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A Validation of the Kinetic Model for Predicting the Composition of Chlorinated Water Discharged from Power Plant Cooling Systems

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**A VALIDATION OF THE KINETIC MODEL FOR PREDICTING
THE COMPOSITION OF CHLORINATED WATER DISCHARGED
FROM POWER PLANT COOLING SYSTEMS**

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A VALIDATION OF THE KINETIC MODEL FOR PREDICTING THE COMPOSITION OF
CHLORINATED WATER DISCHARGED FROM POWER PLANT COOLING SYSTEMS¹

M. H. Lietzke

ABSTRACT

The purpose of this report is to present a validation of a previously described kinetic model which was developed to predict the composition of chlorinated fresh water discharged from power plant cooling systems. The model was programmed in two versions: as a stand-alone program and as a part of a unified transport model developed from consistent mathematical models to simulate the dispersion of heated water and radioisotopic and chemical effluents from power plant discharges.

The model as formulated takes into account the forward and reverse rates of chemical reactions leading to the formation of monochloramine, dichloramine, and organic chloramine (modeled by methyl chloramine). In addition to these three equations, the model also includes a differential equation for the irreversible uptake of chlorine in satisfying the chlorine demand of the water. Input to the computer program consists of the operating characteristics of the cooling system and the chemical composition of the water (amounts of inorganic and organic nitrogen, chlorine demand, pH, and temperature). Output consists of the amounts of the chloramines and total residual chlorine in the discharge water as a function of time.

The results of testing the model using analytical data taken during operation of the once-through cooling system of the Quad Cities Nuclear Station are described. Calculations are also presented on the Three Mile Island Nuclear Station which uses cooling towers.

INTRODUCTION

In a previous report² a description was given of a kinetic model for predicting the composition of chlorinated water discharged from power plant cooling systems. The purpose of the present paper is to present a validation of the model using analytical data supplied by Commonwealth Edison³ taken during operation of the Quad Cities Nuclear Station. In addition to the Quad Cities results, calculations will also be presented on one other operating power station.

DESCRIPTION OF THE MODEL

Since a detailed description of the model has already been published², only the principal features will be mentioned here. The model as formulated takes into account the forward and reverse rates of three chemical reactions leading to the formation of chloramines. These are shown as equations (1), (2), and (3).

The species RNH_2 in equation (3) represents a composite of the organic amines present in the water. Since several of the most common organic amines have very similar rate constants for reaction with hypochlorous acid, they have been modeled as a group using the rate constant for the reaction of methylamine with hypochlorous acid as a stand-in. Of the remaining rate constants k_1 , k_{-1} , and k_2 are known. In lieu of measured

values of k_2 and k_3 , k_3 has been taken equal to k_1 , while k_2 has been assumed to be equal to $1/2 k_1$. These rate constants are functions of both the pH and the temperature of the water.

The rates of the forward reactions resulting in the formation of the chloramines are extremely rapid, while the reverse reactions for the hydrolysis of the chloramines are much slower. For example, in the pH range 7-8 at a temperature of 25° the forward reactions consume the hypochlorous acid in a few minutes, while half-times for the hydrolysis of the chloramines (resulting in the regeneration of the original amines) are measured in hours. The small amount of hypochlorous acid formed by hydrolysis of the chloramines in the cooling system is disregarded in the material balance after the initial consumption of the added chlorine.

In addition to the three chemical reactions leading to the formation of chloramines, the model includes an equation for the rate of irreversible uptake of chlorine in satisfying the chlorine demand of the water. The value of the rate constant for this reaction must be adjusted by trial and error using chlorination data on an actual operating power plant, as will be demonstrated later. Included in the chlorine demand of the water are any substances leading to the irreversible uptake of chlorine. Examples are humic acid, which may constitute up to 90% of the chlorine demand, and other dissolved organics, which might lead to chloroform formation. Hence the rate constant for the overall reaction involving the chlorine demand of the water will depend upon the particular composition of the water when the model is applied.

The chemical reactions involved in the uptake of chlorine in satisfying the chlorine demand of the water are, as a group, very much slower

than the reaction of hypochlorous acid (or hypochlorite) with ammonia or amines. Hence, the calculated values of chloramine concentrations and total residual chlorine in the water, which are the result of very fast reactions, are not very sensitive to the overall rate constant for this reaction. In fact, the rate constant can often be varied by a factor of two with very little effect on the calculated concentration of the chloramines and the total residual chlorine.

In a once-through cooling system the makeup to blowdown ratio is unity and hence chlorine is added to water containing the same concentrations of dissolved substances as the makeup water. In a recirculating system with cooling towers, on the other hand, the chlorine is added to water in which the dissolved substances have become concentrated by a factor equal to the makeup to blowdown ratio. The computer program has been designed to handle either type of configuration. Losses of chlorine by evaporation and by reaction with material attached to the walls of the cooling system are small and have been disregarded.

The mathematical formulation of the model involves the solution of five simultaneous differential equations. Three of these equations involve the formation of the chloramines and their subsequent hydrolysis. A fourth equation involves the irreversible loss of hypochlorous acid in satisfying the chlorine demand of the water, while the fifth calculates the concentration of hypochlorous acid remaining after each time step. The set of five differential equations is solved using a variable step-size Runge-Kutta integration scheme to give the concentrations of NH_2Cl , NHCl_2 , RNHCl , and HOCl remaining in the cooling system after each time step. The concentrations of NH_3 and RNH_2 in the cooling system are calculated after each time step by subtracting the concentrations of NH_2Cl and NHCl_2 from the original concentration of NH_3 and the concentration of RNHCl from the original

concentration of RNH_2 .

VALIDATION OF THE MODEL

In 1973 an in-depth chlorination study was conducted at the Quad Cities Nuclear Station³. The analytical data used in the validation of the model described in this paper were taken at that time. Twelve separate chlorination runs under varying conditions of temperature, pH, chlorine-dose, ammonia concentration, and chlorine demand were used in the calculations.

At the time of the chlorination study the Quad Cities Station was operating on a once-through cooling basis wherein river water was drawn in through a crib-house, circulated through the condensers, and then discharged into a small discharge bay, with the final effluent coming from a large diffuser pipe extending approximately 75% across the Mississippi River. The cooling system consisted of two condensers. Each unit was chlorinated separately with each condenser being split-chlorinated. This resulted in one half of each condenser being chlorinated during a chlorination cycle. The chlorinated water was then diluted with water from the other half of the condenser and with the water flowing through the other condenser before discharge into the discharge bay. Chlorine residuals were not measured at the discharge bay but instead at the center water-box in the condenser. Under the flow conditions during the test, samples were thus taken 25 seconds after chlorination of the water.

The chlorination data supplied by Commonwealth Edison were taken during September and October, 1973. For each run the data included flow rates, temperature and pH of the water, concentration of ammonia, chlorine

dose, and free and combined chlorine residuals measured 25 seconds after chlorination. The chlorine demand of the water was not measured as such. Instead, the free chlorine consumption in 25 seconds was reported. Since these values are approximately proportional to the chlorine demand, they were used in lieu of measured chlorine demand values in the calculations.

The results of applying the model to the chlorination data taken at the Quad Cities Station are summarized in Table I.

In carrying out the calculations the value of the rate constant for the reaction involved in satisfying the chlorine demand of the water was varied from 500 to 2000 liters mole⁻¹ sec.⁻¹. Although the calculated values of the total residual chlorine in the water after 25 seconds did not change much over this range, the best overall fit was obtained with a value of 1600 liters mole⁻¹ sec.⁻¹. This value was used to calculate the chlorine residuals shown in Table I. Note that six of the deviations between the calculated and the observed chlorine residuals are positive and six negative. The sum of the positive deviations is 0.97, while the magnitude of that of the negative deviations is 1.01. If a least squares criterion is adopted as a measure of "goodness of fit" a value for the rate constant closer to 1000 would be used. In this case, however, the overall fit is not as good: the calculated values are slightly closer to the observed values for nine of the cases at the expense of the three cases with the greatest deviations. In any event, the F-ratio test indicates no significant difference between the two sets of calculations.

As mentioned previously, the chlorine residuals shown in Table I were reduced by a factor of four before the water entered the discharge bay. Much further dilution occurred at final discharge through the dif-

TABLE I

Observed and Calculated Values of Total Residual Chlorine 25
Seconds after Chlorination at Quad Cities Nuclear Station

<u>Date</u>	<u>Temp.</u> (0°C)	<u>pH</u>	<u>Chlorine</u> <u>Dose</u> (mg/l)	<u>NH₃</u> (mg/l)	<u>Free Chlorine</u> <u>Consumption</u> (mg/l)	<u>Total Chlorine Residual</u> (calc. mg/l) (obs. mg/l)		<u>Δ</u>
9-18	27.7	7.9	2.00	0.54	1.49	0.98	0.90	+0.08
9-18	27.7	7.9	2.13	0.54	1.63	1.04	0.98	+0.06
9-19	28.1	8.0	1.60	0.58	1.10	0.79	0.57	+0.22
9-20	29.1	8.0	1.75	0.76	1.25	0.87	0.76	+0.11
9-20	29.1	8.0	2.00	0.76	1.25	0.99	1.08	-0.09
9-21	29.0	8.2	2.11	0.23	1.36	0.83	1.10	-0.27
9-24	29.6	8.0	2.16	0.52	1.10	1.07	0.71	+0.36
9-25	21.7	8.2	2.55	0.33	1.55	1.03	1.30	-0.27
9-28	31.4	8.0	2.75	0.40	1.75	1.16	1.22	-0.06
10-1	25.4	7.6	2.33	0.22	1.33	0.89	1.04	-0.15
10-26	25.1	8.15	2.32	0.20	1.32	0.87	1.04*	-0.17
10-27	23.7	8.1	2.42	0.38	1.22	1.08	0.94**	+0.14

* Average of three values: 1.06, 1.10, 0.95

** Average of two values: 0.80, 1.08

fuser pipe into the Mississippi River. Chlorine monitoring⁴ during operation of the Quad Cities Station from August 1976 to January 1977, indicated no detectable total residual chlorine in the Mississippi River upstream or downstream from the station.

FURTHER CALCULATIONS

Three Mile Island Nuclear Station, located near Harrisburg, Pennsylvania, uses both a recirculating (cooling towers) and a once-through river water cooling system. In order to test the chlorination model, data have been taken from a report⁵ on cooling water chlorination practices at this station. The calculations reported here apply to Unit 1 of the recirculating system.

Characteristics of the makeup water, as given in Table 9 of the report, are as follows: pH 7.2; total chlorine demand 2.6 ppm; nitrogen as NH_3 0.17 ppm, temperature 25.5°C. No mention is made of organic amines in the water. Characteristic values for Unit 1 of the recirculating system are: makeup water 11,250 gallons per minute (GPM); blowdown 2000 GPM; volume of the recirculating system 1.3×10^7 G. The blowdown makes up 7% of the total discharge. If it is assumed that the chlorine is instantaneously dispersed and well mixed in the recirculating system, then 6000 lbs. of chlorine per day (assume 2000 lbs. three times a day) in the total recirculating system would amount to 9.2 ppm chlorine in the water of Unit 1 immediately after chlorination.

When the computer program was run for seven successive chlorination cycles the following results were obtained: The makeup to blowdown ratio in the recirculating system is 5.63. Both the chlorine demand and the

ammonia become concentrated in the water by this factor. The amount of chlorine added (9.2 ppm) is relatively high while the concentration of ammonia in the water is relatively low. As shown in Figure 1, when chlorine is added to the water the first time the ammonia is almost immediately consumed, resulting in the formation of both NH_2Cl and NHCl_2 . The remaining HOCl is taken up by the chlorine demand in the water. The amount of NH_2Cl formed is predicted to reach 3.51 ppm, while the NHCl_2 reaches 0.08 ppm. After a little more than two hours hydrolysis and blow-down reduce the NH_2Cl concentration to below one ppm; this value falls to 0.04 ppm after eight hours, while the NHCl_2 concentration falls to less than 0.01 ppm. The pattern is repeated during subsequent chlorination cycles, with the system coming to equilibrium after five cycles. In the sixth and succeeding cycles the maximum predicted amount of NH_2Cl in the system is 3.48 ppm immediately after chlorination and 0.066 at the end of the cycle, while the corresponding amounts of NHCl_2 are 0.48 ppm and 0.05 ppm.

The amounts of total residual chlorine in the discharge from the recirculating system (after dilution) are shown for seven chlorination cycles in Table II. Again equilibrium is reached after five cycles. These values probably represent upper limits because of potential losses of chlorine neglected in the model: e.g., losses due to evaporation, cooling tower drift, and other chemical reactions involving chlorine.

The value used for the rate constant for the reaction involving the consumption of HOCl by the chlorine demand in the water was 500 liters mole⁻¹ sec.⁻¹. This resulted in the total chlorine demand of the water being about 90% satisfied.

Fig. 1. The Amounts of NH_2Cl , NHCl_2 , and NH_3 in the Recirculating System During Eight Chlorination Cycles

CONCLUSION

The results of applying the kinetic model to the chlorination data supplied by Commonwealth Edison on the once-through cooling system at the Quad Cities Nuclear Station provide a validation of the model. As mentioned previously, it was easy to find a rate constant for the reaction involving the irreversible uptake of chlorine in satisfying the chlorine demand of the water such that the observed values of total residual chlorine in the water 25 seconds after chlorination scatter evenly about the calculated values. Since one adjustable parameter is involved in the model, there are eleven degrees of freedom for the twelve chlorination runs used in the calculations. This leads to a value of 0.2 or about 20% for the standard error in the observed values of the total residual chlorine in the water 25 seconds after chlorination. This value is consistent with the scatter shown in the three values of total residual chlorine reported for the same input conditions on 10-26 and the two values on 10-27 in Table I. Sources of error in the observed values would include incomplete mixing of the chlorine in the water and any experimental error in the analytical procedures.

The two examples given in the paper demonstrate that the model may be applied to either once-through cooling system or to cooling systems involving cooling towers.

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