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THE TREATMENT OF COOLING WATERS WITH CHLORINE

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by

Joseph E. Draley*

Environmental Statement Project

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ABSTRACT

The use of chlorine as a defouling agent in power plants requires assurance that aquatic biota will not be harmed. Three requirements are identified: (1) establishment of standards, (2) development of means of predicting the levels of active chlorine species at points of discharge, and (3) monitoring power plant effluents at points of discharge. Various aspects of the problem are considered.

Description of the Problem

The presence of certain bacteria and algae in natural waters leads to the preferential formation and attachment of organic slimes to container walls, and particularly to heated surfaces with which the water comes in contact. In the presence of sunlight at locations such as sluices and other outside water-carrying structures, the slimes are predominantly algae, while bacterial slimes predominate in closed heat-transfer circuits. In power plants it is essential that the heat transfer slimes be removed since they would otherwise seriously interfere with the transfer of heat and adequate flow of water.

The two common methods of removing the slimes are: (a) the passage of objects or suspensions through the fouled heat transfer tubes and (b) the periodic addition of chemicals to the water. Heat-shock defouling has apparently also been used successfully.

The mechanical devices can consist of balls, plugs, or brushes; they are blown through the tubes of heat exchangers such as steam condensers by the force of the flowing fluid or by mechanical devices. Automatic systems are offered by Amertap Corporation and American M.A.N. Corporation. The Amertap system circulates sponge rubber balls in a special bypass cooling water stream. The M.A.N. system employs nonmetallic brushes that are restrained in the tubes by plastic baskets attached to

the ends of each tube. By reversing the flow of the cooling water the operator can automatically "shoot" the tubes with the brushes.

Chemicals added to the water in successful defouling systems have included sulphur dioxide and chlorine. In this country the use of chlorine has predominated, apparently because of its greater effectiveness. Unfortunately the effectiveness of the chemical in defouling is accompanied by a corresponding effectiveness in injuring or killing plant and animal life in natural waters. For this reason it is important that standards for the maximum acceptable concentrations of residual chlorine species in effluent cooling waters be set, the means of predicting concentrations of these species be developed so that proper systems and methods can be designed, and that cooling water effluents be monitored to assure that the standards are not exceeded.

Chlorine is added in short periods to provide what is called "shock" defouling. To be effective about a half part per million of free chlorine is required. This number is not known very accurately because of the fluctuations that normally occur in plant practice; perhaps the important specification is to establish a free chlorine level such that at minima during the short time variations there will with certainty be some free chlorine present. The amount of chlorine (or hypochlorite) solution that must be added to provide the free chlorine depends upon the contents of certain reducing agents and ammonia in the water. The substances that reduce chlorine provide what is called chlorine demand; if the chlorine demand is high and if the ammonia concentration is high, a substantial excess of added chlorine will be required to provide the desired 1/2 ppm of free chlorine. The chloramines produced by the reaction between chlorine and ammonia also can provide shock defouling, but they are less efficient and slower. Under circumstances where the free chlorine defouling is effective in ten minutes it will take of the order of a half hour or an hour to defoul with chloramine. It is risky to undertreat (i.e., use too low a chlorine level) on an experimental basis with the expectation of building up the level later, since deposits which have been allowed to grow under treated conditions are much more difficult to get off later than are "new" deposits [1].

In practice the chlorine is added immediately upstream of the condenser to be defouled so that some of the slower chlorine-removing

reactions will not have taken place during passage through the condenser. This will minimize the amount of chlorine required for defouling, and it allows destructive removal of chlorine by continued reaction with the slower (organic) chlorine demand constituents. This helps to minimize the level of chlorine in the cooling water that is returned to lake, stream, or pond. Another factor that helps to remove the chlorine from cooling waters is the commonly employed practice of splitting the total coolant stream into parts and the chlorination of only one of these partial streams. The untreated streams retain their high chlorine demand and, when remixed with the treated solution after passage through the condenser, provide an improved possibility of complete chlorine removal by reaction with chlorine demand constituents. The split-stream method is often employed in modern power plant chlorination practice, because it makes feasible the use of smaller and less expensive chlorinating equipment.

Simple Equilibria

In order to examine the question of the concentration of chlorine and chlorine-bearing oxidizing species in water discharges it is necessary to examine the chemistry of chlorine and its reactions with certain impurities commonly present in natural waters. Restricting the discussion to dilute solutions, when chlorine is added to water it hydrolyzes very quickly to produce hypochlorous acid and hydrochloric acid as shown in Eq. 1.

The equilibrium constant is such that there is only an insignificant concentration of molecular chlorine at near-neutral pH's. The hypochlorous acid partially ionizes as shown in Eq. 2; a dilute "chlorine" solution thus contains, predominantly, a mixture of hypochlorous acid and hypochlorite ion, with the ratio of the two depending upon pH.

*Equilibrium constants vary with temperature, and there has been variation in results between investigators; in addition the pertinent temperature depends on the location for the application. Constants used here are for about 20-25°C.

The two species are present at equal concentrations at a pH of 7.5.

The presence of ammonia (or ammonium ion, depending on pH, see Eq. 3) in natural waters leads to the rapid formation of chloramines upon addition of chlorine, in accord with Eqs. 4 through 6.

Using the pertinent constants, the equilibrium concentrations of the chlorine- and nitrogen-containing species can be calculated for selected values of chlorine, ammonia nitrogen, and pH. Such values are shown in Table I for a typical chloride ion concentration. Note that the chlorine or ammonia, whichever is present at the smaller concentration, is often nearly completely converted to chloramines. The ratio of mono to dichloramine depends on the total level of ammonia nitrogen and on the pH, as can be seen by the equilibrium shown in Eq. 7.

In all cases, the molecular chlorine concentration is too small to be read with the number of decimal places printed in the table.

Rates of kill of plant and animal life in water largely depend on the concentration of HOCl [2,4], since rates with chloramines are only a few percent of that of the HOCl [2,5,6]. Note in Table I that, for a given level of total residual chlorine, the increasing presence of ammonia progressively decreases the HOCl concentration, and thus decreases rates of kill. However, typical persistence of chloramines (particularly the monochloramine) is considerably greater than that of HOCl in natural environment (see later) and it is not easy to evaluate the biological

*K₆ is not available, but there's little reaction at ordinary pH's.

TABLE I

EQUILIBRIUM CONCENTRATIONS OF IMPORTANT CONSTITUENTS IN CHLORINATED NATURAL WATERS										
UNITS FOR CHLORINE-CONTAINING SPECIES ARE MG/L CL, FOR NON-CL, NITROGEN-CONTAINING SPECIES, MG/L N										
RESIDUAL CHLORINE	CHLORIDE ION	PH	TOTAL AMMONIA	NH4+	NH3	NH2CL	NHCL2	OCL-	HOCL	CL2
1.0000	10.0	6.5	1.000	0.6398	0.0011	0.8209	0.1760	0.0003	0.0029	0.0000
1.0000	10.0	6.5	0.100	0.0001	0.0000	0.0138	0.4783	0.0467	0.4613	0.0000
1.0000	10.0	6.5	0.010	0.0000	0.0000	0.0008	0.0491	0.0873	0.8628	0.0000
1.0000	10.0	7.0	1.000	0.6166	0.0034	0.9252	0.0734	0.0003	0.0011	0.0000
1.0000	10.0	7.0	0.100	0.0000	0.0000	0.0163	0.4734	0.1237	0.3866	0.0000
1.0000	10.0	7.0	0.010	0.0000	0.0000	0.0009	0.0488	0.2304	0.7199	0.0000
1.0000	10.0	7.5	1.000	0.5999	0.0105	0.9729	0.0264	0.0004	0.0004	0.0000
1.0000	10.0	7.5	0.100	0.0000	0.0000	0.0238	0.4586	0.2604	0.2573	0.0000
1.0000	10.0	7.5	0.010	0.0000	0.0000	0.0014	0.0479	0.4782	0.4725	0.0000
1.0000	10.0	8.0	1.000	0.5751	0.0318	0.9905	0.0090	0.0004	0.0001	0.0000
1.0000	10.0	8.0	0.100	0.0000	0.0000	0.0436	0.4189	0.4095	0.1280	0.0000
1.0000	10.0	8.0	0.010	0.0000	0.0000	0.0027	0.0453	0.7254	0.2267	0.0000
1.0000	10.0	8.5	1.000	0.5157	0.0901	0.9963	0.0032	0.0004	0.0000	0.0000
1.0000	10.0	8.5	0.100	0.0000	0.0000	0.0856	0.3348	0.5275	0.0521	0.0000
1.0000	10.0	8.5	0.010	0.0000	0.0000	0.0060	0.0386	0.8695	0.0859	0.0000
0.1000	10.0	6.5	1.000	0.9592	0.0017	0.0981	0.0017	0.0000	0.0002	0.0000
0.1000	10.0	6.5	0.100	0.0649	0.0001	0.0803	0.0166	0.0003	0.0028	0.0000
0.1000	10.0	6.5	0.010	0.0003	0.0000	0.0081	0.0327	0.0054	0.0538	0.0000
0.1000	10.0	7.0	1.000	0.9554	0.0053	0.0994	0.0005	0.0000	0.0001	0.0000
0.1000	10.0	7.0	0.100	0.0621	0.0003	0.0915	0.0071	0.0003	0.0010	0.0000
0.1000	10.0	7.0	0.010	0.0001	0.0000	0.0093	0.0313	0.0144	0.0450	0.0000
0.1000	10.0	7.5	1.000	0.9441	0.0165	0.0998	0.0002	0.0000	0.0000	0.0000
0.1000	10.0	7.5	0.100	0.0602	0.0011	0.0967	0.0026	0.0004	0.0004	0.0000
0.1000	10.0	7.5	0.010	0.0001	0.0000	0.0117	0.0268	0.0309	0.0306	0.0000
0.1000	10.0	8.0	1.000	0.9102	0.0503	0.0999	0.0001	0.0000	0.0000	0.0000
0.1000	10.0	8.0	0.100	0.0577	0.0032	0.0986	0.0009	0.0004	0.0001	0.0000
0.1000	10.0	8.0	0.010	0.0001	0.0000	0.0158	0.0186	0.0500	0.0156	0.0000
0.1000	10.0	8.5	1.000	0.8177	0.1429	0.0999	0.0000	0.0000	0.0000	0.0000
0.1000	10.0	8.5	0.100	0.0517	0.0090	0.0992	0.0003	0.0004	0.0000	0.0000
0.1000	10.0	8.5	0.010	0.0001	0.0000	0.0203	0.0096	0.0638	0.0063	0.0000
0.0100	10.0	6.5	1.000	0.9943	0.0017	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	6.5	0.100	0.0960	0.0002	0.0096	0.0002	0.0000	0.0002	0.0000
0.0100	10.0	6.5	0.010	0.0071	0.0000	0.0067	0.0010	0.0002	0.0021	0.0000
0.0100	10.0	7.0	1.000	0.9906	0.0055	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	7.0	0.100	0.0956	0.0005	0.0099	0.0001	0.0000	0.0001	0.0000
0.0100	10.0	7.0	0.010	0.0066	0.0000	0.0083	0.0006	0.0003	0.0009	0.0000
0.0100	10.0	7.5	1.000	0.9789	0.0171	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	7.5	0.100	0.0944	0.0016	0.0099	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	7.5	0.010	0.0062	0.0001	0.0091	0.0002	0.0003	0.0003	0.0000
0.0100	10.0	8.0	1.000	0.9439	0.0521	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	8.0	0.100	0.0910	0.0050	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	8.0	0.010	0.0059	0.0003	0.0094	0.0001	0.0004	0.0001	0.0000
0.0100	10.0	8.5	1.000	0.8479	0.1481	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	8.5	0.100	0.0818	0.0143	0.0100	0.0000	0.0000	0.0000	0.0000
0.0100	10.0	8.5	0.010	0.0053	0.0009	0.0095	0.0000	0.0004	0.0000	0.0000

KA=3.2D-08, KB=1.81D-05, KCHLORAMINE=3.6D+09, K2=1.33D+06, KCHLORINE=2.54D+03

damage to be expected from the low-level presence of chloramine versus that from "free chlorine."

The values in Table I were calculated on the assumption that none of the species was lost by any mechanism other than those in the equations shown. In fact, there are other processes by which chlorine-containing compounds are lost. Realistic calculation of quantities of the species expected in waters depends on the rates of these processes, as well as on the rates of formation of the species.

Reaction Rates

As has been remarked, the chlorine-hypochlorite ion interactions (Eqs. 1 and 2) are nearly instantaneous and can be so considered. The ammonia base reaction (Eq. 3) is in the same category. It follows that certain concentration ratios (HOCl/Cl_2 , HOCl/OCl^- and $\text{NH}_3/\text{NH}_4^+$) can be treated as constants for any given pH. The reaction between ammonia and hypochlorous acid (Eq. 4) probably occurs only as written, that is the ammonium ion and hypochlorite ion are probably not involved. This is judged to be the case by examination of the reaction rate as a function of pH. This is maximum at a pH of 8.3 (where the product of the concentrations of molecular ammonia and hypochlorous acid is maximum) and decreases rapidly at higher and lower pH values. For example, at 25°C, with 0.8 ppm of chlorine and 0.32 ppm of ammonia nitrogen, about 1 minute is required for reaction of 99% of the chlorine, whereas at pH 5 approximately 210 minutes and at pH 11 approximately 50 minutes are required. The rate of the reaction also varies considerably with the temperature [4]. The 25°C rate constant given by Morris [7] for Equation 4 is $5.1 \times 10^6 \text{ liter mol}^{-1} \text{ sec}^{-1}$. Multiplying this by the concentrations of NH_3 and HOCl gives the reaction rate in mols/liter-second. The reaction activation energy is given as 3 kcal/mol. The reaction rate constant for the formation at 25°C of the dichloramine, Equation 5, is $3.4 \times 10^2 \text{ liter mol}^{-1} \text{ sec}^{-1}$, and the activation energy is 7.3 kcal/mol. The formation of the dichloramine is accelerated by the presence of H^+ and acetic acid (effects of other weak acids undetermined), varying linearly with their concentrations [7].

The loss of "free chlorine", in the form of hypochlorous acid, by decomposition to form oxygen in accordance with Eq. 8 is relatively

slow in the absence of light, but is catalyzed by ultraviolet illumination. For the average light intensities in a cell employed in research studies by Hancil and Smith[8], the time in seconds required to reduce the concentration from its initial value c_0 to c is approximately as given in Eq. 9. The rate of reaction depends on the rate

$$t = 7.8 \ln \frac{c_0}{c} \quad (9)$$

of absorption of light, which is directly dependent upon the concentration of either hypochlorous acid or the hypochlorite ion (rate apparently the same for both) and on the light intensity. From Eq. 9 it can be calculated that under the experimental conditions 31 sec. would be required to reduce the concentration of "free chlorine"* from a typical defouling value of 0.5 ppm to 0.01 ppm, a level at which fish in natural waters are perhaps no longer harmed by intermittent exposures with frequencies typical of defouling water treatments. Reaction times are greater by a factor of the order of 50 to 200 in the dark.

At equilibrium, the chlorate ion and the perchlorate ion are considerably more stable than the hypochlorite ion (see Eqs. 10 and 11)

*As noted earlier, uncombined useful chlorine is typically present in the forms of the hypochlorite ion and hypochlorous acid. The concentration of molecular chlorine that would have the same oxidizing capacity as is present in the OCl^- and HOCl is called the "free chlorine" level. The actual chlorine content of the OCl^- or HOCl is only half of the free chlorine level, since in these forms the chlorine has twice the oxidizing capacity per gram as has elemental chlorine (valence changes from +1 to -1 during the reduction reaction vs. the change from 0 to -1).

but the production of these ions from the hypochlorite ion is slower than Reaction 8 so the anions containing chlorine at higher oxidation states are normally not observed in chlorine solutions.

The chlorine in chloramines formed by reactions such as 7 and 8 still retains about half of its oxidizing potential (the driving force for oxidation) and these chemicals are effective bacteriocides, also harmful to natural water flora and fauna. If the free chlorine concentration reaches a level greater than 8 or 10 times the concentration of that of the nitrogen in chloramines, both free and combined chlorine are removed by the "breakpoint" reaction. The details of this reaction have not been completely determined and demonstrated, but the oxidation-reduction process is at least approximately as shown in Eq. 12 [9].

The nitrous oxide is largely lost to the atmosphere. The rate of the breakpoint reaction depends on the ammonia nitrogen level in the water (and perhaps on the quantities of other constituents present as well); at about 30 parts per million a few minutes is sufficient, while below one part per million, of the order of 1/2 hour is required [10]. Although this reaction is an effective means of removal of chlorine and chloramines under some circumstances, it probably has little significance in power plant use of chlorine for defouling, where the chlorine added is generally insufficient to initiate the breakpoint reaction.

Chloramines are also lost in natural waters and in such devices as cooling towers by evaporation. Quantitative rates are not available, but the dichloramine is said to be the most volatile; normal

practices are said to maintain a "zero" level of chloramines. Some free chlorine is also lost by the evaporation of molecular HOCl . No quantitative data on rates of loss are known. The evaporative loss of molecular chlorine is normally negligible due to its low concentration in the solution.

There are additional substances in natural waters that are oxidizable by free or combined active chlorine.* These include inorganic reducing agents, (S^- , Fe^{++} , Mn^{++} , NO_2^-) for which reaction rates are rapid, and a wide range of organic substances and organisms. The rate at which the organic materials react with chlorine is quite variable, depending on composition and state of physical aggregation. The overall situation is summarized by the identification of a "chlorine demand" for a natural water. This is the quantity of free or combined active chlorine that will be destroyed by reacting with the constituents of the water. Because of the varying rates of reaction, it is necessary to specify the contact time at which the chlorine demand is measured. The five-minute chlorine demand might be considerably greater than the one-minute chlorine demand.

Need for Information

As stated earlier, there are needs for standards; methods of prediction, supported by the necessary data; and monitoring, possibly requiring the development of methods or equipment.

It is understood that the national Environmental Protection Agency is preparing recommended criteria for the maximum concentration of active chlorine, presumably for combined and uncombined chlorine, that is acceptable in water discharged to natural waters. The criterion of acceptability will be the effects of active chlorine on marine biota, perhaps emphasizing effects on fish. The EPA criteria presumably will facilitate the establishment of standards.

*When chloramines oxidize other substances, ammonia (or ammonium ion) is re-formed.

If chlorine treatment is to be used for power plant cooling water, and its advantages do provide an incentive to continue chlorination, it will be necessary to develop plant designs and operating procedures that will make it possible to meet standards. This development will in turn require the development of procedures for calculating the active chlorine species to be expected under power plant conditions of water chemistry, operations, temperature, time, etc.

If once-through condenser cooling is used, it will be necessary to calculate realistic decay rates for chlorine residuals after leaving the condenser, considering the effects of mixing with untreated water some minutes before discharge to river or lake. This will require determination of rates of the pertinent reactions discussed above, as functions of water impurities and other conditions applicable to power plant usage, including:

Formation of chloramines,

Decomposition of HOCl to form oxygen,

Reaction of free and combined chlorine with organic impurities,

Evaporative losses for several species, representative of behavior in lakes and rivers, discharge canals and basins.

If a cooling lake is employed, and process water is dumped into it as well as condenser cooling water, it will be necessary only to show that all residual chlorine has decayed at the blowdown point. The same processes as above will occur, with available times and accessibility of light being much greater.

The use of a cooling tower requires demonstration that any residual chlorine in the blowdown, and in the process water discharge, meets standards at the point of discharge to river or lake. In addition, it becomes necessary to show that the active chlorine (HOCl or chloramines) evaporated or in the drift of the cooling tower is negligible. Again the same reactions are of potential importance.

Monitoring at the point of discharge will require analytical methods with adequate accuracy. For levels corresponding to standards that seem probable at this time, of the order of a few parts per billion, laboratory methods might not be available for use with natural waters, and the monitors that might be necessary to obtain data unbiased by the passage of excessive time between sampling and finished analysis are believed to be undeveloped.

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