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**THERMAL DISCHARGES: CHARACTERISTICS AND CHEMICAL
TREATMENT OF NATURAL WATERS USED IN POWER PLANTS**

William L. Marshall

OAK RIDGE NATIONAL LABORATORY

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FEBRUARY 1971

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FOREWORD

This study was performed during the summer of 1970 as a contribution of the Task Force on the Program Plan on Thermal Discharges and Effects under the leadership of Marvin M. Yarosh. The work was supported as a part of the Environmental Quality Program of the Oak Ridge National Laboratory.

THERMAL DISCHARGES: CHARACTERISTICS AND CHEMICAL TREATMENT OF NATURAL WATERS USED IN POWER PLANTS

William L. Marshall

ABSTRACT

Several factors relating to the discharge of thermal waters to the environment from electrical power plants are reviewed. A survey of the chemical constituents of natural waters with respect to dissolved solids and gases, and their expected behavior on throughput of natural water coolants, is presented. The current practices in chemically treating natural waters for use as coolants are described in relation to the ultimate discharge of these chemicals to the environment. All types of thermal power plants are considered briefly, including dual-purpose plants that also desalinate water. Knowledge of chemical additives in thermal discharges is important for studies of the combined effect on the ecology of changes both in temperature and composition of natural waters.

1. INTRODUCTION

In the evaluation of aqueous thermal discharges to the environment, it is important to consider the combined effects of increased temperature, the natural constituents of water, and any substances added in the utilization of the water. The largest industrial use of cooling water is in thermal electrical power plants, where the rise in water temperature for once-through cooling is generally from 5 to 15°C. It is the purpose of this report, therefore, to present information on the constituents of natural waters and the resultant compositions of thermal discharges to the environment when these waters are used for cooling thermal power plants. Current practices of the thermal power plant industry in treating natural waters for use as coolants are reviewed in order to allow a better evaluation of the ecological effects of these thermal waters on the environment.

2. CHARACTERISTICS OF NATURAL WATERS

2.1 Chemical Composition of Natural Bodies of Water¹

The quantity of salts in open, natural bodies of water (i.e., those bodies of water which have a continual turnover of their water content through a process other than evaporation and precipitation) is usually in the range up to 200–300 mg/liter [approximately 200–300 parts per million (ppm) parts by weight of water solution], but the content in individual water bodies will vary enormously. A weighted mean average of all rivers has been given as 100 mg/liter.² These dissolved inorganic salts are for the most part composed of the same cationic and anionic species that are present in the largest quantity in ocean water, for example, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- , SO_4^{2-} , CO_3^{2-} , and HCO_3^- .^{1,3} Since the waters are open, any excess of chemicals due to the presence of contacting beds of readily soluble salts would have long before dissolved in geological time, and have been removed to the ultimate reservoir, the ocean. In the above sense, the ocean is considered a closed system with a mean chemical content of about 35,000 mg of dissolved solids per liter. The chemical content of estuaries or of seas will vary from approximately the above mean content of the ocean to the range of concentration of total dissolved salts given above for open lakes and rivers, depending upon the dilution effect at the particular site under consideration.

¹ G. Evelyn Hutchinson, *A Treatise on Limnology*, vol. I – *Geography, Physics, and Chemistry*, Wiley, New York, 1957.

² *Ibid.*, p. 553.

³ H. U. Sverdrup, M. W. Johnson, and R. H. Fleming, *The Oceans*, Prentice-Hall, New York, 1942.

Closed lakes are those bodies of water that do not have a continually flowing effluent, and thereby are able to concentrate dissolved substances through evaporation.⁴ In contrast to open lakes, the concentration of dissolved substances may be very high, whereby many separate salts may saturate the lake. The salts first saturating a lake will be those of low solubility, like CaSO_4 or CaCO_3 if the lake is in contact with beds of these salts. The rate of change in concentration of salts in these closed lakes will depend upon the relative difference between the rate of rainfall and rate of evaporation within the surrounding watershed, including the lake. In geological time, the lake therefore may be concentrating or diluting its salt content, with lakes undergoing the former process being the more predominant. There are relatively few very large closed, inland bodies of water; the Great Salt Lake, the Dead Sea, and the Caspian Sea are three of the more famous ones.¹ The extent of dissolved substances in two of these bodies of water (Great Salt Lake and Dead Sea) greatly exceeds that of the ocean and produces a saturated brine for both lakes. The concentration of dissolved salts in the Caspian Sea is lower than that for the ocean but considerably exceeds that of open bodies of water.

Although rainwater is the primary source of the water in open lakes and rivers, the ratio of dissolved salt components (or ionic species) generally is not the same as that in rainwater.⁵ In passing over a land surface, for example, over a limestone-dolomite area, the rainwater with its CO_2 content will dissolve such salts as CaCO_3 or MgCO_3 . In addition, through ion exchange mechanisms with the soil, ion adsorption on organic peaty material, and through other leaching processes, the effluent water will change its chemical composition. It is of interest to note that the total dissolved solids in rainwater appear to originate mostly from turbulent evaporation from the ocean, whereby dissolved salts are entrained into the vapor and retained in cloud particles.⁵ Rainfall may then deposit these salts ultimately into open waters. The concentration of chloride ion, as an example of usually the most abundant ion in rainwater, may vary from 70 to 700, 15 to 30, 3 to 5, 0.5 to 1.5, and <0.3 mg/liter at distances inland from an ocean of <0.1 , 1 to 2, 100, 1000, and 2000 km respectively.⁶

The concentration of major cationic species in open waters will tend to have a ratio $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$. The concentration of major anionic species will show ratios of $\text{CO}_3^{2-} > \text{Cl}^- \geq \text{SO}_4^{2-}$ for hard-water lakes and $\text{Cl}^- \geq \text{SO}_4^{2-} > \text{CO}_3^{2-}$ for soft-water lakes, although sometimes $\text{CO}_3^{2-} > \text{SO}_4^{2-}$ in a hard-water lake containing a very large amount of chloride ion.⁷ Nitrate ion and soluble silica will also usually be found in natural waters, where the former originates predominantly from the biological oxidation of compounds containing nitrogen and partly from the atmosphere, and the latter from dissolution processes. Many other ionic species of much lesser concentration may be present in open waters.

Estuaries are in a distinctly different class with respect to dissolved salts. Because of an interaction of tidal flow with river flow, which may vary widely due to the potentially wide variation of rainfall in the respective watershed, the chemical composition and concentration of estuary waters can show widely varying diurnal changes, as well as cyclical changes of much longer duration at times of flood or drought.

2.2 Dissolved Oxygen, Carbon Dioxide, and Nitrogen⁸⁻¹¹

The content of dissolved oxygen, necessary to maintain both animal and plant life in natural waters, is widely dependent upon the extent of vegetation within the natural water and on the temperature. The

⁴ Reference 1, p. 564.

⁵ Ibid., p. 541.

⁶ Ibid., p. 545.

⁷ Ibid., p. 562.

⁸ Ibid., chaps. 9, 10, and 16.

⁹ P. A. Krenkel and F. L. Parker (eds.), *Biological Aspects of Thermal Pollution*, Vanderbilt University Press, Nashville, Tenn., 1969.

¹⁰ F. L. Parker and P. A. Krenkel (eds.), *Engineering Aspects of Thermal Pollution*, Vanderbilt University Press, Nashville, Tenn., 1969.

¹¹ F. L. Parker and P. A. Krenkel, *Thermal Pollution: Status of the Art*, report No. 3, Department of Environmental and Water Resources Engineering, Vanderbilt University, Nashville, Tenn., December 1969.

equilibrium solubility of O_2 from an atmospheric mixture of gases at $25^\circ C$ and 1 atm is 8.3 mg per liter of pure water.¹² However the rate of absorption of oxygen into bulk water from the atmosphere is a very slow process. (It would appear that the oxygen and other gases dissolve readily only in the surface layer of water.^{9-11,13} Convection currents then carry the dissolved gas to the bulk of the liquid; thereby, a fresh layer of less saturated water continually reaches the surface and absorbs gas. Turbulent surfaces, therefore, greatly increase the rate of dissolution of gas.) Because of this slow process, and where the epilimneal (upper layer) temperature shows only small changes with time (e.g., 1 or $2^\circ C$ per month would be considered small), the dissolved oxygen concentration may be undersaturated. The amount of undersaturation may vary from 60 to 80% of saturation depending upon the temperature, the number of fish and bacteria, and the extent of underwater vegetation; these factors dictate the continuing demand for oxygen [the biological oxygen demand (BOD)]. Of course, any man-made discharges (which contain nutrients, vegetation, or bacterial life that increases oxygen consumption) to natural waters will increase the total demand for oxygen, and thereby increase the extent of undersaturation of oxygen. Ultimately, those species incapable of surviving under these conditions of low oxygen content will disappear, with a subsequent new attainment of equilibrium between surviving species, the dissolved oxygen (at ecological equilibrium), and the altered system.

Carbon dioxide in an ecological system is a necessary constituent of natural waters for photosynthesis in plants.¹⁴ Although its solubility at $25^\circ C$ in pure water from pure carbon dioxide gas (plus water vapor) at 1 atm is 36 times that of oxygen by weight (26 times by molar ratio CO_2/O_2),¹² it is only 0.052 times that of O_2 (0.038 times by molar ratio)¹² from a natural air composition containing 0.03 vol % of CO_2 and 20.99% O_2 at 1 atm air pressure.³ [The value "about 200 times that of oxygen" stated elsewhere¹⁴ (p. 654 of ref. 13) would appear to originate from the dissolved weight per liter of CO_2 saturating water from a pure 1 atm of CO_2 divided by the dissolved weight per liter of O_2 saturating from a natural air composition at 1 atm. This ratio at $25^\circ C$ is equal to 175 but does not appear useful for comparisons; it most certainly is an error of presentation. (The solubilities of CO_2 from natural air given in Table 79, p. 654, of ref. 13, are expressed as milligrams of CO_2 per liter of water.)] Like oxygen, the usual concentration of carbon dioxide in natural waters may be somewhat below its saturation value. The concentration of carbon dioxide usually dictates the normal extent of acidity of a natural water; this acidity may range in most cases from a pH [$-\log$ concentration of H^+ (moles per liter)] of 6.0 to 8.0. In very extreme cases, however, the pH may range from 1.70 in some volcanic lakes containing free sulfuric acid to 12.0 or more in some closed alkaline lakes. These extreme values of pH represent rare conditions and should therefore be of little concern here.

The solubility of nitrogen in pure water from air at $25^\circ C$ and atmospheric pressure is 14.5 mg N_2 per liter of water, or 1.74 times that of O_2 by weight (2.0 times by molar ratio).¹² As a gas, nitrogen does not appear to be at all vital to life processes, but of course is a necessary constituent of all life when combined with other elements.

Partly because of the slowness in the rate of evolution of gases in general from water, all three of the above gases, O_2 , CO_2 , and N_2 , may sometimes supersaturate water. This supersaturation may occur in several ways. Excess oxygen and carbon dioxide production by plant, fish, and animal life in the water can

¹² A. Seidell and W. F. Linke, *Solubilities of Inorganic and Metal-Organic Compounds*, vols. I and II, American Chemical Society publication, Washington, D.C., 1965. The solubilities and relative solubilities of oxygen, nitrogen, and carbon dioxide gases in (pure) water given in the text were evaluated from the data reported and compiled in these two volumes, and a composition of natural air given in ref. 3, p. 187.

¹³ G. Evelyn Hutchinson, *A Treatise on Limnology*, vol. I - *Geography, Physics, and Chemistry*, pp. 575-92, Wiley, New York, 1957.

¹⁴ *Ibid.*, chap. 10.

produce supersaturation. Nitrogen may also be produced by bacterial action under particular conditions. In another mechanism, turbulent water falling over a ledge (a waterfall) into a deep trough may become saturated with the various gases during the period of turbulence. Gas bubbles carried with the water into the trough will be hydrostatically compressed; thereby, additional gas may dissolve.¹⁵ The subsequent movement of this gas-saturated water toward the surface, with a decreasing hydrostatic pressure, may then produce gas supersaturation. Cold water, containing dissolved gases, that warms up can also produce gas supersaturation if the respective equilibrium limits of gas solubility are exceeded. These two latter processes can occur naturally with flowing water (in streams, rivers) or can be caused by man-made constructions. Thus turbulent water flowing over a dam spillway into a deep trough, like that for particular dams on the Columbia River (Oregon), would be an example. Cold water taken from the bottom of a man-made lake to drive a hydroturbine and subsequently warmed up near the surface of the outflow river would be another example of the potential occurrence of supersaturation. Gas supersaturation is of vital significance to aquatic life since it can cause a condition ("gas bubble disease") in fish somewhat similar to "the bends" in man.¹⁶⁻¹⁸ Gas bubbles produced in the blood that has become supersaturated with gas under these conditions can cause death.

3. TREATMENT OF COOLANT WATERS IN THERMAL POWER PLANTS; INPUTS TO AN ECOLOGICAL SYSTEM

3.1 Once-Through Cooling of Power Plant Condensers

With respect only to the physical input to the ecological system, the chemical composition (including gas concentration in the water) of natural waters used in once-through cooling systems does not appear to be changed by present thermal electrical power plant practices. Generally, the concentration of a dissolved solid is so far removed (usually several orders of magnitude lower than the solubility limit) from its saturation value that any change in concentration must arise from a process such as corrosion (oxidation-reduction) within the power plant condenser coolant system. In modern practice, however, corrosion is negligible in once-through coolant systems. The dissolved concentration of gases in coolant water does not appear to be changed significantly by once-through cooling processes.¹⁹ This lack of effect arises both from the usual undersaturation of oxygen and carbon dioxide in natural waters (although supersaturation can indeed occur; see Sect. 2.2) and from the very slow rate of evolution of a gas such as O₂, CO₂, or N₂ from water if the water becomes momentarily supersaturated at an elevated temperature within the condenser. The acidity of the water also is little affected since no significant loss of CO₂ occurs. Although the natural concentration of dissolved substances may not change during the once-through cooling process, the effluent (outfall) may differ in composition from its receiving water. If water is withdrawn from the hypolimnion of very deep, still lakes, this water may be essentially devoid of dissolved gases (and of life), and therefore the effluent discharged on the surface, although not supersaturated with

¹⁵Reference 11, Appendix, p. A-7.

¹⁶G. R. Snyder, *Thermal Plants, Thermal Pollution, and Fish - the Problem in the Columbia River and the Pacific Northwest*, U.S. Bureau of Commercial Fisheries, Biological Laboratory, Seattle, Wash., 1968.

¹⁷W. S. Davis and G. R. Snyder, *Aspects of Thermal Pollution That Endanger Salmonid Fish in the Columbia River*, U.S. Bureau of Commercial Fisheries, Seattle, Wash., 1967.

¹⁸W. J. Ebel, "Supersaturation of Nitrogen in the Columbia River and Its Effect on Salmon and Steelhead Trout," *Fishery Bulletin* 68(1), 1 (1969).

¹⁹F. L. Parker and P. A. Krenkel, *Thermal Pollution: Status of the Art*, report No. 3, Department of Environmental and Water Resources Engineering, Vanderbilt University, Nashville, Tenn., chap. III, pp. 37-42, December 1969.

gases, would still have a detrimental effect on life. Many electrical power plants draw once-through coolant water from the hypolimnion (but not from the excessively deep, still lakes) and discharge it to the epilimnion. However, many of the new state water quality regulations are requiring that withdrawn waters be returned to the same water strata from which they were taken.

In the usual practice for the treatment of once-through water from open rivers or lakes, the gas chlorine is added as a bactericide and algicide (combined term: biocide) about three times a day (shock treatment) for approximately a 30-min period for each addition.²⁰⁻²² The residual chlorine (that is, that amount not consumed in killing algae and bacteria on condenser tubes) is kept below 0.1 to 0.5 ppm in the effluent, depending upon the condition of the water, which is partly related to the season of the year (see below). Algae and bacteria form slimes on condenser tubes. These slimes drastically lower both the thermal and mechanical efficiency of the condenser, and in the extreme could essentially stop the flow of coolant. Chlorine is the most generally accepted biocide for once-through condensers. When ocean or estuary waters are used for once-through cooling, the dosage of chlorine may be increased to as high as 4-5 ppm to prevent mussel and crustacean growth (that form scales on condensers) and to 12 ppm to deter eels and jellyfish.²² Again, for these waters the shock treatment may be used for approximately 30-min periods several times a day, or for a single 4-hr period. These approximate concentrations of chlorine appear in the effluent and are then diluted by the external body of water. Sometimes, but rarely, sodium hypochlorite is used in place of free chlorine.

In many instances, natural coolant water is sufficiently free from algae and slime-forming bacteria that it is unnecessary to add a biocide.²³ Where a biocide is needed (for most once-through coolant waters), the concentration required (0.1 to 0.5 ppm) to eliminate slimes will vary with the season; the highest concentration is usually required in the spring when algae blooms may occur. Some power plants may require the addition of a biocide only at that time of year.

The condensers of some plants may be designed so that hot water can be flushed periodically through the condenser tubing in order to remove slimes or crustaceans.²⁴ This thermal shock method has been used, but not too frequently. In another method, sponge rubber balls of diameters varying from 0.5 to 1 in. to fit the condenser tubes are circulated through the tubes of the condenser.^{25,26} Initially, sponge rubber balls that are partly coated with tungsten carbide may be circulated through tubes for an extensive cleaning of the condenser. These balls are later replaced by the standard sponge rubber balls for continuous use. The process²⁷ is currently used extensively in electrical power plants in Europe, and also is used in many electrical power plants in the United States. Both the thermal shock and rubber ball methods for preventing slime formation eliminate the need for biocides and the consequent input of these chemicals (chiefly Cl_2) to the environment.

²⁰Fischer and Porter Company Application Bulletin 90-49-18, *Chlorine Shock Treatment for Slime and Algae Control*, publication 14435, Fischer and Porter Co., Warminster, Pa. (January 1963).

²¹G. V. James, *Water Treatment: a Guide to the Treatment of Water and Effluents Purification*, The Technical Press, Ltd., London, revised 1965.

²²W. H. Betz and L. D. Betz (eds.), *Handbook of Industrial Water Conditioning*, 4th ed., W. H. and L. D. Betz, Gillingham and Worth Sts., Philadelphia, Pa., 1953.

²³See, for example, *The Bull Run Steam Plant*, Tennessee Valley Authority technical report No. 38 (Nov. 27, 1967).

²⁴J. G. Dobson, "The Control of Fouling Organisms in Fresh and Salt Water Circuits," *Trans. Amer. Soc. Mech. Eng.* 68, 247 (April 1946).

²⁵J. R. Maurer, "The Use of Stainless Steel Tubing in Condensers and Related Power Plant Equipment - a Progress Report," *Combustion* 39, 2 (July 1967).

²⁶A. Heidrich, J. J. Roosen, and R. G. Kundle, *Calorimetric Evaluation of Heat Transference by Admiralty Condenser Tubes*, report No. 65-WA/CT-2, The American Society of Mechanical Engineers (Sept. 1, 1966).

²⁷The Amertap Corporation, Garden City, N.J.

3.2 Water Discharges Other than Once-Through Coolant

3.2.1 Discharges (Blowdowns) from Cooling Towers. Although the use of cooling towers with electric power plants is rather extensive in Europe (chiefly, natural draft evaporative types), relatively few of these towers are used for thermal power plant operations in the United States, but their use is increasing. In continual operation of a cooling tower, selected chemicals usually are added to the water to prevent corrosion of metal parts, to inhibit slime-forming bacteria and algae, to inhibit deterioration of wood used in the construction of the towers, and to prevent scale deposition of CaCO_3 , Ca(OH)_2 , MgCO_3 , Mg(OH)_2 , and similar precipitates.^{21,22} The chemicals used and their amounts depend on the quality of the water used in the particular cooling tower and on the economic justification for their use. Evaporative-type cooling towers may concentrate the water by the vaporization of as much as 1 m³ (of liquid) per second per 1000 MW(e) output.²⁸ Consequently, makeup water must be continually added, with additional chemicals. Also, intermittent or continual liquid discharges (blowdowns) to the environment must be made to prevent the increasing concentration of chemicals (both added and naturally present) upon the vaporization of the water.

Blowdowns usually are discharged directly either to a river or to an open body of water; or where both cooling towers and once-through cooling are employed, they are discharged to the once-through coolant. The blowdown ultimately is discharged to the environment in either case. Where particular highly toxic chemicals may have been used, these substances might be removed by chemical means before the blowdown is discharged to a water body. In the past, the incentive for removing obviously toxic substances probably originated only from adverse reaction from the local population.

Blowdowns can be discharged also to a reservoir (e.g., a lined pit) or closed lake where the chemicals are concentrated by natural evaporation of water. No immediate discharge to the outer environment would occur under these conditions. However, upon continuing evaporation of water, solid precipitates might ultimately need to be physically removed to other locations.

3.2.2 Chemical Treatment of Waters Used in Cooling Towers.^{21,22} Water used for recycling in cooling towers is treated more elaborately than once-through waters. Since the water not lost by vaporization is recycled through the condenser, particular chemicals can be added that would not be economically feasible otherwise. Aside from economy, other chemicals are required for these systems that are not required for a once-through coolant. In routine operation, the chromate ion in sodium chromate (Na_2CrO_4) may be added to maintain from 25 to 50 ppm chromate in order to prevent corrosion of the condenser surfaces and any other metal parts in the system. Prior to routine operation, approximately 600 to 1200 ppm chromate (in Na_2CrO_4 , the most economical chromate compound) may be circulated in the coolant water at the operating temperature for periods varying from 48 hr to two weeks.^{21,22} With this procedure, the metal surfaces are passivated (protected) against corrosion; a chromium oxide passive film is thus placed on the metal surfaces. The concentration of chromate ion may then be reduced to that given above for routine operation. Also, many different, for the most part proprietary, organic-based compounds are used to inhibit corrosion. There are many types, with subtle differences for particular water qualities and for particular cooling tower designs. Some of these compounds are used also as additives to once-through cooling waters, although the economics of these additions will limit the amount that can be added. Probably the most widely used substances at the present time are the organic polyphosphate compounds. Some other proprietary compounds used are labeled "silicate," "silicate-condensed phosphate," "chromate-condensed phosphate," "organic-zinc," "chromate-zinc," "chromate-zinc-organic," "nitrate-borate-organic," "organic-

²⁸F. L. Parker and P. A. Krenkel (eds.), *Engineering Aspects of Thermal Pollution*, chap. 9, Vanderbilt University Press, Nashville, Tenn., 1969.

zinc-condensed phosphate," and "buffered chromate."²⁹ "Silicate" usually refers to sodium silicate, commonly termed "water glass." Sodium ferrocyanide and sodium nitrite are sometimes used as corrosion inhibitors, but rarely.^{21,22}

Most conventionally constructed evaporative cooling towers contain wood. In these towers, the dosage of chlorine as a biocide is limited to about 0.5 ppm or less because of the deteriorative effect of chlorine on wood. An evaporative cooling tower provides ideal conditions (e.g., warmth, sunlight, air, moisture) for the growth of algae and fungi (slimes), and therefore biocides must be used in larger quantity than for once-through coolant water. In the recent past, organic compounds that contained combined mercury, tin, arsenic, or lead were used somewhat extensively. At the present time these biocides, which are highly toxic to fish and animal life when discharged in the blowdown to the environment, are very seldom used. Instead, proprietary organic compounds, which are presumed, evaluated, or stated to be less toxic to fish and animal life, are now used predominantly as biocides.³⁰

Where the water to be used in a cooling tower is sufficiently hard (i.e., the water contains moderately high concentrations of calcium, magnesium, sulfate, or carbonate ions which may produce scale-forming precipitates upon increasing concentration or at high temperature), sodium hexametaphosphate (a polyphosphate), glassy silicate (a mixture of sodium silicates), or other related substances are added to complex the compounds with the troublesome elements in order to prevent or inhibit scale formations by CaSO_4 , CaCO_3 , MgCO_3 , Mg(OH)_2 , Ca(OH)_2 , or other substances. The compound ethylenediaminetetraacetic acid (EDTA) has also been used for this purpose in special applications, but the relatively high cost of this substance prohibits its widespread use.^{29,30}

The acidity (pH) of cooling tower water usually is adjusted, if necessary, to a pH of 6.5 to 8.0 by the addition of sodium hydroxide solution. Commonly, very dilute sulfuric acid solution is added first to decompose carbonate ions (a scale former where Ca^{2+} or Mg^{2+} is also present) to CO_2 (removed) and water; sodium hydroxide is then added (a back titration) to readjust the pH to 6.5–8.0. Ammonia solution is usually never added to adjust the pH since corrosion of metal alloys containing copper is accelerated. In this corrosion process, aqueous ammonium hydroxide reacts with CuO (an insoluble protective film) to produce a soluble $\text{Cu(NH}_3)_4^{2+}$ complex that ultimately would be discharged to the environment.^{21,22,31} Copper as an alloy constituent of condensers is widely used, and as the Cu^{2+} ion [which might arise from soluble $\text{Cu(NH}_3)_4^{2+}$] it is highly toxic to fish and animal life.

A typical discharge from a recirculating tower may contain about 1500 to 10,000 ppm of total dissolved solids (TDS) in the effluent.²² For a once-through cooling tower, rarely used because of high operating cost, where sulfuric acid may be added to the throughput water to remove carbonate ion, the TDS is usually about 500 to 600 ppm. Sodium hydroxide is added in the treatment to readjust the pH to 6.5–8.0; thus the resulting sodium sulfate is included in the above TDS.

3.2.3 Water Desalination: Dual-Purpose Thermal Power Production Systems. Desalinated water can be produced as a by-product of steam-cycle electrical power production by using ocean or brackish water as the coolant and extracting heat from the turbine cycle for distillation of the coolant water. A program is in progress on the design of very large scale dual-purpose power plants (i.e., plants producing both electrical energy and pure water).³² The water discharged back to the environment from these dual-purpose plants

²⁹ *Corrosion in Cooling Waters*, Drew Chemical Corporation technical bulletin No. 2161-68, 552 Fifth Ave., New York, N.Y. (1968).

³⁰ *Biocides*, Drew Chemical Corporation technical bulletin No. 2223-68, 552 Fifth Ave., New York, N.Y. (1968).

³¹ M. G. J. Desensy, "Materials for Seawater Cooling," *Chem. Eng.* 77, 182 (1970).

³² United States–Mexico–International Atomic Energy Study Team, *Nuclear Power and Water Desalting Plants for Southwest United States and Mexico*, document No. TID-24767, CFSTI, U.S. Bureau of Standards, U.S. Department of Commerce, Springfield, Va. 22151.

will be a more concentrated brine (by a factor of about 2 to 3 times by volume for ocean water). Although no large dual-purpose plant is yet in operation, the chemicals that might be added to the source coolant water probably would be the same as those added in conventional water desalination processes. Thus, in the usual practice, sulfuric acid is added to prevent alkaline scale formation, as described in Sect. 3.2.2. In addition, proprietary polyglycol substances are added to prevent foaming of ocean or brackish water on distillation.

3.2.4 Closed-Cycle Boiler-Water Turbine Systems.^{33,34} The designs of steam-cycle electrical power plants are usually of two classes: (1) the subcritical pressure steam cycle with a boiler temperature ranging from 260 to 540°C and (2) the supercritical pressure steam cycle with a boiler temperature of about 540 to 565°C. Fossil fuel plants are designed for both classes, whereas present-generation light water nuclear fuel plants are predominantly designed for subcritical pressure and relatively low temperatures of 260 to 370°C. The requirements for boiler water quality are different for these two classes.

For the supercritical pressure class, in order to inhibit corrosion and scale formation, the boiler water must contain considerably less than 1 ppm of total dissolved solids, for example, in the order of parts per billion (ppb). Thus the water must be "polished" extensively before its addition to the boiler system. This water must be essentially "electrical conductivity water," that is, equivalent to very pure water used for determining a background conductance required for exact determinations of electrolyte conductances in water. To obtain this purity, the initial, preliminarily purified water may be "flash evaporated" and passed through a cationic-anionic mixed-bed exchange resin. All gases (i.e., O₂, N₂, CO₂, and the other gases of air) are removed by the flash evaporation process. In usual present-day practices, during power plant operation a side stream or full flow of boiler water is passed through a mixed-bed resin for continual purification. At intervals the mixed-bed resin must be regenerated, and this is done by passing moderately concentrated sodium chloride or sulfuric acid through the bed. The spent regenerating solution (eluent) from this process must then be discharged to the environment, usually by direct discharge to a once-through coolant effluent.

The water quality for subcritical boilers, with provisions for blowdown, does not need to meet the highly restrictive standards required for supercritical pressure steam generators. The problem of corrosion is not as severe, and particular chemicals can be added to inhibit corrosion. However, for most operations it is important that free oxygen gas be removed because this gas can cause and induce considerable corrosion. Relatively pure water may be obtained commercially, for example, from a city water system supply, and substances such as morpholine,²¹ hydrazine,²¹ or catalyzed sodium sulfite (a commercial preparation of Na₂SO₃ with about 0.5 ppm CoSO₄ catalyst added)³⁵ are usually added to remove oxygen by chemical reaction (reduction of oxygen and simultaneous oxidation of the additive). For the latter reagent (Na₂SO₃), approximately 7 to 10 times the weight of dissolved oxygen concentration is added; this process leaves about 0.5 ppm of Na₂SO₃ as a residual impurity. The acidity is adjusted to a pH of 6 to 7 by addition of sulfuric acid; water of a pH higher than 7 (i.e., an alkaline solution) will embrittle the steels conventionally used for boiler construction. The above additives to low-temperature boiler water eventually are discharged to the environment, usually by injection into the once-through coolant effluent.

3.2.5 Closed-Cycle Primary Coolant Loops. In nuclear-fueled electrical power reactors, the heat generated by the reactor is transferred to the boiler-turbine (secondary) cycle by means of a primary

³³ J. A. Signorelli, "Perspectives on Steam Cycles for Nuclear Power Plants," *Nucleonics* 23, 45 (April 1965); D. K. Davis, "Nuclear Steam Systems," *Proc. Amer. Power Conf.* 27, 302 (1965).

³⁴ Paul Cohen, *Water Coolant Technology of Power Reactors*, USAEC monograph (under direction of the American Nuclear Society for the Atomic Energy Commission), Gordon and Breach Science Publishers, New York, 1969.

³⁵ Nalco Product Bulletin B-19, *Nalco 19 Chemical Deaerator*, Nalco Chemical Company, Chicago, Ill.

coolant cycle. The water used in this primary cycle must be purified ("polished") extensively as described in Sect. 3.2.4 for water used in supercritical pressure steam cycles. This requirement for primary loops of nuclear power plants is needed not only for the inhibition of corrosion (although the primary containment loops are constructed of highly corrosion-resistant alloys) but to eliminate those impurities that would become radioactive. Boric acid (H_3BO_3), however, is conventionally added to provide an initial concentration of about 1800 ppm as boron.³⁶ Boron with its high affinity for neutrons acts as a shim material in the control of the reactor. The buildup of neutron poisons within the core of the reactor is partially offset by the controlled chemical removal of boron from the primary coolant. The main nuclear reaction by which the boron functions is

In a typical power reactor operation, the initial boron operating concentration of about 1800 ppm would be reduced to about 10 ppm at the end of the power production operational cycle. Several other compounds containing elements of high thermal neutron capture (for example, gadolinium, cadmium, samarium, and europium)³⁷ have been considered but to the present have not been used in an operation as a constituent of a dissolved salt. A rather sophisticated discussion of all current details of primary loop coolant technology, including all chemical additives tested or considered, is that by Cohen,³⁴ many references are given. Since for nuclear power plants the past emphasis has been on the prevention of radioactive contamination of the environment, the discharges (blowdowns) from primary loops always are retained in a closed system, although the water content may be evaporated.

As for conventional boiler waters, the same chemicals and by-products are used and produced from the purification of these primary-cycle waters and from the regeneration of mixed-bed ion exchange resins. These added substances in water solution also are usually discharged to the once-through coolant water for dilution and incorporation into the effluent.

4. CONCLUSION

In this report, a review of the nature of the constituents of natural waters and the current practices in the thermal power industry in treating these waters for use as coolants has been presented. A judgment of the relative merits of the various treatments is not attempted. It is hoped, however, that this review will be useful to those undertaking further studies on the ecological effects of chemical-thermal discharges to the environment.

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³⁶Reference 34, p. 161.

³⁷Ibid., p. 168.

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