42	90.0	-	0.16
42	0.00	-	96.7	-	0.15
47	-	0.34	103.3	-	0.14
52	0.00	-	113.3	-	0.12
57	-	0.27	125.0	-	0.10
65	-	0.21	135.0	-	0.08
69	0.00	-	145.0	-	0.07
75	-	0.16			
85	-	0.13			
94	0.00	-			
97	-	0.10			
109	-	0.09			
116	0.08	-			
127	-	0.07			
139	-	0.06			

^aAfter turning on chlorine feed.

Fig. 2. Chlorination Run No. 1: April 9, 1973. (Condenser exit temperature 100°F, pH 7.10-7.60.)

Fig. 3. Chlorination Run No. 2: April 10, 1973. (Condenser exit temperature 89°F, pH 7.20-7.60.)

chlorine to decrease to about 0.01 or 0.02 ppm, the sensitivity limit of the procedure used. (The accuracy of the procedure is not well known; there is no way to be certain that the small concentrations read towards the end of the decay period were truly combined chlorine or that no large errors were made.)

Although only Run 1 was made at the conditions typical at the plant, total residual chlorine had been measured under nominally identical conditions a few weeks earlier. The run was done with Unit 2 rather than Unit 1; the water was sampled at the condenser exit, but not at the cooling-tower basin. Data were similar to the curve in Fig. 2 for the total chlorine at the condenser outlet. The maximum was again 0.63 ppm, and the level dropped below the limit of sensitivity in about three hours.

Run 2 was made on the morning of April 10, with the injection rate of chlorine increased, in the hope that the free-chlorine level would be higher and that the loss in this species during passage through the cooling tower could be estimated. In some ways the results were as anticipated, although the free-chlorine level was very erratic, showing unaccountable swings between 0 and significant values. This time there were a few readings of free chlorine in the cooling-tower sluice, also erratic (not shown in Fig. 3). The irregularity might have been caused by the unusually long time since the last chlorination (23 hr, rather than the usual 12). Perhaps unusually heavy deposits had formed and pieces dislodged sporadically during the cleaning, leading to depletion of the free chlorine in solution by rapid reaction with the dislodged material. At the condenser exit, the maximum recorded total residual-chlorine concentration was 0.90 ppm.

Subtracting the maximum free-chlorine value provides an estimated maximum combined chlorine value of 0.64 ppm, about 0.1 ppm greater than that in Run 1. The peak combined-chlorine level estimated in the same way for the cooling-tower-sludge water was 0.51 ppm, about 43 percent below the maximum at the condenser.

4. APPLICATION OF CALCULATIONAL MODELS

Separate calculational models were used to fit the data for the increase in chlorine content during the period of addition of chlorine and for the decay after addition of chlorine was stopped. Concerning the build-up, the slow increase in combined (or total) chlorine and the rapid decline after chlorine addition was stopped indicate consumption by reducing substances in the system that are themselves being depleted (see Figs. 2 and 3). On this basis, the following expression was developed in which the combined-chlorine concentration had a maximum value at the condenser that was lower than that corresponding to the rate of chlorine injection by an amount K :

$$C_{\text{tot}} = (C_0 - K)\{1 - \exp[-A(t - t_0)]\} + C_{\text{free}}. \quad (1)$$

This constant is the sum of the free chlorine that remains unreacted and the amount of chlorine that was reduced by rapid-acting chlorine-demand constituents. This maximum amount of combined chlorine was diminished by reaction of the free or combined chlorine with such things as deposits on surfaces. The braced term of Eq. 1 is developed for the case in which a constant fraction of the reactive wall material is removed for each constant-time interval. It is necessary to use t_0 to accommodate the times of passage (of injected chlorine solution and of circulating water from the point of chlorine injection to the sample point) and possible inaccuracies in watch synchronization. Finally, the total residual chlorine is the sum of the combined chlorine so estimated and the free chlorine remaining.

This equation was fitted to the data for the buildup of chlorine at the condenser for Runs 1 and 2. Referring to Fig. 2, using three points determines the constant A. The remaining constants, t_0 , K, and C_{free} , could have wide ranges of values and still provide essentially the same curve. There was, however, a requirement for certain interrelationships. For Run 1, the condition chosen to finalize the constants was that the free chlorine had the constant value equal to the average of those observed, 0.09 ppm. The fit to the data was excellent, as can be seen in Fig. 2, where the line drawn is that of the equation from five minutes onward. The line is dashed after the first 24 min, since the derivation of the equation did not consider the effect of chlorinating water that had been chlorinated on a previous pass around the system. Since the average total passage of water through the system is 22 min (the volume divided by the circulating flow rate) and there is a 2-min period from the point of chlorination to the sampling, no points for times greater than 24 min were used in determining the values of the constants. If the basis for the model is correct, the extended dashed line suggests that cleaning the condenser would be essentially complete only after another 20-30 min of chlorination.

For Run 2, the value of A was again selected by passing the line through three of the data points before 24 min. In the absence of a clear method for selecting values for the remaining constants, the value of K for Run 2 was established as the same as that for Run 1. Choosing the same value instead for fast chlorine demand might have been better; the difference in constants would have been only slight. Again, the dashed line is an extrapolation beyond the first 24 min of the run. Again, the data suggest that cleaning the walls of all significant amounts of chlorine-consuming

growths would require an additional period of chlorination. The values of the parameters are tabulated in Table 4. All the constants appear to be at least reasonable in magnitude, and there is fairly good correlation between the values used for the two runs. During time increments of about 14 min (reciprocal of $A = 0.07$), the quantity of chlorine-destroying material is reduced by a factor of e . By the choice of K , the level of the free chlorine (assumed to be constant during the buildup) was 0.05. In view of the irregular values obtained, there is no way to determine whether this is a good or poor approximation. In fact, if other values for the last four parameters in the table had been selected, so as to use a significantly larger value for C_f , they would still have been in the reasonable range in light of the lack of precision in the results. For example, a value of 4 for t_0 in Run 2 leads to a value of 0.13 for C_f and 0.71 for K . As shown in Table 4, for the parameters chosen, the values of $K - C_f$ are almost the same for Runs 1 and 2. This quantity should be a measure of the total concentration of the substances in the circulating water that quickly destroy chlorine before it can produce chloramines or react with organic deposits.

After the initial sharp decay period, the more gradual loss of combined chlorine from the system was fitted to an equation first used in August 1972 in an effort to estimate chlorine levels during and after treatment of the recirculating-water system for a proposed nuclear power plant for which a license has been requested.³ Chlorine species were assumed to be lost by blowdown and by reaction within the system--as by reaction with reducing substances, evaporative loss in the cooling tower, or sunlight-catalyzed decomposition to form oxygen (for free chlorine). The loss within the system is given by a term, F , the fraction lost per average pass

through the recirculating-water system. On the basis of mass balance and the assumption of uniform composition throughout the system at any one time, the following expression was derived:

$$V \frac{dC}{dt} = C_M M - C(B + FR), \quad (2)$$

where V is the volume of the system, C the concentration varying with time t , C_M the concentration in the makeup at flow rate M , B the blowdown rate, and R the recirculating-water flow rate. For the present application, where there is no addition of chlorine, the first term on the right side is 0, and integration yields the following result (the requirement for uniformity in the system also vanishes):

$$C = C_0 \exp \frac{-L(t - t_0)}{V}, \quad (3)$$

where L , the loss factor, is defined as $B + FR$.

Application of this expression to the decay period of the two lines in each of Figs. 2 and 3 provided excellent fits to the data; in fact, the lines were drawn from the equation. They were extended backward in time from the first point fitting the data as dashed lines in the figures. The constants used for these lines are given in Table 4. For Run 1, the actual

TABLE 4. Values for Parameters in Equations 1 and 3

		<u>Run 1</u>	<u>Run 2</u>
Equation 1 (buildup)	A	0.067	0.074
	t ₀	5.0	3.0
	C _f	0.09	0.05
	K	0.64	0.64
	K - C _f	0.55	0.58

	<u>Condenser</u>	<u>Basin</u>	<u>Condenser</u>	<u>Basin</u>
Equation 3 (decay)	V, gal	5.5 x 10 ⁶	Same	Same
	B, gpm	4000	Same	0
	R, gpm	2.48 x 10 ⁵	Same	Same
	F	0.44	0.35	0.40
	t ₀ , min	60	80	70
	C ₀ , min	0.11	0.10	0.19

blowdown rate (about 4000 gpm) was used; for Run 2, since there was no blowdown, B was assigned a value 0. The only constant to which an independent value was assigned was F. Note that this factor varied from 0.35 to 0.44-- a small range, given the differences in circumstances at the condenser and in the cooling-tower basin and differences in the rate of addition and the level of chlorine for the two runs.

It is encouraging that relatively simple calculational models provide a good approximation to the buildup and decay of chlorine during these experiments. The decay curve used (value of F) indicates that the free chlorine in the condenser discharge during Run 1 probably was converted to chloride by reaction with something in the system before going through the cooling tower, since the fraction lost per pass (and for chloramines this very likely means loss by evaporation in the cooling tower) was 0.4 rather than 0.5 (see Section 2). The applicability of the factor 0.4 to other natural-draft cooling towers should be determined. A logical basis (depending on the chemical constitution of the recirculating water) for the quick-acting chlorine demand of 0.6 ppm for the two runs would be desirable. Unfortunately, the only chemical analyses available are for the river water. There might be enough reducing species, such as manganous ion, ferrous ion, nitrite ion, and some organic substances, to add up to this level of quick-acting chlorine demand. If this correlation could be shown, it would provide confidence in the use of this equation in predicting the buildup of chlorine in recirculating systems, at least during the first passage of water through the system.

ACKNOWLEDGMENTS

The cooperation and participation of personnel of the American Electric Power Service Corporation (AEP) and the Appalachian Power Company are gratefully acknowledged. Mr. R. W. Reeves, head of the Environmental Engineering Division of the AEP, together with T. A. Miskimen of the same organization, made necessary arrangements. Mr. J. A. Moore, Manager, and Mr. M. Vaughan, Chief Chemist, at the Amos Plant authorized the necessary nonstandard operations. Messrs. Gary Crawford and Emil Hoffman, both AEP, did the analyses.

REFERENCES

1. Joseph E. Draley, The Treatment of Cooling Waters with Chlorine, ANL/ES-12 (Feb 1972).
2. George Clifford White, Handbook of Chlorination, Van Nostrand-Reinhold, New York, Cincinnati (1972).
3. U. S. Atomic Energy Commission, Final Environmental Statement Related to Construction of Davis-Besse Nuclear Power Station, Docket No. 50-346 (Mar 1973).