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THREE MILE ISLAND NUCLEAR STATION - DOCKET NO. 50-289

Supplemental Testimony on Chlorine Releases

By

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Contention 6

It is contended that the plant should not be operable if and at such times when the cooling towers create any fog or misting that would create a hazard to vehicular and aircraft traffic. It is further contended that the applicant should be required to establish a cooling system by the use of the cooling towers that would minimize chlorination but would be the most efficient system as the state of the art will allow.

My testimony is addressed to the need for chlorination, the quantities of chlorine that will be released under well controlled state-of-the-art operating procedures, and the relationship of these quantities to the limits imposed in the Technical Specifications for Unit One. The remainder of the contention is addressed by supplemental testimony of Dr. J. D. Buffington and Dr. James E. Carson.

The presence of certain bacteria and algae in natural waters leads to the preferential formation and attachment of organic slimes to

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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 algal, while bacterial slimes predominate in closed heat-transfer surfaces. In power plants it is essential that the slimes be removed since they would otherwise seriously interfere with the transfer of heat and adequate flow of water, with resultant loss of plant efficiency and increase in the cost of power.

The removal is most commonly effected by the periodic addition of small concentrations of chlorine or a hypochlorite solution. In either case, hypochlorous acid,  $\text{HOCl}$ , is the primary active agent. This substance and the hypochlorite ion in equilibrium with it are the chlorine species present in greatest concentration in an aqueous solution formed by the addition of either chlorine or a hypochlorite to water. The hypochlorous acid-hypochlorite mixture in solution is called "free chlorine," with the concentration given as that of molecular chlorine having the same oxidizing capacity as the hypochlorous acid-hypochlorite actually present.

When ammonia (and ammonium ion) and certain organic compounds are present in water to which chlorine is added, the free chlorine reacts

with them to form compounds called chloramines, in which the chlorine retains some of its oxidizing potential, defouling capacity, and toxicity. With ammonia, the reaction is typically rapid, resulting in nearly complete conversion to the monochloramine ( $\text{NH}_2\text{Cl}$ ) in less than half a minute. The rate of reaction depends on concentrations of the ammonia and hypochlorous acids and the pH.<sup>1</sup>

Chemical defouling is accomplished by killing at least some of the organisms that largely comprise the slime. Unfortunately, agents that are toxic to slime bacteria are also toxic to other aquatic organisms, so it is desirable to manage defouling treatments so as to release as little of the toxic substance to the natural water as possible. Chlorine has a good combination of high toxicity to fouling organisms and a natural instability in water so that free chlorine persists only short periods before it decomposes to form chloride ion and free oxygen. The time of persistence is markedly reduced in the presence of light.<sup>2</sup> For example, under the ultraviolet illumination conditions of the laboratory study by Hancil and Smith,<sup>3</sup> an initial free chlorine concentration would decrease by a factor of 10 in about 18 seconds. Reaction times are greater by a factor of the order of 50 to 200 in the dark.<sup>2</sup> Chloramines, sometimes referred to as combined chlorine, also decompose in natural waters to form near-innocuous chloride. Decomposition times are longer than for free chlorine, ranging from a few hours to a few days.

Natural waters contain a variety of substances that react with chlorine (thereby reducing the chlorine to chloride). The quantity of chlorine reduced (per unit quantity of water) in a given exposure period is called the "chlorine demand" of the water for that period. This is a variable quantity, depending on variations in chemical and biological content of the water. For the Susquehanna River, the 15 minute chlorine demand was  $2.1 \pm 0.97$  (std. deviation) ppm for a series of 29 determinations between May 29, 1968 and November 7, 1969, given in the Final Environmental Statement (FES) Appendix 3.

In considering the discharge of chlorine from Three Mile Island Unit 1 at this time, it is assumed that Unit 2 will not be continuously discharging water to the river, and therefore such flow cannot be counted on to dilute (or provide chlorine demand for any residual chlorine to react with) chlorine in the Unit-1 discharge. It is recognized that this condition might not be representative of the situation later, when Unit 2 might be operating. The present analysis is therefore conservative with respect to the concentration of chlorine expected in the discharge to the river.

The analysis of expected chlorine releases for Unit 1 draws heavily on experience at other plants, especially at the John E. Amos Plant<sup>4</sup>, a coal-burning station in the Kanawha River in West Virginia. Chlorine-release data for this plant are the only known published data of this type for a cooling tower system; behavior very similar to that in the Amos Plant is projected for TMI. During the addition of chlorine to the Unit-1

circulating water system, the concentration of free chlorine at the condenser outlet will perhaps be fairly constant and the concentration of combined chlorine will probably continuously increase to a maximum equivalent to a major fraction of the concentration of ammonia nitrogen in the recirculating water. Following termination of chlorination, free chlorine would no longer be expected in blowdown taken downstream of the condenser, and the concentration of combined chlorine would be expected to decline first quickly, then more slowly. Detectable residual chlorine could be present in the blowdown for a couple of hours after chlorination had ceased.

It is probable that meeting the terms of the Unit-1 Technical Specifications will require that periods of chlorination be chosen so that the normal chlorine demand of the river water will be present in the effluent from the service water systems while chlorine is being released in the cooling tower blowdown and that the chlorine demand in the cooling tower blowdown will not be lowered by the presence of chlorine in the recirculating water system while chlorine is being released in the effluent from the service water systems. These conditions are therefore assumed in the analysis that follows. The analysis is based on the flowrates shown in Figure 8 of the FES.

It is considered possible that the addition of chlorine to the system ahead of the condenser can be regulated to provide a free chlorine level as low as 0.1 ppm at the condenser outlet while providing adequate de-

fouling for the condenser and the cooling towers. In the absence of knowledge of the concentration of ammonia nitrogen in the recirculating water, we shall use in our analysis a value of 0.5 for the maximum combined chlorine in the blowdown, immediately before chlorine injection is halted.

The 0.1 ppm free chlorine in the 2000 gpm blowdown will be diluted to 0.012 immediately upon mixing with the service water streams. By using an equivalent amount of the chlorine demand constituents of the service water, the free chlorine will probably be destroyed before discharge to the river. The 0.5 ppm maximum combined chlorine in the blowdown will be 0.058 ppm immediately after dilution with the service water streams. If one-third of the remaining 15-minute chlorine demand (about 2.04 ppm) in the service water is assumed effective in destroying combined chlorine before discharge to the river, there will be a considerable excess of this demand predicted, (factor of 10), and no measurable residual chlorine will exist in the discharge. The rate of destruction by chlorine-demand constituents cannot be predicted accurately, but when the loss of combined chlorine in the forced-draft cooling tower is considered, it is probable that circulating water chlorination will not lead to combined chlorine levels in the discharge to the river in excess of a few thousandths of a part per million. This is less than the maximum level deemed harmless for the Susquehanna River (see below).

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When service water is chlorinated, it is again considered possible that careful control of chlorine injection rates will lead to a free chlorine level at the point of discharge of the service water systems being treated of about 0.1 ppm. Referring to Figure 8 of the FES, the 15250 gpm combined discharge of the two service water systems will be diluted with the cooling tower blowdown (2000 gpm) and the chlorine demand of the cooling tower blowdown will probably destroy the free chlorine before discharge to the river. The chlorine demand of the cooling tower blowdown is estimated to be 2.88 ppm, the result of concentrating the demand of river water in the cooling tower circuit by a factor of 5.6<sup>\*</sup>, then losing an estimated three-fourths of that by reaction with oxygen in the cooling tower. There would thus be a calculated 3.8 times as much chlorine demand available in the cooling tower blowdown as required by the free chlorine in the service waters (assuming all the demand would be available to react before reaching the river).

Again the level of combined chlorine (in the service water discharge) is unknown because the ammonia nitrogen concentration (in the river water) is unknown at this time. The combined chlorine is therefore assumed to be 0.6 ppm, a value deemed likely to be at least approximately correct. If one-third of the remaining 15-minute chlorine demand in

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\* This is the calculated concentration factor for the rates of makeup and blowdown shown in Fig. 8 of the FES.

the cooling tower blowdown is again assumed effective in destroying combined chlorine before reaching the mechanical-draft cooling tower, there would remain 0.45 ppm of residual chlorine in the water. This might be reduced to 0.23 ppm by the loss of 50% of the combined chlorine in passage through the forced-draft cooling tower (an estimate based on observations for a natural draft tower<sup>4</sup>). This is in excess of the maximum level deemed harmless for the Susquehanna River for releases not greater than 2 hours per day (see next paragraph).

The Staff's determination\* of the maximum concentrations of combined chlorine in the plant discharge that could be predicted not to cause significant harmful effect on biota in the Susquehanna River was based substantially on the interim criteria of William A. Brungs<sup>5</sup> for receiving waters. The Brungs criteria for waters not containing sensitive species such as trout and salmon allow total residual chlorine releases not to exceed 0.2 ppm for a period of 2 hours per day and not to exceed 0.01 ppm for continuous discharge, with free chlorine essentially absent. These criteria have been applied by the staff to discharges to the river.

The estimates of chlorine releases from Unit 1 to the Susquehanna River indicate no expected violations of the staff criteria due to the chlorination of the circulating water system, but possible violations due to chlorination of the service water systems. By the terms of the technical specifications, plant operators will be required to record continuously

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\* See Supplemental Testimony by J. D. Buffington.

the concentrations of chlorine in the discharge to the river and in the cooling tower blowdown, and to comply with the criteria, with the exception of a ninety-day period (see below). The limit of two hours per day during which chlorine in the plant discharge will not exceed 0.2 ppm will be confirmed by direct monitoring, which will assure that releases from the nuclear and secondary service systems meet the criterion.

The release of chlorine in the cooling tower blowdown as well as in the service water effluent might result in a total duration of chlorine discharge from the plant in excess of two hours per day. In this event, it will be necessary to assure that for those periods in excess of two hours per day the chlorine in the cooling tower blowdown will not lead to discharges to the river in excess of 0.01 ppm. This concentration is believed to be below the limit of accuracy of known monitors. The method chosen is to limit the total residual chlorine in the cooling tower blowdown to 1 ppm. This number is believed conservatively to meet the 0.01 ppm criterion, in accord with the analysis above, so long as there is normal chlorine demand in the effluent water from the service water systems.

During a 90-day period, the company will determine the minimum chlorine releases associated with acceptable cleaning of service water system components and confirm the adequacy of the 1 ppm limit or establish an alternative limit. During this period, releases up to 0.5 ppm total residual chlorine will be permitted for periods not to exceed two hours

per day.

If compliance with the criteria is effected using optimized normal operating procedures (as already outlined by the Applicant), aquatic life is expected to be unharmed and there would be no measurable benefit to be sought by the institution of special measures to reduce or minimize chlorine levels in the plant discharge. In the event it proves impossible to comply with the criteria using normal operating procedures, other means can be employed in an effort to comply and to minimize chlorine releases. The following means could be considered (although additional problems might be created by each of them): (1) Mixing pumped river water with the discharge stream before it reaches the river; this will dilute and allow reaction between chlorine and chlorine-demand constituents in the untreated river water; (2) adding a retention pond to allow time for decay; (3) changing the location of chlorination so that it will be possible to chlorinate one of the two service water systems at a time; water from the untreated service water system will then serve the function of the river water in (1); (4) adding dechlorination chemicals as required. If, unexpectedly, violation of the criteria is caused by chlorination of the circulating water system, it is possible that the violation could be avoided by taking blowdown from the cooling tower basin or by prohibiting blowdown during those periods when the level of chlorine in the recirculating water system is too high.

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## REFERENCES

- (1) J. Carrell Morris, "Kinetics of Reactions Between Aqueous Chlorine and Nitrogen Compounds," pp. 23-53 in Principles and Applications of Water Chemistry, Ed. by Samuel D. Faust and Joseph V. Hunter, John Wiley and Sons, 1967.
- (2) See for example, Joseph E. Draley, "The Treatment of Cooling Waters with Chlorine," ANL/ES-12, February 1972.
- (3) Vladislav Hancil and J. M. Smith, Ind. Eng. Chem. Process Des. Develop., 10, 515-523 (1971).
- (4) J. E. Draley, "Chlorination Experiments at the John E. Amos Plant of the Appalachian Power Company: April 9-10, 1973," ANL-ES-23.
- (5) William A. Brungs, U. S. Environmental Protection Agency, National Water Quality Laboratory, "Review of Literature on the Effects of Residual Chlorine on Aquatic Life," to be published in J. Water Pollution Control Federation.