STEAM

1. Introduction

Steam [7732-18-5], gaseous H_2O, is the most important industrially used vapor and, after water, the most common and important fluid used in chemical technology. Steam can be generated by evaporation of water at subcritical pressures, by heating water above the critical pressure, and by sublimation of ice. Steam is used in electric power generation; for driving mechanical devices; for distribution of heat; as a reaction medium; as a solvent; as a cleaning, blanketing, or smothering agent; and as a distillation aid. It is so widely used because water is generally available and steam is easy to generate and distribute. It has high latent heat, moderate density, and, except for thermal characteristics, nonpolluting properties. Steam provides easy control of temperature in processes and heating applications because the temperature is a function of pressure, which is easy to control.

Steam is generated from water by boiling, flash evaporation, and throttling from high-to-low pressure. The phase change occurs along the saturation line such that the specific volume of steam is larger than that of the boiling water. Thermal energy, ie, the heat of evaporation, is absorbed during the process. At the critical and supercritical pressures, the water–steam distinction disappears, and the fluid can go from water- to steam-like properties without an abrupt change in density or enthalpy. The heat of evaporation under these conditions becomes zero.

Properties of steam can be divided into thermodynamic, transport, physical, and chemical properties. In addition, the molecular structure and chemical composition of steam are of interest. It was at the start of industrialization, ~1763, that thermodynamic relationships were first measured by Watt. A century later, in 1859, Rankine published his *Manual of the Steam Engine*, which gave a practical thermodynamic basis for the design and performance of steam engines.

The thermodynamic and physical properties of pure steam are well established over the range of pressures and temperatures used. The chemical properties of steam and of substances in steam, their molecular structures, and interactions with the solid surfaces need to be more fully explored.

2. Physical Properties

2.1. Official Properties. The physical properties of steam have long had considerable commercial importance. The expected efficiency of steam turbines depends on them. The first steam tables for practical use were based on Regnault's data (1) and began to appear toward the end of the nineteenth century. A thermodynamically consistent set of equations for fitting data was devised in 1900 by H. L. Callendar and was adopted by Mollier and others. The library of the United States National Institute of Standards and Technology (NIST) contains six different steam tables published between 1897 and 1915. The necessity of international property formulations was recognized as early as 1929, when the First International Steam Table Conference was held in London. As of this writing (2006), 14 international conferences on the properties of steam have been held. In 1972, the International Association for the Properties of Steam (IAPS) was formed. At the 12th International Conference on Properties of Water and Steam (ICPWS), IAPS changed its name to the International Association for Properties of Water and Steam (IAPWS), an association of national committees that maintains the official standard properties of steam and water for power cycle use. In the United States, the national committee is sponsored by the American Society of Mechanical Engineers (ASME).

IAPWS maintains two formulations of the properties of water and steam. The first is an industrial formulation, the official properties for the calculation of steam power plant cycles (2). This formulation is appropriate from 0 to 100 MPa (0 to 14504 psia) and from 0 to 800°C (32 to 1472°F). In addition, there is a region from 800 to 2000°C (1472 to 3632°F) and 0 to 10 MPa (0 to 1450 psia), which is appropriate for use in combustion turbines. Because there is considerable industrial cost in changing from one set of properties to another, this formulation is revised every 25–30 years. This formulation is used in the design of steam turbines and power cycles and in computerized fluid dynamics. Millions of calls to the steam properties routines based on this formulation may be made in a single design calculation, thus the computational speed of the industrial formulation remains a significant issue. The IAPWS maintains a second formulation of the properties of water and steam for scientific and general use from 0 MPa (extrapolating to ideal gas) at 0°C (0 psia at 32°F) to the highest temperatures and pressures for which reliable information is available. This latter formulation is revised as new data become available. Because the normal use of this formulation is for modest numbers of calculations, computational speed is not an issue. This second formulation agrees with the industrial formulation within the tolerance of the industrial formulation. The general and scientific formulation is made available in the United States by NIST (3). The IAPWS conducts a conference every 4 years, and the official properties formulations and releases as well as guidelines on other properties of steam and water have been

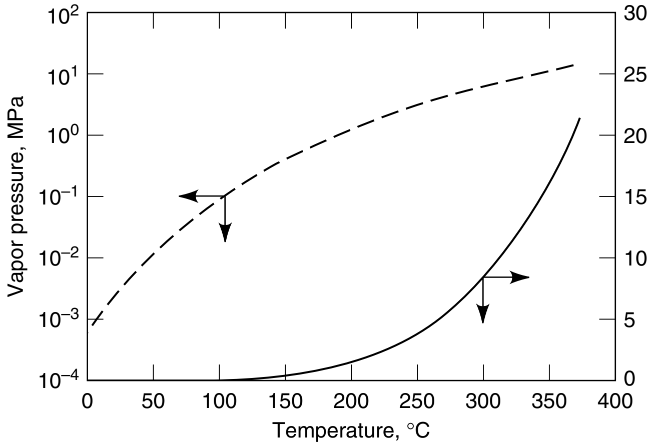

Fig. 1. Vapor pressure of ordinary water, where (—) represents linear and (– – –) logarithmic scale. To convert MPa to psi, multiply by 145.

published in the conference proceedings (4), but are now maintained on their website (5).

2.2. Thermodynamic Properties. Ordinary water contains three isotopes of hydrogen [1333-74-0], ie, ^1H, ^2H, and ^3H, and three of oxygen [7782-44-7], ie, ^{16}O, ^{17}O, and ^{18}O. The bulk of water is composed of ^1H and ^{16}O. Tritium [15086-10-9], ^3H, is present only in extremely minute concentrations. The concentrations of deuterium [16873-17-9], ^2H, ^{17}O, and ^{18}O in water and steam are 0.015574(5), 0.03790(9), and 0.20004(5) atom percent, respectively (6). The thermodynamic properties of heavy water (water with all hydrogens replaced by deuterium, D_2O) are subtly different from those of ordinary water. The IAPWS has special formulations for heavy water. The properties given herein are for ordinary water having the usual mix of isotopes.

Vapor Pressure. Vapor pressure is one of the most fundamental properties of steam. Figure 1 shows the vapor pressure as a function of temperature for temperatures between the melting point of water and the critical point. This line is called the saturation line. Liquid at the saturation line is called saturated liquid; liquid below the saturation line is called subcooled. Similarly, steam at the saturation line is saturated steam; steam at higher temperature is superheated. The properties of the liquid and vapor converge at the critical point, such that at temperatures above the critical point, there is only one fluid. Along the saturation line, the fraction of the fluid that is vapor is defined by its quality, which ranges from 0 to 100% steam. When both steam and water are present, the liquid phase in the steam is generally called "moisture" and the steam "wet steam".

Density. The density of saturated water and steam is shown in Figure 2 as a function of temperature on the saturation line. As the temperature approaches the critical point, the densities of the liquid and vapor phase approach each other. This fact is crucial to boiler construction and steam purity because the efficiency of separation of water from steam depends on the density difference.

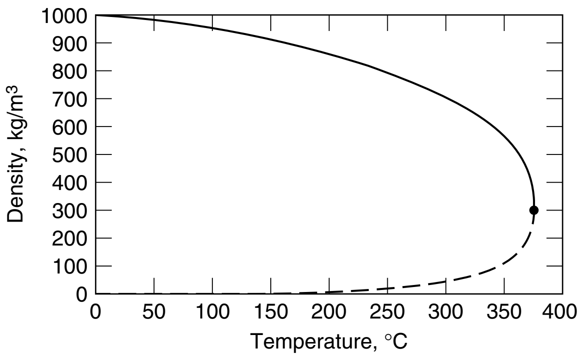

Fig. 2. Density on saturation line of (—) water and (– – –) steam, where (●) represents the critical point.

Internal Energy, Enthalpy, and Entropy. The enthalpies and internal energies of steam and water on the saturation line are shown in Figure 3. Like the density, these converge at the critical point. The entropy along the saturation line is shown in Figure 4. Many plots of enthalpy, internal energy, and entropy are possible, but the Mollier chart (Fig. 4) combines these in a useful way. Before the advent of computer programs to generate values of properties, Mollier charts printed in very large sizes allowed accurate reading of values for equipment design. The heat capacity at constant pressure, C_p, defined as the derivative of enthalpy with respect to temperature, is shown in Figure 5. The value of C_p becomes very large in the vicinity of the critical point. The variation is much smaller for the heat capacity at constant volume, C_v, also given in Figure 5.

Speed of Sound. The speed of sound (Fig. 6) is important to choking phenomena, where the flow of steam is no longer simply related to the difference in pressure.

2.3. Transport Properties. Viscosity, thermal conductivity, the speed of sound, and various combinations of these with other properties are called transport properties, which are important in engineering calculations. Thermal

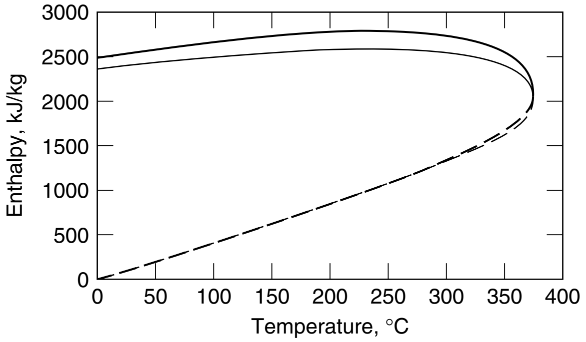

Fig. 3. Enthalpy (bolded line) and internal energy of (– – –) water and (—) steam. To convert kJ to kcal, divide by 4.184.

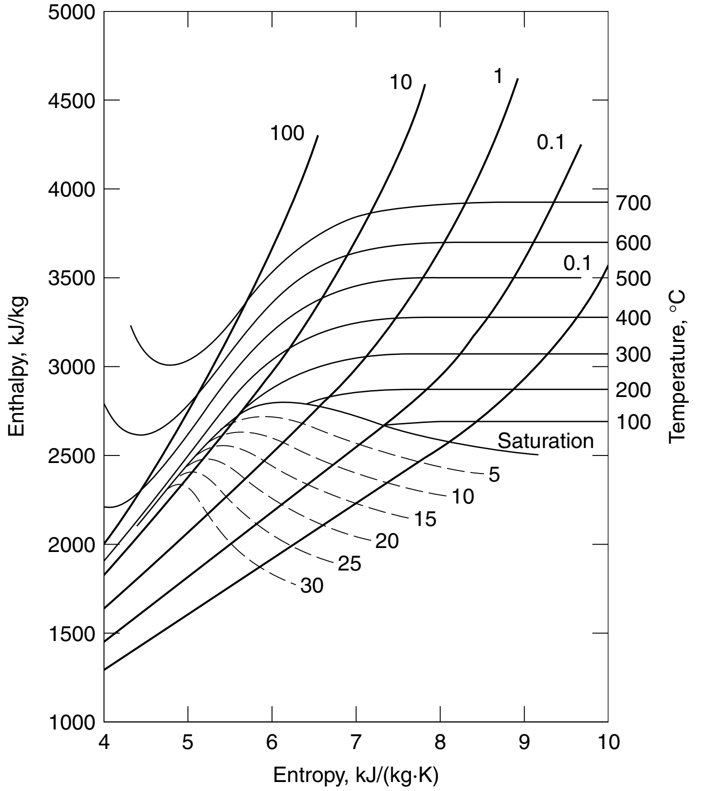

Fig. 4. Mollier chart, where the numbers on the solid lines represent pressure in MPa, and the values associated with the dashed lines represent percentages of moisture. To convert MPa to psi, multiply by 145. To convert kJ to kcal, divide by 4.184.

conductivity (Fig. 7) is important to the design of heat-transfer apparatus. The viscosity, which is the resistance to flow under pressure, is shown in Figure 8. The sharp declines evident in each of these properties occur at the transition from liquid to gas phase, ie, from water to steam. When new formulations of the transport properties, in process at the time of writing are available, they may be found on the IAPWS website (5).

2.4. Miscellaneous Properties. *Surface Tension.* The surface tension between water and steam is shown in Figure 9.

Dielectric Constant. The dielectric constant, a physical property having great importance to the chemical properties of hot water and steam, is shown as a function of temperature in Figure 10. Along the saturation line, the steam and water values converge at the critical point. The ability of water to dissolve salts results from the high dielectric constant. The precipitous drop in water dielectric constant in the region of the critical point is very important to the solubility of salts in water near the critical temperature. Many salts exhibit declining solubilities as the critical temperature is approached, and then exceeded. The drop in dielectric constant is largely a result of the decline in density. The dielectric constant on the 1-kg/dm^3 isochore, ie, the density at 25°C, declines with the

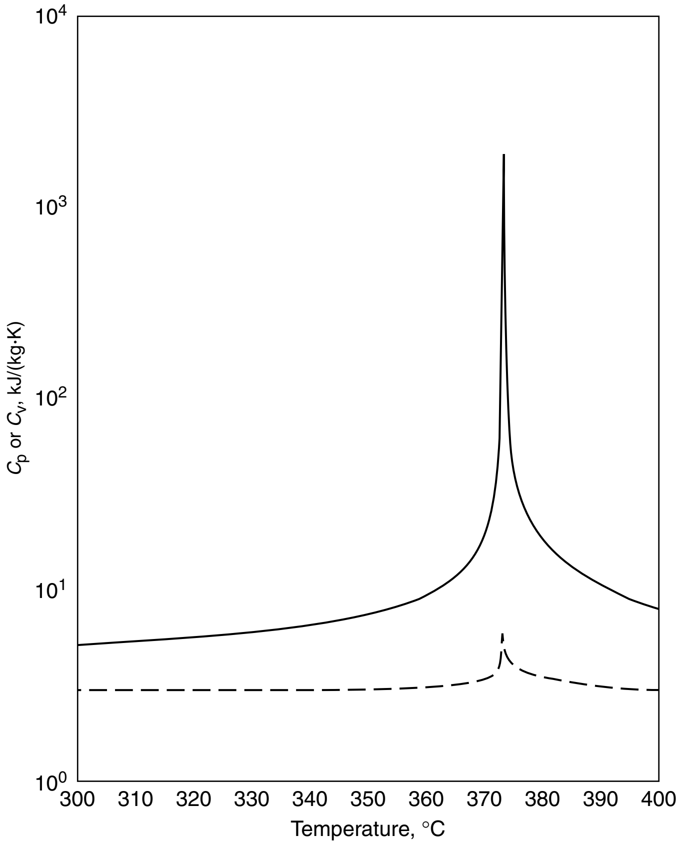

Fig. 5. Heat capacities at (—) constant pressure, C_p, and at (– – –) constant volume, C_v, on the 22.0-MPa (3190-psi) isobar. To convert kJ to kcal, divide by 4.184.

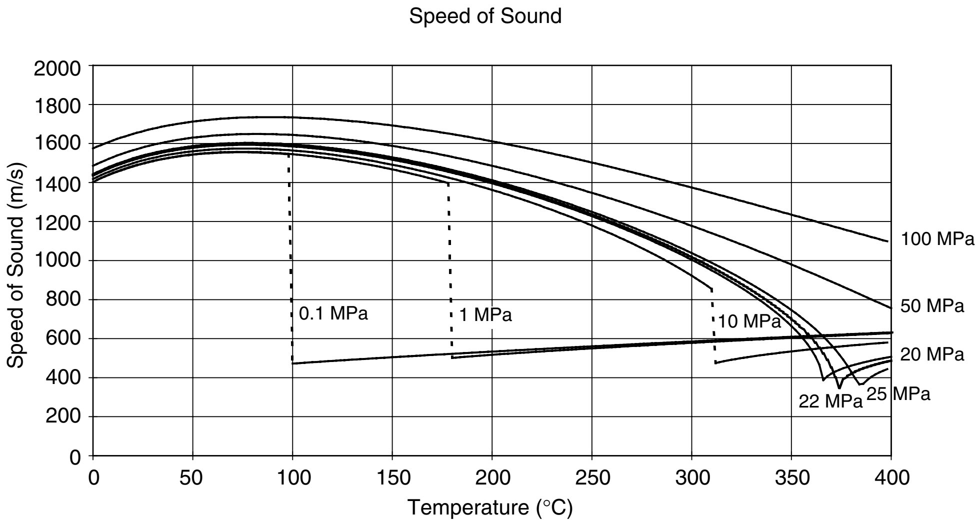

Fig. 6. Speed of sound in water and steam as a function of temperature. Values given correspond to pressures in MPa. To convert MPa to psi, multiply by 145.

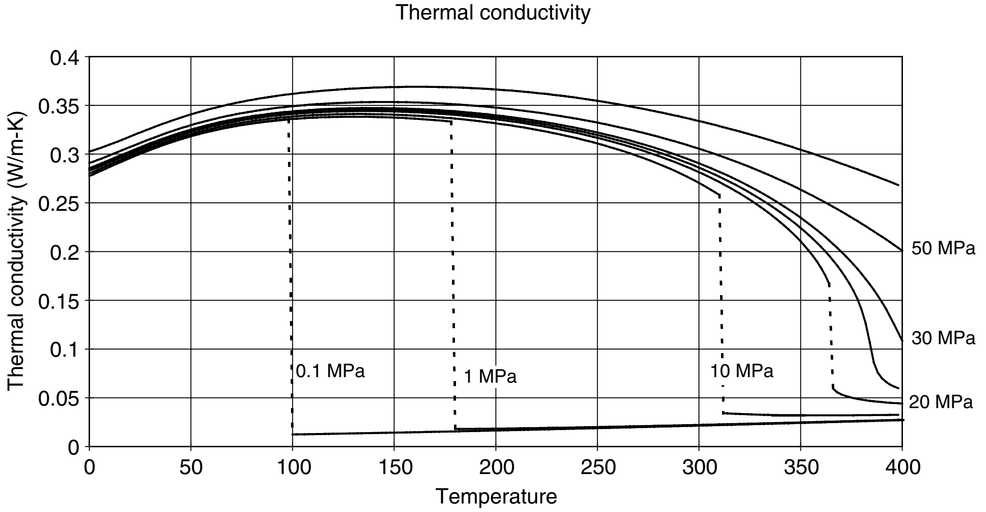

Fig. 7. Thermal conductivity of water and steam as a function of temperature. Values given correspond to pressures in MPa. To convert MPa to psi, multiply by 145.

increase in temperature, but not as much as does the dielectric constant on the saturation line. The isochore does not show the sharp drop at the critical temperature.

Ion Product. The ion product of water is the product of the molality of the hydrogen and hydroxide ions, $K_{\mathrm{w}} = m_{\mathrm{H}^+} m_{\mathrm{OH}^-}$. Its temperature variation is shown in Figure 11. The ion product increases with temperature to 250°C, and

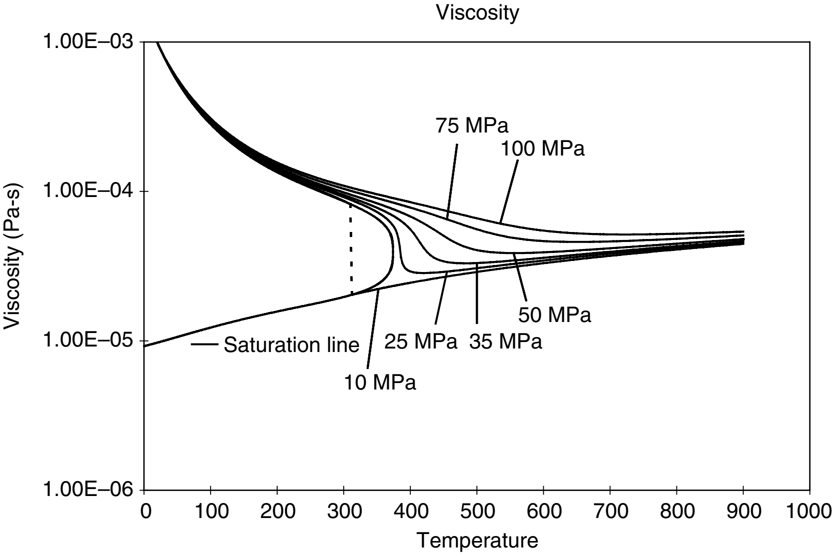

Fig. 8. Viscosity of water and steam as a function of temperature. Values given correspond to pressures in MPa. To convert MPa to psi, multiply by 145.

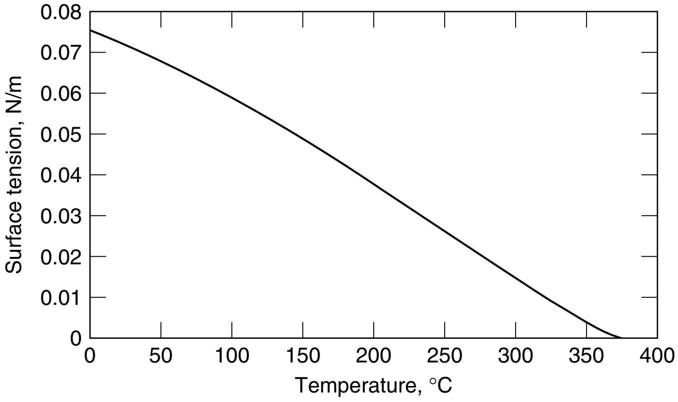

Fig. 9. Surface tension between liquid water and steam along the saturation line.

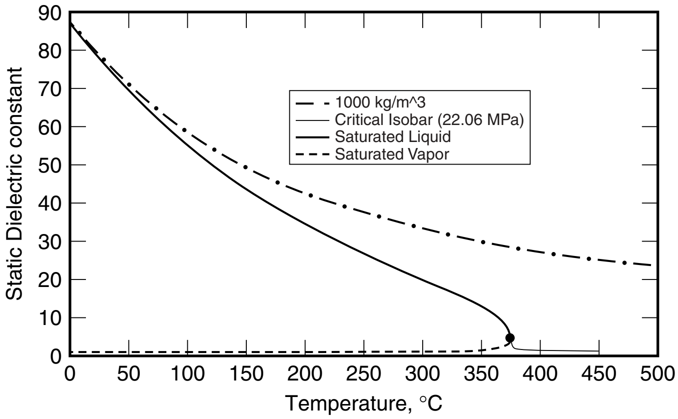

Fig. 10. Dielectric constants of (—) water and (– – –) steam on the saturation line, where (●) corresponds to the critical point, and (–·–) along the 1-kg/dm^3 isochore. Above the critical point, the critical isobar (22.05 MPa, 3199 psi) is extended.

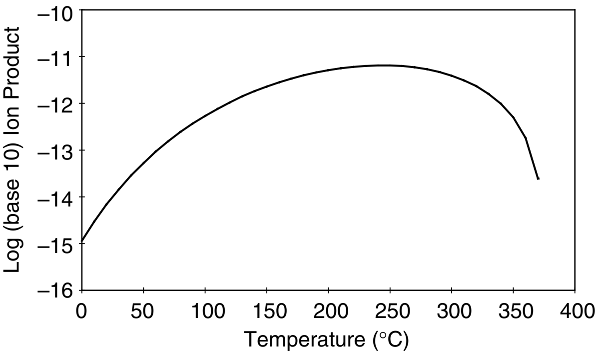

Fig. 11. Ion product of water at saturation line.

then declines. The initial increase is the temperature effect, and the later decline is due to the decline in the dielectric constant of water. This variation means that neutral pH, which is the square root of the ion product, varies with temperature.

3. Chemical Properties

3.1. Molecular Nature of Steam. The molecular structure of steam is not as well known as that of ice or water. During the water–steam phase change, rotation of molecules and vibration of atoms within the water molecules do not change considerably, but translational movement increases, accounting for the volume increase when water is evaporated at subcritical pressures. There are indications that even in the steam phase some H_2O molecules are associated in small clusters of two or more molecules (7). Values for the dimerization enthalpy and entropy of water have been determined from measurements of the pressure dependence of the thermal conductivity of water vapor at 358–386 K (85–113°C, 185–235°F) and 13.3–133.3 kPa (100–1000 Torr, 1.9–19.3 psia). These measurements yield the estimated upper limits of equilibrium constants, K_n, for cluster formation in steam, where n is the number of molecules in a cluster.

n	K_n, kPa$^{-(n-1)}$
3	1.9×10^{-8}
4	5.8×10^{-11}
5	3.8×10^{-12}
6	2.8×10^{-15}

3.2. Solvent. The solvent properties of water and steam are a consequence of the dielectric constant. At 25°C, the dielectric constant of water is 78.4, which enables ready dissolution of salts. As the temperature increases, the dielectric constant decreases. At the critical point, the dielectric constant is only 5.4, which is similar to the dielectric constants of many organic compounds at 25°C. The solubility of many salts declines at high temperatures. As a consequence, steam is a poor solvent for salts. However, at the critical point and above, water is a good solvent for organic molecules.

Solubility of Salts in Steam. Although the solubility of salts in steam is small, it has great significance to corrosion of steam system components, particularly steam turbines. Much of this information, also of interest to geochemists and cosmochemists, is published in geochemistry journals, such as *Geochimica et Cosmochimica Acta.* Most of the available work has been collected by Harvey and Bellows (8). In recent years, there has been considerable investigation of the equilibrium distribution of salts across the vapor–liquid phase boundary (9–12). Historically, this work was entirely for single solute systems. For many solutes, the distribution ratio in dilute solutions can be described by equation 1:

$$\log D = m \log(\rho_v/\rho_l) \tag{1}$$

where $D = c_v/c_l$, the ratio of the concentration of solute in the vapor phase, c_v, to the concentration of solute in the liquid phase, c_l; ρ_v is the density of the vapor; ρ_l, the density of the liquid; and m, a coefficient, which has been related to a coordination number (13). In careful work, the change in the critical point pressure and temperature with concentration of dissolved species must be considered. The Ray diagram (Fig. 12) shows the distribution of solutes as a function of density ratio for various metal oxides, salts, and silica (13,14). The slopes in Figure 12 are the m values for the distribution equation (eq. 1). At the critical point, the distribution ratio is 1. As the density ratio declines, the distribution ratio declines. The data were collected at relatively high concentrations and for pure materials only. Dissociation and common ion effects in the liquid phase are not included in this treatment, so the reliability of Figure 12 at values of $\rho_l/\rho_v > 10$ is questionable. When the system contains more than one solute, the

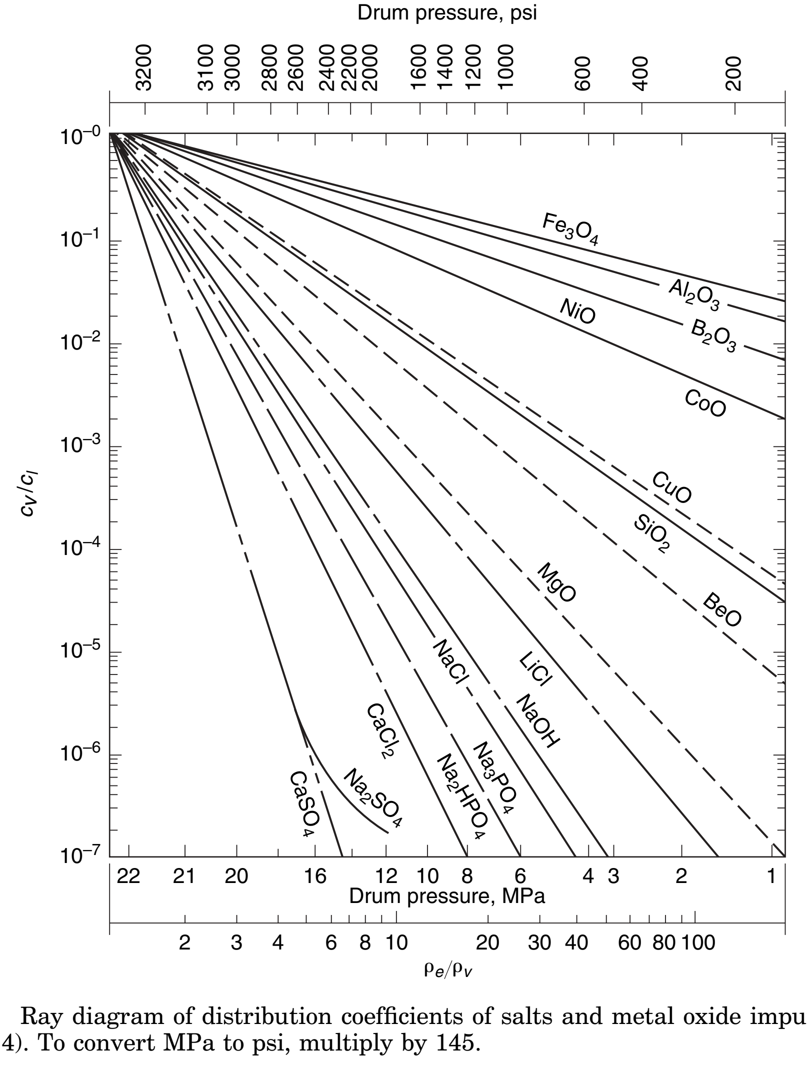

Fig. 12. Ray diagram of distribution coefficients of salts and metal oxide impurities in steam (14). To convert MPa to psi, multiply by 145.

distribution cannot be represented so simply, as common ion effects occur. Only a few such systems have been studied.

Ammonium Chloride. Work on the distribution of ammonium chloride [12125-02-9] between the vapor and liquid phases (15) suggests that the Ray diagram is sometimes an oversimplification. In most steam systems, there is much more ammonia than any other impurity. In particular, there is more ammonia than hydrogen chloride. The volatility of ammonium chloride is therefore expressed by the following chemical equation:

$$NH_4^+(aq) + Cl^-(aq) \rightarrow NH_4Cl\ (g) \qquad K = a\,(NH_4Cl)/a\,(NH_4^+)a\,(Cl^-)$$

where a is the activity of the species in the parentheses. The distribution coefficient for ammonium chloride is shown in Figure 13 for equation 2:

$$\log K = -20.24 + 18207/T - 10.48\log(\rho_l/\rho_v) \qquad (2)$$

where T is in K and the densities are of pure water or steam. Investigations of sodium salts at low concentrations suggest that similar treatments may be required for most species (10,15,16).

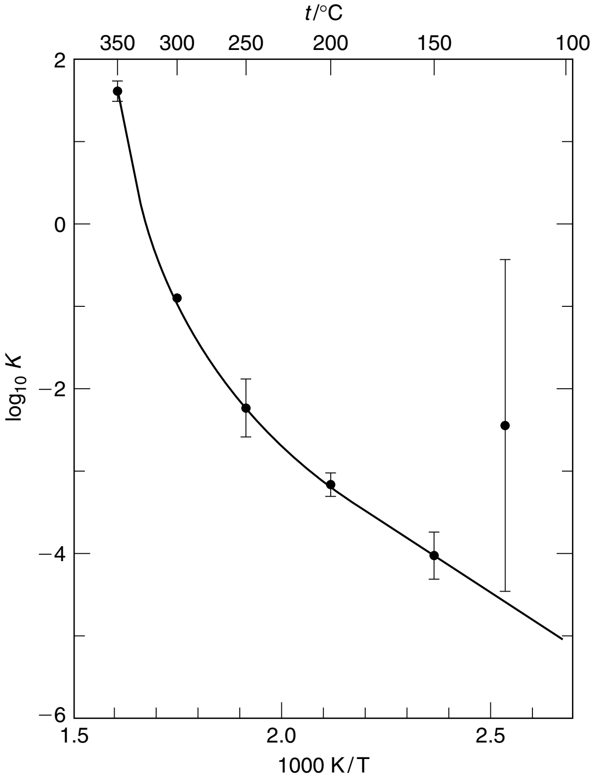

Fig. 13. Thermodynamic partitioning coefficient for ammonium chloride (15).

Metal Oxides and Hydroxides. The metal oxides tend to have very low solubilities at the critical point, evidenced by the small slope in Figure 12. For the most part, these oxides may be considered as solid suspensions. Copper oxides and alumina under some conditions are exceptions to this rule. Solubilities of the metal oxides are available (17,18). Cupric hydroxide has a distribution ratio near unity from the critical point to at least 1.62 MPa or 202°C (234 psia or 396°F) (10). Although its solublity in liquid water is not particularly high, it is believed to be the primary species by which copper is transported from the boiler to the steam turbine.

Sodium Chloride. Sodium chloride, a corrodent of many materials, is the archetype contaminant and has been studied more than other salts. The solubility of sodium chloride in superheated steam is shown at the conditions of a typical steam turbine expansion in Figure 14. The solubilities were measured in the region of higher solubility. As the steam expands, sodium chloride becomes considerably less soluble. The solubility, X_s, as mole fraction can be represented by equation 3 (8).

$$\ln(X_s) = -7.928 - 4852.47/T + (4.49961 - 0.0013/T)\ln\rho - \ln P \qquad (3)$$

where ρ is the molar density of steam in mol/L, T is the temperature in K, and P is the pressure in MPa. There is a combined effect of decreasing density and decreasing temperature.

Silica. Silica is not actually a corrodent of turbines. However, it can deposit on and cause blocking of turbine passages, thus reducing turbine capacity and efficiency. As little as 76 μm (3 mils) of deposit can cause measurable loss in turbine efficiency. Severe deposition can also cause imbalance

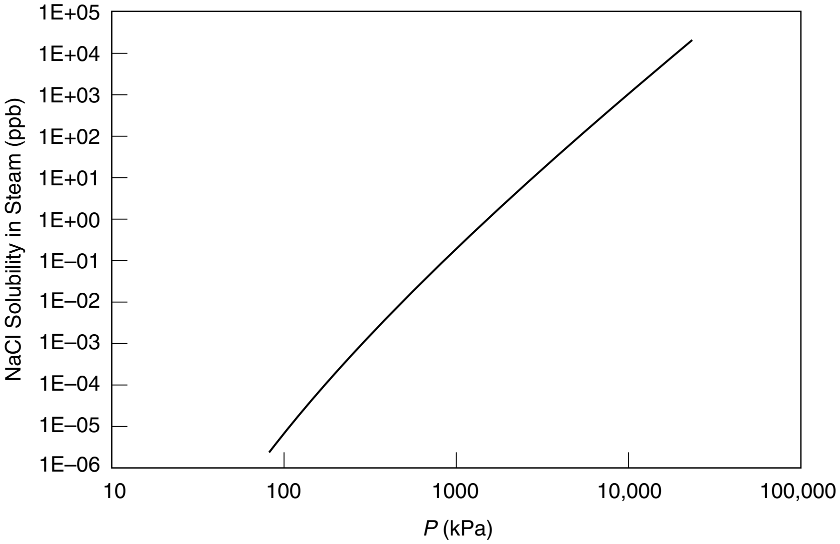

Fig. 14. Solubility of NaCl as a function of pressure on typical turbine expansion line (7). To convert kPa to psi, multiply by 0.145.

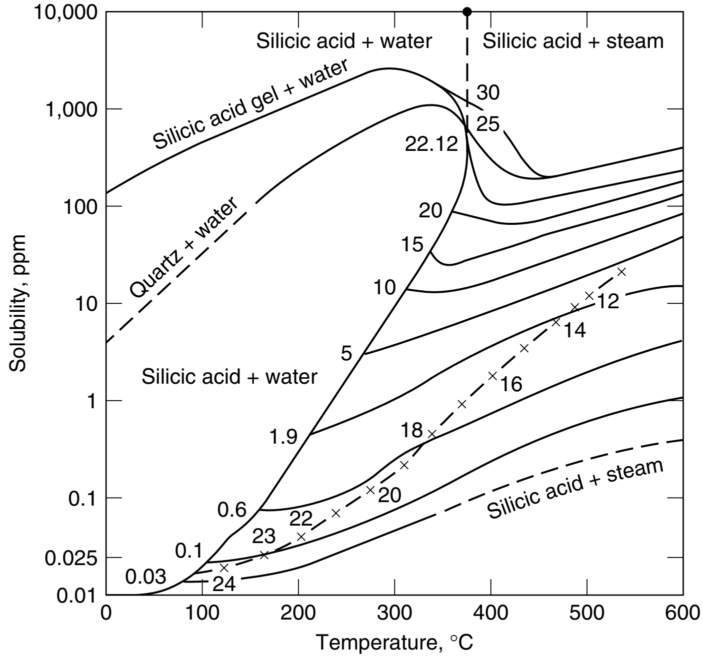

Fig. 15. Silica solubility diagram (19) where (–×–) is the turbine expansion line and (●) is the critical point. Numbers represent pressure in MPa. To convert MPa to psi, multiply by 145.

of the turbine and vibration. The solubility in steam and water is shown in Figure 15, as is a typical steam turbine expansion. Silica is rarely a problem except in low pressure turbines unless the concentrations are extraordinarily high. However, if a turbine is frequently started, and the silica in the steam is high at startup, deposits can develop at the low pressure end of the high pressure turbine.

Moderately Volatile Materials. For moderately volatile materials, such as the amines commonly used in feedwater and boiler water chemical treatment, the distribution ratios vary from 0.1 to 30; for gases, the ratios are much higher. The distribution ratios of amines and organic acids are generally temperature dependent. The distribution ratios for ammonia [7664-41-7], morpholine [110-91-8], and acetic acid [64-19-7] are shown in Figure 16 as examples.

Gases. At low temperatures and pressures, most gases are relatively insoluble in water and tend to appear in the steam phase. Only those gases that ionize to some extent violate this rule. However, as the temperature approaches the critical point of water, the solubility of gases increases. The IAPWS maintains a Guideline on the Henry's Constant and Vapor–Liquid Distribution for some common gases (5).

3.3. Reactant.

Steam can behave as an oxidant. The partial pressure of oxygen generated by the dissociation of steam into hydrogen and oxygen is shown in Figure 17.

Steam reacts with salts so that the salts dissociate into the respective hydroxide and acid. For sodium salts, the sodium hydroxide is largely in a liquid solution and the acid is volatile. Figure 18 shows the concentration of

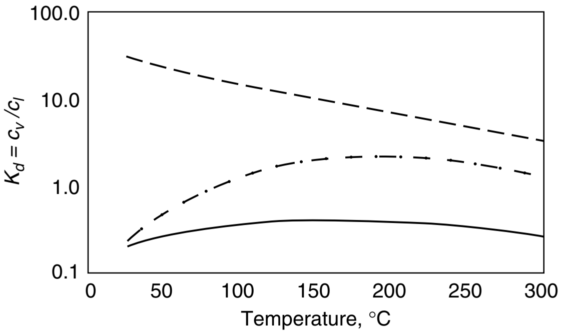

Fig. 16. Distribution of (– – –) ammonia, (–·–) morpholine, and (—) acetic acid between water and steam (17).

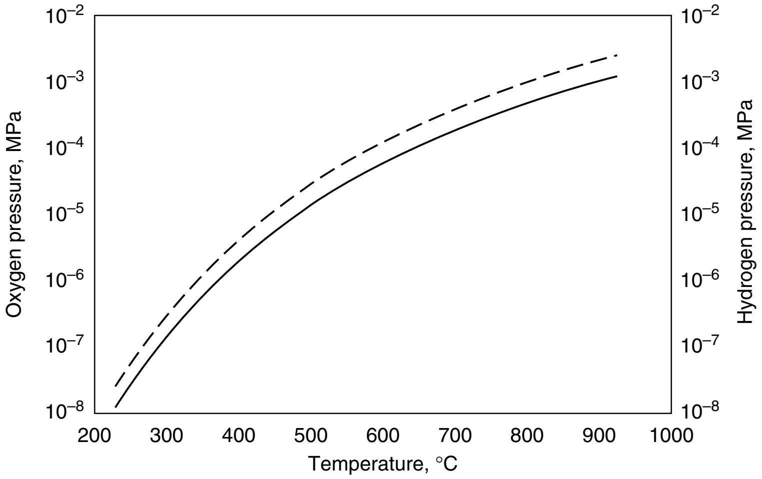

Fig. 17. Oxygen (—) and hydrogen (– – –) partial pressure in steam at 3 MPa (435 psi) (20). To convert MPa to psi, multiply by 145.

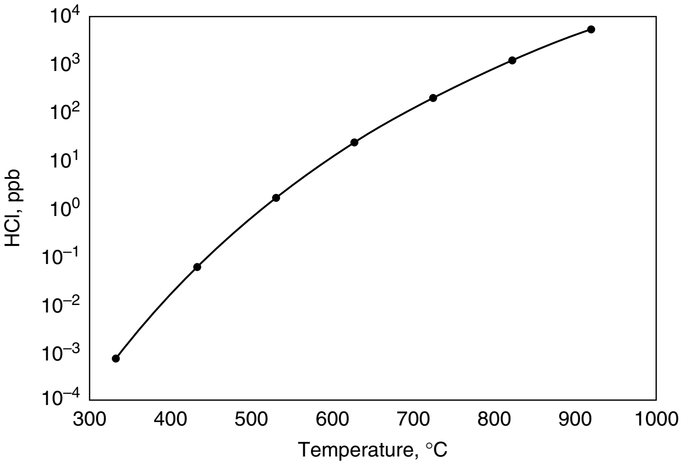

Fig. 18. Hydrochloric acid in steam due to hydrolysis of sodium chloride (20).

hydrochloric acid [7647-01-0], HCl, in steam due to hydrolysis of sodium chloride. Although the amount is not large, it can be measured.

4. Generation

4.1. Equipment. *Simplified Cycle.* A simplified conventional fossil steam cycle appears in Figure 19. Here, "conventional" is used to denote a boiler and turbine cycle, as opposed to, eg, a combined cycle, which is also fossil fueled. The water accumulates in the bottom of the condenser, called the hotwell. It goes through a feed pump to pressurize it. The pressurized water passes through one or more feedwater heaters, which raise the temperature. The water then enters the boiler where heat from the fuel converts it to steam. The steam expands through the engine, usually a turbine, which extracts work. In the middle of the turbine, some of the steam is extracted to supply heat to the feedwater heater. The remainder expands through the turbine and is condensed. The rejected heat is carried away by the condenser coolant, which is usually water, but sometimes air. The condensed steam then returns to the hotwell to repeat the cycle.

Steam Generators or Boilers. Steam is produced in a boiler or steam generator. The term steam generator is used when the heat source is nuclear power and is often used for fossil-fired boilers, particularly supercritical once-through units, where the fluid changes gradually from liquid- to vapor-like properties without a distinct change of phase. Boilers using hot gas as a heat source are generally called heat recovery steam generators (HRSGs). The design (21,22) of steam generators and boilers is complicated and is treated herein in an overview.

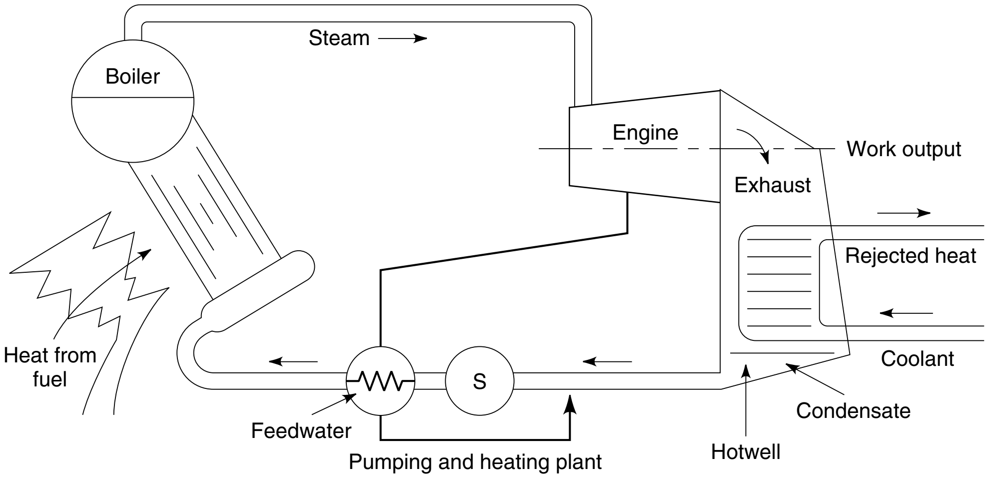

Fig. 19. Schematic of a simplified steam (S) cycle (21).

In fossil-fuel-fired boilers, there are two regions defined by the mode of heat transfer. Fuel is burned in the furnace or radiant section of the boiler. The walls of this section of the boiler are constructed of vertical, or near vertical, tubes in which water is boiled. Heat is transferred radiatively from the fire to the waterwall of the boiler. When the hot gas leaves the radiant section of the boiler, it goes to the convective section. In the convective section, heat is transferred to tubes in the gas path. Superheating and reheating are in the convective section of the boiler. The economizer, which can be considered as a gas-heated feedwater heater, is the last element in the convective zone of the boiler.

Recirculating or Drum Boilers. There are two basic types of boilers: recirculating and once-through. The difference between the boiler types is the manner in which heat is absorbed from the fuel to generate steam. In a recirculating boiler, shown schematically in Figure 20, water enters the boiler at the bottom of the waterwall. Approximately 25–33% of the water boils by the time it reaches the top of the waterwall. In the steam drum, the steam is separated from the remaining water. The mixture of steam and water passes through steam-separating devices, eg, baffles, cyclones, or corrugated plates, where the direction of flow changes rapidly. Steam follows the change in direction but water hits the metal and is drained away. The efficiency of this process depends on the density difference between the steam and the water. With increasing pressure, the density difference decreases, and the efficiency of the separation also decreases. The steam goes to the superheater, and then to the turbine or process. The water separated from the steam is recirculated to the bottom of the boiler. The water flow in a recirculating boiler may be either convective or forced. Convective flow relies on the difference in the average densities of the water in the downcomer and the water and steam in the waterwall. In forced circulation, the natural circulation is aided by a pump. Because the steam is separated from the water, nonvolatile impurities, usually solids, concentrate in the water. A small portion of the water, usually 2% or less, is removed

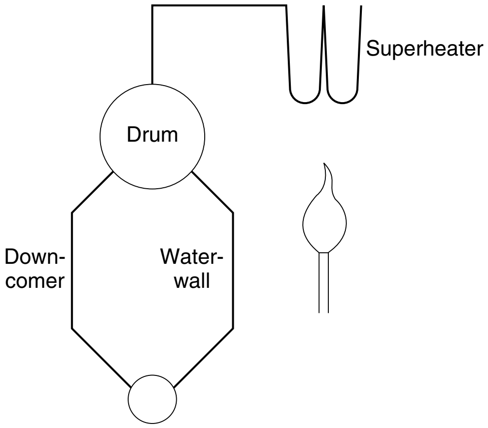

Fig. 20. Schematic of a simplified fossil-fuel-fired recirculating steam generator.

(blown down) to reduce these impurities. Blowdown is a dilution process because the concentration of the impurities in the makeup water is lower than in the boiler water.

Once-Through Steam Generators. In a once-through system the feedwater enters the steam generator at the bottom of the waterwall and passes out of the boiler through the superheater. Most once-through steam generators are supercritical [>23 MPa (3300 psia)]. Once-through steam generators require extremely pure feedwater, because no purification of the water occurs in the boiler. Subcritical once-through boilers require the same high-purity feedwater, but do not provide as high efficiency as the supercritical unit.

Nuclear Steam Generators. There are three basic types of nuclear heat sources. Most common are pressurized water reactors having steam generators (Fig. 21). In this system, the nuclear reactor heats water in a high pressure loop, typically 14.1–17.2 MPa (2045–2495 psia). The water is circulated through tubes in a steam generator. On the outside of the tubes, water is boiled to steam, which goes to the steam turbine. In recirculating steam generators, the steam is saturated. In once-through steam generators, the steam has ~28°C (50°F) superheat. In boiling-water reactors, the second type, the nuclear heat is used to boil the feedwater directly. In gas-cooled reactors, the third type, the gas takes the same role as the pressurized water in a pressurized-water reactor (PWR) and transfers the heat to the steam generator. Typical nuclear turbine inlet conditions range from 5.0 to 7.3 MPa (725–1059 psia) at saturation temperatures of 264–289°C (507–552°F) and ~0.25% moisture.

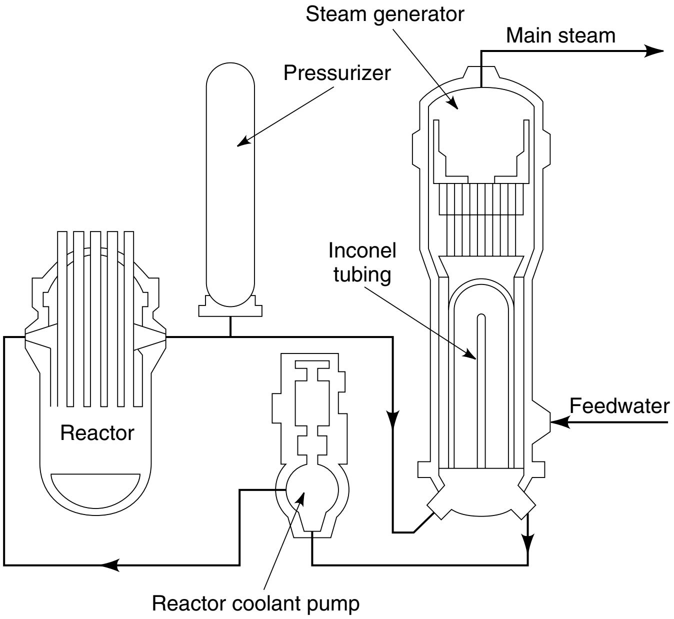

Fig. 21. Schematic of a pressurized-water-loop reactor coolant system.

Heat Recovery Steam Generators. Heat recovery steam generators (HRSGs), a special class of boilers where essentially all heat transfer takes place convectively, are used to extract energy from hot gas streams. One of the principal uses is extraction of heat from the exhaust gases of a combustion turbine. Turbine exhaust gas typically exceeds 540°C (1004°F) and may be as high as 621°C (1150°F). Careful design of the HRSG allows the gas leaving the HRSG to approach the feedwater temperature within 28°C (50°F). High heat-transfer rates in modern HRSGs are assisted by finned tubing. The HRSGs may have horizontal gas path with vertical tubing or vertical gas path with horizontal tubing. The horizontal gas path design requires more land area, but the vertical gas path design is more prone to problems with liquid and vapor distribution in the tubes leading to corrosion, poor heat transfer, and leaks. Most HRSGs are recirculating boilers, but some once-through HRSGs have been built.

Feedwater Heaters. Feedwater heaters use steam from the turbine to preheat the feedwater before it reaches the boiler. Feedwater heaters increase efficiency of steam cycles because heat comes from a source having a lower temperature than the fire in the boiler. Although feedwater heaters may be either shell and tube or direct contact, most are of shell-and-tube construction. Water flows through the inside of the tubes. Steam is admitted to the shell where it condenses, warming the water inside the tubes. The steam entering the feedwater heater first passes over the tubes containing the water that is about to leave the heater, then to tubes containing the cooler water entering the heater. The condensed steam is collected in a drain, which is either cascaded to a lower temperature feedwater heater or collected and pumped forward into the main feedwater stream. In a direct-contact or deaerating heater, the water is sprayed through a steam space and flows down trays in thin layers. Steam is admitted at the bottom and flows upward countercurrent to the water. Dissolved gases are removed from the water in direct-contact heaters and must be vented.

Condenser. Water-cooled condensers are constructed of tubes between tubesheets (Fig. 22). Cooling water is pumped from the source into the inlet waterbox, through the tubes, and through the outlet waterbox. Tight joints between the tubes and tubesheet are necessary to prevent ingress of the cooling water. Total cooling water leakage as small as 4 L/day of fresh water can produce unacceptable impurity concentrations in feedwater for nuclear steam generators. Careful selection of condenser materials is required for long-term reliability. Double tubesheets having condensate between the two sheets are a method of reducing the likelihood of cooling water leaks. The cooling water may be drawn from lakes or rivers or may be recirculated from cooling towers. Cooling water chemistry is complex due to precipitation and microbiological considerations. It is treated in handbooks by water treatment chemical vendors (23–25).

Air-cooled condensers are used more frequently as cooling water sources are being exhausted. Air-cooled condensers consist of large numbers of finned tubes. Air is forced past the outside of the tubes and the steam condenses on the inside. Cooling water leakage is not a problem when air-cooled condensers are used, but air in-leakage can be a bigger problem than for water-cooled condensers.

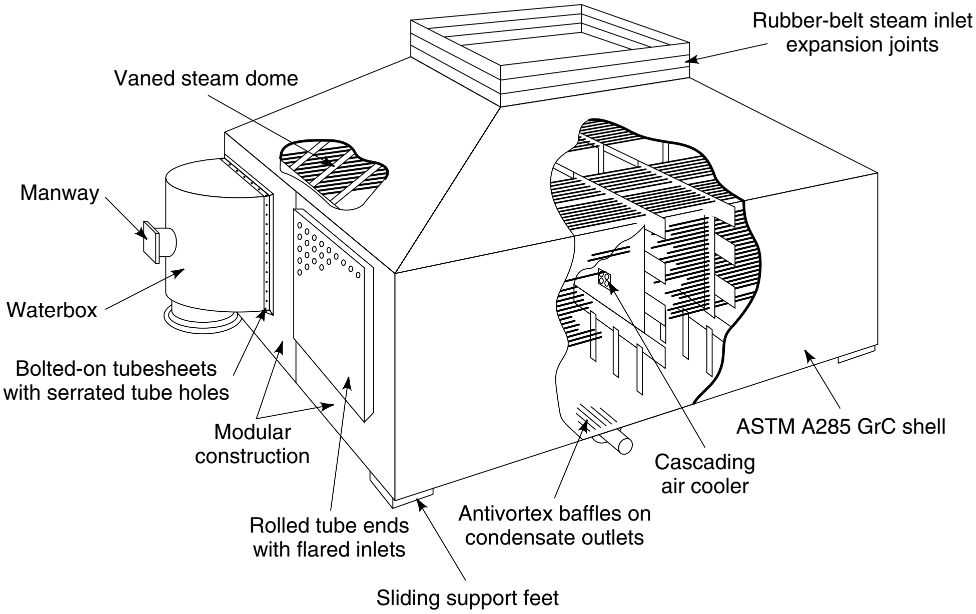

Fig. 22. Schematic of a condenser.

4.2. Water Chemistry in Steam-Generating Systems.

Specifications. Steam Purity. The usual function of steam purity limits is to protect the turbine or other steam user from deposition and subsequent corrosion. In systems where the steam is used for chemical processes, the specific process may create additional requirements for steam purity. For example, in food processing, regulations may limit or prohibit hydrazine in the steam, so ascorbic acid or sodium sulfite must be used as an oxygen scavenger. When steam is sent to processes and returned as condensate, it may be necessary to add pH control agents to the steam to control corrosion at various points in the process and condensate return system. Table 1 gives typical steam purity recommendations for steam turbine protection. In addition to the normal limits, most vendors have time-limited excursion ranges, which provide tolerance for upset conditions and the higher impurity concentrations commonly found on

Table 1. **Steam Purity Recommendations**

Parameter	Normal operation	Typical shutdown limit
conductivity, μS/cm		
hydrogen cation exchanged	≤0.2	1.0
sodium, μg/kg	1–10	50
silica, μg/kg	10–20	50
iron, μg/kg	20	
copper, μg/kg	2	
chloride	3–10	
sulfate	3–6	

the startup of a boiler system. The recommendations are derived from a blend of theoretical considerations of solubility of salts in steam, practical limits on water purity, and experience with what has proved successful. It has recently been shown that the rate of deposition of impurities from steam is an important aspect of the process (26). The development of steam purity limits is available (27,28).

Boiler Water. The steam purity limits define boiler-water limits because the steam cannot be purified once it leaves the boiler. For a once-through boiler, the boiler water must have the same specifications as the steam. A recirculating boiler is a still, and there can be considerable purification of the steam as it boils and is separated from the water in the steam drum. The process of separation is not perfect, however, and some water is entrained in the steam. This water, called mechanical carryover, contains impurities in the same proportions as the boiler water, and its contribution to steam impurity is in those proportions. Typical mechanical carryover is $<0.25\%$ and often $<0.1\%$, but operating conditions in the boiler can affect the mechanical carryover. In addition to mechanical carryover, chemicals can be carried into the steam due to solubility. This is called vaporous carryover. Total carryover is the sum of mechanical and vaporous carryover. The boiler-water specification must be such that the total carryover conforms to the steam purity requirements. For salts, eg, sodium phosphate and sodium chloride, vaporous carryover is not a significant problem below $\sim$15 MPa (150 bar, 2176 psia). As boiler pressures approach the critical point, vaporous carryover increases rapidly. Above 15 MPa, boiler solids concentrations must be carefully controlled to minimize vaporous carryover. Most boilers operating over 18 MPa (180 bar, 2611 psia) use all volatile treatment to prevent deposition of salts in turbines. Boiler-water limits for utility boilers are listed in Table 2. Recommendations from American Boiler Manufacturers' Association (ABMA) for boiler-water limits for drum-type boilers and associated steam purity for watertube boilers are listed in Table 3.

In addition to the requirement to conform to steam purity needs, there are concerns that the boiler water neither corrode the boiler tubes nor produce deposits, known as scale, on these tubes. The boiler water pH is an important parameter, both in the bulk water and under deposits, where the pH adjacent to the metal may be considerably different from the bulk water pH. If deposits and contaminants are reasonably well controlled, then the bulk water pH is a

Table 2. **Boiler-Water Limits for Utility Boiler**[a,b]

Elements, ppm	All-volatile treatment	Phosphate
sodium	0.7	1.7
chloride	0.28	0.9
sulfate	0.28	1.6
silica	13	13
phosphate		2.2

[a] At 17.2 MPa (2500 psi).

[b] Ref. 27.

Table 3. **ABMA Recommended Boiler-Water Limits**[a]

	Boiler-water limits, ppm			Steam limits, ppm
Drum pressure, MPa[b]	Total dissolved solids[c]	Total alkalinity	Suspended solids[c]	Expected total dissolved solids[c,d]
		Drum boilers		
0.1–2.2	700–3500	140–170	15	0.2–1.0
2.2–3.2	600–3000	120–600	10	0.2–1.0
3.2–4.2	500–2500	100–500	8	0.2–1.0
4.2–5.3	400–2000	80–400	6	0.2–1.0
5.3–6.3	300–1500	60–300	4	0.2–1.0
6.3–7.0	250–1250	50–250	2	0.2–1.0
7.0–12.5	100	[e]	1	0.1
12.5–16.3	50		[f]	0.1
16.3–18	25		[f]	0.05
18.0–20.1	15		[f]	0.05
		Once-through boilers		
≥9.8	0.05	[f]	[f]	0.05

[a] Ref. 29.

[b] To convert MPa to psi, multiply by 145.

[c] Values are maximum.

[d] Values are exclusive of silica.

[e] Dictated by boiler-water treatment.

[f] Not applicable.

good estimate of the pH of the water adjacent to the metal. Three important components of boiler tube scale are iron oxides, copper oxides, and calcium salts, particularly calcium carbonate [471-34-1]. Calcium carbonate in the feedwater tends to produce a hard, tenacious deposit. Sodium phosphate is often added to the water of recirculating boilers to change the precipitate from calcium carbonate to calcium phosphate and control the pH.

Feedwater. The feedwater for a steam cycle must be purified. The degree of purity depends on the pressure of the boiler. Higher pressure boilers require higher feedwater purity. There is some trade-off between feedwater purity and boiler blowdown rate. However, increasing blowdown rate to compensate for lower feedwater purity is expensive, because blowdown water has been heated to the saturation temperature. Typical feedwater specifications for utility boilers are given in Table 4. To some extent turbine steam purity requirements determine the feedwater purity requirements. The boiler-water silica required to maintain adequate steam purity for higher pressure steam turbines is considerably less than the boiler could tolerate if deposition in the boiler were the only issue.

Makeup. Makeup water is the water supplied to replenish the steam system for any losses. In most systems, it is introduced into the condenser or the feed pump suction. In steam systems where the makeup is a small fraction of the total feedwater, its purity may be somewhat lower than the feedwater requirement because it is diluted by condensate. In systems where there is little condensate return, such as heating steam supplies, the makeup purity must be essentially the same as the feedwater.

Table 4. **Utility Feedwater Specifications for Normal Operation**[a]

Parameter	Reducing chemistry Recirculating boiler	Reducing chemistry Once-through boiler	Oxidizing chemistry Once-through boiler
pH			
all-ferrous metallurgy	9.0–9.6	9.0–9.6	8.0–8.5
mixed Fe–Cu metallurgy	8.8–9.3	8.8–9.3	
cation-exchanged conductivity, μS/cm	≤0.2	≤0.2	≤0.15
iron, ppb	≤10	≤10	≤5
copper, ppb	≤2	≤2	
oxygen, ppb	≤5	≤5	50–150

[a] Refs. 27 and 30.

Water Treatment. Water and steam chemistry must be rigorously controlled to prevent deposition of impurities and corrosion of the steam cycle. Deposition on boiler tubing walls reduces heat transfer and can lead to overheating, creep, and eventual failure. Additionally, corrosion can develop under the deposits and lead to failure. If steam is used for chemical processes or as a heat-transfer medium for food and pharmaceutical preparation, there are limitations on the additives that may be used. Steam purity requirements set the allowable impurity concentrations for the rest of most cycles. Once contaminants enter the steam, there is no practical way to remove them. Thus all purification must be carried out in the boiler or preboiler part of the cycle. The principal exception is in the case of nuclear steam generators, which require very pure water. These tend to provide steam that is considerably lower in most impurities than the turbine requires. A variety of water treatments are summarized in Table 5. Although the subtleties of water treatment in steam systems are beyond the scope of this article, uses of various additives may be summarized as in Table 6.

Reducing Chemistry. Most steam systems are maintained in a reducing state to avoid oxidation of the steel piping and other components. Oxidation is further suppressed by raising the pH, which is commonly controlled by using ammonia, although amines, eg, morpholine, cyclohexylamine, ethanolamine, and dimethylamine, are also used. Amines are not generally employed for systems having superheat temperatures ≥538°C (1000°F) because these tend to decompose to organic acids, which can be corrosive. Most feedwater is treated with hydrazine to reduce the oxygen concentration to the 1–5 μg/kg (ppb) range. Carbohydrazide, hydroquinone, and methylethylketoxime are also used as oxygen scavengers. In plants where the steam may be in contact with food, sodium sulfite, ascorbic acid, or erythorbic acid is commonly used as an oxygen scavenger due to lower or minimal toxicity.

Feedwater treatment is designed to protect the feedwater system and, to some extent, the boiler. Most systems contain carbon steel piping. Carbon steel corrosion (Fig. 23**a**) is considerably slower at a pH between 9.0 and 11.0. In all-ferrous feedwater systems, the preferred pH range is therefore 9.2–9.6, although

Table 5. **Water Treatment Schemes**

Program	Characteristics	
	Favorable	Unfavorable
phosphate		
conventional, Na_3PO_4 (+NaOH)	hardness salts converted to a form readily removed by bottom blowdown; relatively high levels of suspended solids successfully controlled; acids neutralized; surface passivation by PO_4^{3-}	high pressure boilers cannot tolerate intentional formation of boiler sludge; required alkalinity levels are too high for operation >10.4 MPa (1500 psig); oil or organic contamination produces highly adherent deposit; possible under-deposit corrosion by NaOH
coordinated, $[Na]:[PO_4] < 3$	caustic corrosion may be eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4^{3-}	in boilers containing deposits, chemical interaction of iron and phosphate can lead to caustic corrosion; at very low $[Na]:[PO_4]$ molar ratios (<2.1), corrosion by phosphoric acid possible
congruent, $2.6 < [Na]:[PO_4] < 2.8$	caustic and acid corrosion eliminated; deposit form makes for easy removal; produces low solids levels and high steam purity; acids neutralized; surface passivation by PO_4^{3-}	control of the $[Na]:[PO_4]$ molar ratio may be difficult; continuous feed and blowdown may be required
NaOH or LiOH	acid neutralization	can cause rapid corrosion when concentrated in high quality regions or under deposits; vaporous carryover in steam at higher pressures; difficult to analyze
chelates, ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA)	optimum heat-transfer and boiler efficiency obtained under good feedwater-quality conditions; elimination of boiler sludge prevents formation of adherent deposits involving oil/organics	inability to analyze free chelant residual accurately can lead to overfeed and s ubsequent corrosion,[a] does not complex iron or copper under normal boiler-water pH conditions; presence of oxygen in boiler water can cause dechelation and excessive corrosion; limited to lower pressure boilers (see text)

Table 5. (*Continued*)

Program	Characteristics	
	Favorable	Unfavorable
all-volatile[b]	near-zero solids in boiler water and high purity steam realized under ideal feedwater conditions; having some corrosion protection; no carryover of solids; no surface concentration; condenser leakage detection by sodium measurement; boiler deposition of corrosion products easy to remove by chemical cleaning	feedwater contamination may exceed inhibiting ability of volatile fed, leading to boiler corrosion; introduction of contaminants into feedwater produces deposits they may be hard to remove; marginal acid neutralization, particularly when using ammonia in wet steam regions; interference with condensate polishing; corrosion of copper alloys by ammonia and oxygen; organic acid decomposition products of organic amines
oxygenated treatment	no interference of additives with condensate polishing; low corrosion rates of ferritic steels	requires extremely low concentrations of impurities in feedwater; no corrosion protection in case of an upset; corrosion of copper alloys; precise control required

[a] Condition is heightened when treatment is applied to deposit-bearing boiler.
[b] Such as, ammonia, morpholine, cyclohexylamine, and ethanolamine (ETA).

Table 6. **Water Treatment Additives**

Additive	Effect
sodium orthophosphate	pH control; hardness precipitation
sodium hydroxide, lithium hydroxide	pH control (acid neutralization)
neutralizing volatile amines (ammonia, morpholine, cyclohexylamine, diethanolamine, ethanolamine, etc)	pH control of feedwater and boiler water, possibly steam condensate
hydrazine	oxygen scavenging
sodium sulfite	oxygen scavenging
sludge conditioners	dispersion of sludge for easy removal by blowdown in drum boilers, inhibiting of scale formation
synthetic sulfonated polymer, synthetic carboxylated polymer, polyacrylic acid	<6.9 MPa (1000 psi)
carboxymethyl cellulose, organophosphonate	<4.1 MPa (600 psi)
lignin	<2.1 MPa (300 psi)
oxygen or hydrogen peroxide	improve surface passivation in all-ferrous high purity water systems
filming amines (octadecylamine and some of its salts)	surface protection against condensate corrosion
antifoams (polyglycols, polyamides)	reduce foaming and carryover in boilers

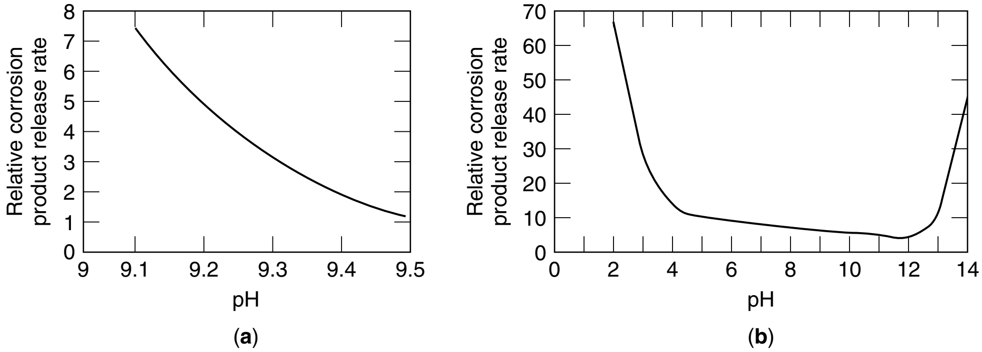

Fig. 23. Corrosion rates of carbon steel as a function of pH of (**a**) the feedwater (31) and (**b**) boiler conditions (32).

some systems are operated at a pH as high as 10. In systems where copper alloys are present, high concentrations of ammonia accelerate corrosion of the copper alloys. In those systems, the preferred pH is 8.8–9.2. There is a trend away from copper and copper alloys in the design of new steam generating systems.

For once-through boilers, the treatment must be without solid residues, so all-volatile treatment [AVT or AVT(R), where R indicates reducing] is used. The AVT, which is also used in some drum boiler systems, relies on the feedwater chemical additives, ammonia and hydrazine, to provide water appropriate to the boiler. Because the additives are volatile, they do not accumulate in the boiler and provide only minimal protection during contaminant ingress. Most plants using AVT have some form of condensate polisher to remove impurities from the condensate.

Boiler tubes are susceptible to corrosion due to contaminant ingress. Controlling the pH of the boiler water by judicious addition of low volatility pH control agents (eg, trisodium phosphate) can reduce corrosion. Figure 23**b** shows the rate of carbon steel corrosion as a function of pH at boiler conditions. If feedwater impurities or faulty chemical additions cause the boiler pH to move outside the acceptable range, corrosion can be rapid and boiler tube failure may occur in a matter of hours. If the boiler does not fail immediately, it can also be damaged by hydrogen embrittlement, which makes it subject to failures during thermal transients, eg, startup.

In drum boilers, sodium hydroxide (caustic), sodium phosphate, or both may be added for pH and scale control. Sodium hydroxide is used more in Europe than in the United States, where sodium phosphate treatment is usually preferred. In boilers operating >4 MPa (580 psia), caustic concentrations must be carefully controlled to prevent highly corrosive deposits from forming. In the lowest pressure boilers, phosphate treatment may be used to compensate for lower purity feedwater. As the boiler pressure increases, the allowable phosphate concentration decreases, and at 16.5 MPa (2400 psia) or above, equilibrium phosphate treatment may be used. In this treatment, caustic is added to a low phosphate concentration in the boiler to maintain the proper pH (33).

In lower pressure boilers, a variety of additional treatments may be appropriate, particularly if the steam is used in chemical process or other nonturbine application. Chelants and sludge conditioners are employed to condition scale and enable the use of feedwater with a higher impurity content. When the drum pressure is less than 7 MPa (1015 psia), sodium sulfite may be added directly to the boiler water as an oxygen scavenger. It has minimal effect on the oxygen concentration in the system before the boiler.

The selection of boiler-water treatment is also dependent on the type of cooling water. When cooling water reaches the boiler, various compounds precipitate before others. For example, seawater contains considerable magnesium chloride. When the magnesium precipitates as the hydroxide, hydrochloric acid remains. In some lake waters, calcium carbonate is a significant impurity. When it reaches the boiler, carbon dioxide is driven off in the steam and calcium hydroxide is formed. If the cooling water tends to form acid in the boiler, either caustic or phosphate may be added to counteract the effect. When the cooling water tends to form base, only phosphate treatment is appropriate. Many drum boilers that are operated on AVT have provision for phosphate or caustic treatment during condenser leaks because the amines used in AVT have neither significant buffering capacity nor precipitate conditioning properties in the boiler.

Oxidizing Chemistry. In high pressure boilers systems having the ability to maintain hydrogen cation-exchanged conductivity near or <0.1 μS/cm, the feedwater may be treated with oxygen. The process is called Oxygen Treatment, OT. Oxygen is added either as gaseous oxygen or as hydrogen peroxide. The pH may be neutral or elevated with ammonia. The goal of this treatment is to maintain all iron alloy surfaces in a passivated state. The rate of carbon steel corrosion as a function of oxygen is shown in Figure 24. At the low (0.1 μS/cm) cation conductivity, the corrosion rate drops over an order of magnitude as the oxygen concentration is increased from 0.02 to 0.2 mg/kg (ppm). When higher anion concentrations inhibit passivation, the increased oxygen causes faster corrosion. Oxygenated water treatment has been used in Germany since the 1970s and has become widespread throughout the world since 1990. This treatment regime requires systems having no copper alloys. This practice is most advantageous for once-through boiler systems. In recirculating boiler systems, it is very difficult to maintain the hydrogen cation-exchanged conductivity low enough in the boiler

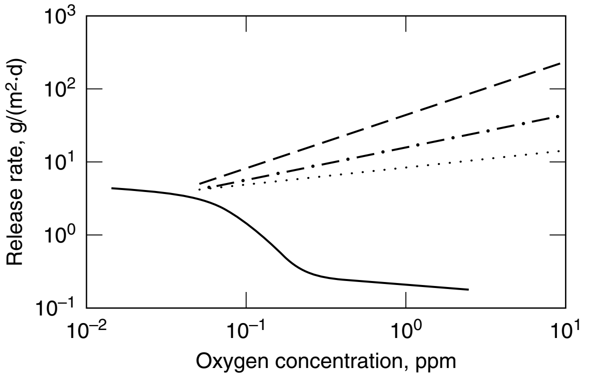

Fig. 24. Corrosion rates of carbon steel as a function of oxygen concentration at cation conductivity values of (—) 0.1, (· · · ·) 7, (–·–) 87, and (– – –) 850 μS/cm (34).

water. Thus the oxygen must be flashed in the drum to prevent boiler corrosion. Nonetheless, some recirculating systems have been successfully operated on oxygenated water treatment.

Another oxidizing treatment is All Volatile Treatement (Oxidizing), AVT(O). As in the case of the OT, cation exchanged conductivity must be maintained <0.15. Instead of injecting oxygen, however, the reducing agent (oxygen scavenger) feed is simply stopped. The oxygen concentration in the feedwater is allowed to float at the value set by the condenser deaeration, commonly $<25\ \mu g/kg$. The goal is to maintain the iron in the passive state. The AVT(O) is frequently used in systems with recirculating steam generators.

Other Water Treatment Issues. Attemporation. Maintaining steam temperatures at correct values may require a process called attemporation, where water is sprayed into the inlet, midpoint, or outlet of the superheater or reheater to lower the temperature of the exiting steam. Attemporation bypasses the drum of a recirculating boiler. Any impurities in the feedwater are sent directly to the turbine. Copper fouling of turbines is commonly associated with high rates of attemporation. Attemporation can also allow salts from a condenser leak to bypass the boiler and deposit on the turbine.

Condensate Polishing. In order to maintain the feedwater purity required for once-through boilers, but also as an aid to maintaining feedwater purity for drum boilers and nuclear steam generators, condensate polishers are used. Condensate polishers are large ion-exchange systems designed to pass high flows. These reduce contamination, but do not protect a system against large contaminant ingress. When there is massive contaminant ingress, condensate polishers provide time for an orderly shutdown.

Makeup. Makeup treatment depends extensively on the source water. Some steam systems use municipal water as a source. These systems may require dechlorination followed by reverse osmosis and ion exchange. Other systems use wellwater. In hard water areas, these systems include softening before further purification. Surface waters may require removal of suspended solids by sedimentation, coagulation, flocculation, and filtration. Calcium may be reduced by precipitation softening or lime softening. Organic contaminants can be removed by absorption on activated carbon. Details of makeup water treatment may be found in many handbooks (23–25), as well as in technical literature from water treatment chemical suppliers.

Water and Steam Purity Monitoring. To maintain appropriate steam and water purity requires analysis at the concentrations of interest. Details of monitoring systems, including the need for special nozzles to sample steam can be found in Supplement 19.11 to the ASME Power Test Code (35). Feedwater and steam purity for most boiler systems approaches the detection limit of on-line monitoring instruments. One of the most reliable monitoring devices is electrical conductivity. Pure water has a resistivity of $18\ M\Omega{\cdot}cm$ or a conductivity of $0.055\ \mu S/cm$ $(1\ S = 1/\Omega)$. Ammonia or an amine added to raise the pH also raises the conductivity. The agreement between the pH predicted from measured conductivity and the measured values of pH is one measure of water purity. By passing the sample stream through a cation resin in the hydrogen form, the ammonia or amine is removed and all the other cations are converted to hydrogen. The conductivity of the resulting stream (hydrogen−cation-exchanged conductivity, commonly called cation conductivity) is a measure of the total anions in the solution. Carbon dioxide may contribute a large fraction of this conductivity. Degassing the stream after the cation exchange removes the carbon dioxide and other volatile species. The resulting conductivity is essentially a measure of the dissolved solids. Conductivities $<1\,\mu S/cm$ should be measured on continuous streams with on-line instrumentation. The measurement of pH in high purity water is difficult and pH between 8 and 11 may often be more reliably calculated from the specific and cation conductivity using equation 4:

$$\mathrm{pH} = \log_{10}(s - a\,c) + 8.57 \tag{4}$$

were s is the specific conductivity, c is the cation exhanged conductivity, and a is a constant, near 0.3, that depends slightly on the ions causing the cation exchange conductivity.

Sodium and chloride may be measured using ion-selective electrodes. On-line monitors exist for these ions. Silica and phosphate may be monitored colorimetrically. Iron is usually monitored by analysis of filters that have had a measured amount of water flow through them. Chloride, sulfate, phosphate, and other anions may be monitored by ion chromatography using chemical suppression. On-line ion chromatography is used at many nuclear power plants.

Deposition of Contaminants from Steam in Turbines. Impurities in steam may deposit whenever the concentration exceeds the solubility limit. Considerable work has been done on the nucleation of steam droplets on impurities, leading to concentrated solutions. The time available for the nuclei to combine to form macroscopic droplets is limited, and one expects that most of the nuclei will reach the condenser before they collide with another impurity bearing nucleus. However, the author believes that the limiting mechanism is mass transfer from the bulk steam to the surface. Papers on both subjects can be found (16).

5. Uses

5.1. Power Production. Steam cycles for generation of electric power use various types of boilers, steam generators, and nuclear reactors; operate at subcritical or supercritical pressures; and use makeup and often also condensate water purification systems, as well as chemical additives for feedwater and boiler-water treatment. These cycles are designed to maximize cycle efficiency and reliability. The fuel distribution of steam power sources installed in the United States, both conventional and combined heat and power, from 2000 to 2003 are as follows: coal, 56.6%; oil, 3.1%; natural gas, 16.5%; nuclear, 22.6%; miscellaneous (including wood, waste, solar, and geothermal), 1.6%. The 2004 summer peak generation in the United States was 730 GW (36). The predominant use of natural gas for power production is in combined cycle plants.

Modern power cycles have turbine throttle pressures of 16.5 MPa (2400 psig) or 24.1 MPa (3500 psig) with the throttle and reheat temperatures in the range 537–566°C (1000–1050°F). The lower pressure is used for subcritical recirculating boilers, the higher pressure for supercritical once-through boilers. Ultrasupercritical boilers use higher temperatures and pressures and research

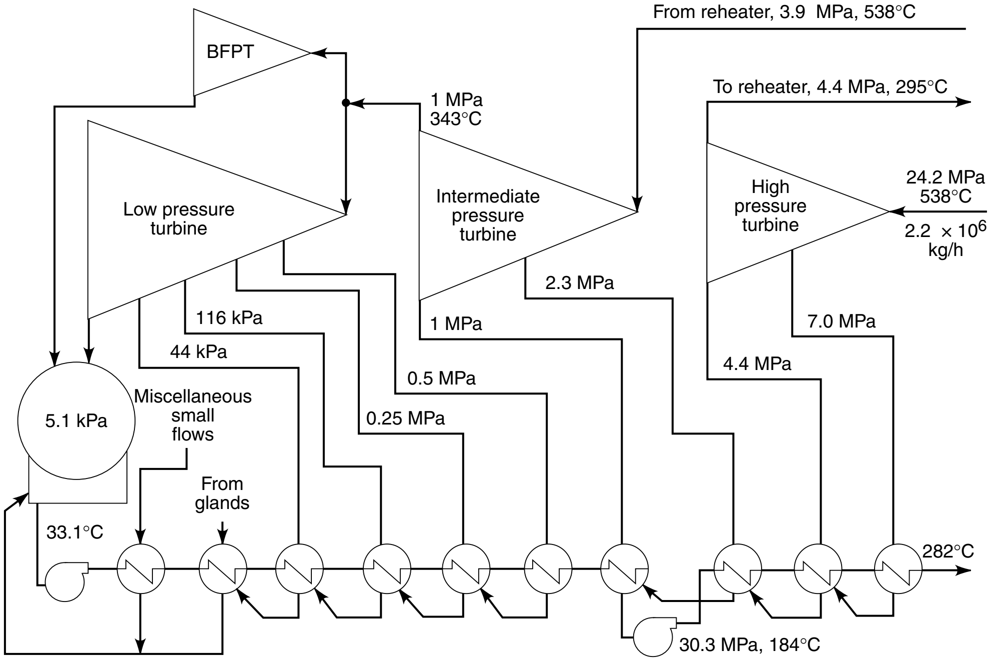

Fig. 25. Schematic of large fossil steam turbine system, where BFPT = boiler feed pump turbine. To convert MPa to psi, multiply by 145.

is in progress to extend the throttle conditions to 35 MPa (5076 psia) and 760°C (1400°F). A cycle schematic for a typical 16.5 MPa (2400 psig) plant is shown in Figure 25. The number of feedwater heaters, which may vary between five and seven and is occasionally eight, is a compromise between efficiency and capital cost. The cycle schematic shows *P*, *T*, and flows at multiple locations. Fossil turbines generally operate at 3600 rpm (60 Hz) or 3000 rpm (50 Hz) using two-pole generators. Nuclear turbines, and some older large fossil low pressure turbines, generally operate at 1800 (60 Hz) or 1500 (50 Hz) using four-pole generators, which produce double the frequency of two-pole generators for a given speed.

Turbines. The structure of steam turbines varies with the size. Very large (>500 MW) utility turbine systems have several individual turbines, usually classified as high pressure (HP), from throttle pressure to typically 4.8 MPa (696 psia); intermediate pressure (IP), typically from 4.8 MPa (696 psia) to 1.0 MPa (145 psia); and low pressure (LP), typically from 1.0 MPa (145 psia) to condenser pressure of 5.0 kPa (38 Torr, 1.5 in. Hg). On smaller turbines, typically in the range of 100–420 MW, a combined HP–IP turbine is joined with an LP turbine. Still smaller turbines, typically <125 MW, have a total combination of HP–IP–LP in a single cylinder or case.

Turbine Construction. Large steam turbines are generally designed as a rotor inside one or two cylinders or casings. The low pressure nuclear turbine having a partial integral rotor (Fig. 26) illustrates many of the features of both older and newer turbines. The rotor carries multiple rows of blades (or buckets); the cylinder carries the same number of diaphragms of stationary blades and

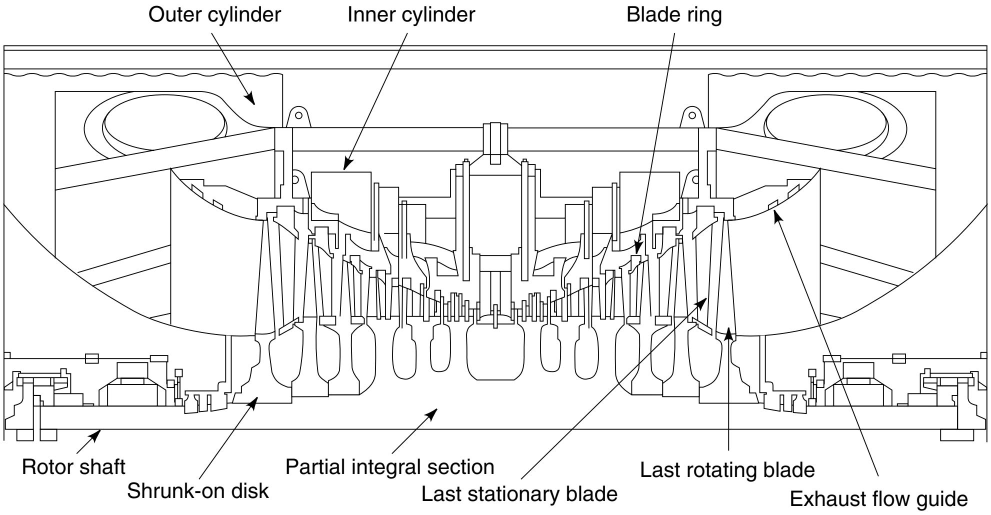

Fig. 26. Schematic of a nuclear low pressure turbine having a partial integral rotor.

acts as a pressure vessel. The stationary blades may also be called vanes or nozzles. A row of stationary blades followed by a row of rotating blades is called a stage. A typical turbine has 20–25 stages varying in height from ~2 cm at the inlet to >130 cm at the exhaust. The low pressure stages may be multiplied in a double, quadruple, or sextuple flow. Each blade row, stationary and rotating, contains from 80 to 150 blades. This amounts to thousands of blades, each of which is a precision airfoil. The stationary blades direct the expanding steam in the proper directions so that the rotating blades efficiently convert the energy into torque. The difference between the rotating and stationary blades is significant. The rotating blades experience centrifugal stress, whereas the stationary blades do not. Because a principal source of operating stress in the rotating parts is usually the rotation, stress corrosion cracking thus occurs more in rotating parts than in stationary ones.

Modern utility turbines are generally rather massive devices. The longest turbine systems may exceed 30 m. Turbine cylinders are pressure vessels. The high pressure cylinder of a fossil unit must withstand 16.5–24.1 MPa (2400–3500 psig) at 538°C (1000°F), at which temperatures and pressures creep becomes significant during the design life, even for the thick metal walls. To reduce the pressure and temperature differentials, either the exhaust or the extraction steam from the HP turbine is used to pressurize and cool the cavity between the inner and outer cylinders. In spite of the various cooling and pressure distribution features, the high pressure inner and outer cylinders are still massive castings and do not tolerate rapid temperature changes without experiencing low cycle fatigue and cracking. Because the cylinders cannot be operated above rated temperature for extended times without significantly reducing the creep life of the parts, careful control of steam temperature is necessary. High and intermediate pressure cylinders are usually made from chromium–molybdenum, CrMo, steel. To allow the opening of the turbine for maintenance, cylinders are cast in upper and lower halves and bolted together for operation.

The bolts are high strength, high temperature materials that are susceptible to stress corrosion cracking if a liquid phase is present. The intermediate pressure inner and outer cylinders are also cast. Low pressure turbines have an inner cylinder that contains pressure and an outer shell that contains a vacuum. Low pressure inner and outer shells are usually fabricated structures. The rotary seals between the turbine shaft and cylinders are steam glands. In a gland, steam is leaked through a labyrinth to a low (subatmospheric) pressure point (37). Air also goes to the low pressure point, which is the gland condenser.

Rotor bodies are generally made from low alloy steels. A nuclear low pressure rotor weighs >90 metric tons. High pressure and intermediate pressure rotor bodies, made from 0.9 to 1.5% Cr, from 0.7 to 1.5% Mo, from 0.2 to 0.35% V steels in single forgings (37), are machined to accept blade attachments of various types. Low pressure rotor bodies are generally made from 3.25 to 4.0% Ni, from 1.25–2.0% Cr, from 0.25–0.6% Mo, from 0.05–0.15% V steel (37). When first designed, low pressure rotor bodies (everything except the blades) have often been larger than the largest available forgings. The early bodies of a given design are built up, whereas the later bodies of a design are single forgings. One method of buildup is to weld disks together; the other is to shrink disks on a shaft. The first method has all the problems associated with welding; the second creates crevices in high stress regions. The partial integral rotor (Fig. 26) shows the intermediate stage where the center part is a single forging but the last several disks are shrunk-on. As of the 1990s, forging technology permits monoblock rotors in all applications. To reduce weight, low pressure rotor bodies are forged with a disk on shaft shape. The outer rims of the disks are machined to accept the blades.

Low pressure stationary blades are made from 12% Cr steel and their supporting structures are usually made from carbon steel. Stationary blades are commonly welded into diaphragms. The diaphragms are caulked either into blade rings that mount in the turbine cylinder, or directly into the cylinder. Rotating blades are commonly made of 12 or 13% Cr alloy. One manufacturer uses 17–4 PH (17% Cr and 4% Ni, precipitation hardened with Cu) for long low pressure blades. Increasingly, titanium is used for stress reduction due to its light weight, for corrosion resistance, or both. Blades in high pressure, intermediate pressure, and the first stages of low pressure turbines are generally machined. The airfoils of long (28 cm or longer) blades in the last several stages of the LP turbine are generally precision-forged and the attachment area machined to complement the attachment of the rotor body. The attachment area of rotating blades is a crevice and prone to the problems associated with crevices. Details of turbine design and the aerodynamics of turbines are available (37).

Rankine Cycle Thermodynamics. Carnot cycles provide the highest theoretical efficiency possible, but these are entirely gas phase. A drawback to a Carnot cycle is the need for gas compression. Producing efficient, large-volume compressors has been such a problem that combustion turbines and jet engines were not practical until the late 1940s.

The Rankine cycle overcomes the problem of an efficient gas compressor by compressing the liquid. Efficient pumps are much easier to construct than efficient compressors. Figure 27**a** shows the Rankine cycle on a pressure–volume (P–V) diagram; Figure 27**b**, the cycle on a temperature–entropy (T–S) diagram

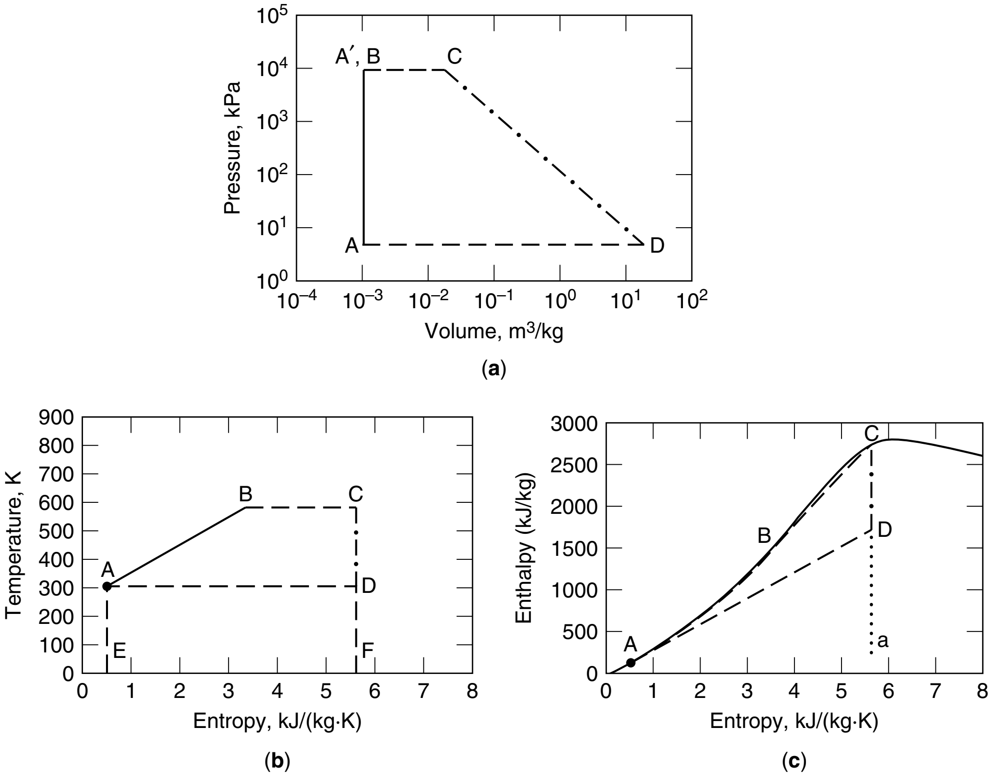

Fig. 27. Rankine cycle in terms of (**a**) pressure and volume; (**b**) temperature and entropy; and (**c**) Mollier (enthalpy vs entropy) chart, where adiabatic (isentropic) compression is represented by line AA′ in (**a**) and by (•) in (**b**) and (**c**). (– – –) represents isobaric heating or heat rejection, including vaporization; (–·–) represents isentropic expansion; and (—) in (**c**) is the saturation line. Heat rejection is from point D to point A. To convert kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184.

for a cycle between 5 kPa (0.73 psia) and 10 MPa (1450 psia; 1435 psig). This is near the highest pressure for which a simple Rankine cycle is practical. First the pressure is increased adiabatically from 5 kPa to 10 MPa. This compression of the liquid water raises the temperature and enthalpy slightly (0.7°C or 2.8 kJ/kg), but the amounts are so small that the difference cannot be easily distinguished on most temperature–entropy or Mollier (enthalpy–entropy) charts (Fig. 27**c**) that represent the rest of the cycle. This process is represented as points A and B in Figure 27. The compressed liquid is heated along the isobar to the boiling point 311°C (592°F) at point B. The fluid is then boiled isothermally to point C. The steam is expanded reversibly (isentropically) to D, where the pressure is 5 kPa and the temperature is 32.9°C. The steam is then isothermally condensed back to point A.

The efficiency of the Rankine cycle, $\eta = W/Q$, where W is the work produced and Q is the heat input can be derived (37–39) as follows:

$$\eta = (h_{\mathrm{C}} - h_{\mathrm{D}})/(h_{\mathrm{C}} - h_{\mathrm{A}}) \qquad (5)$$

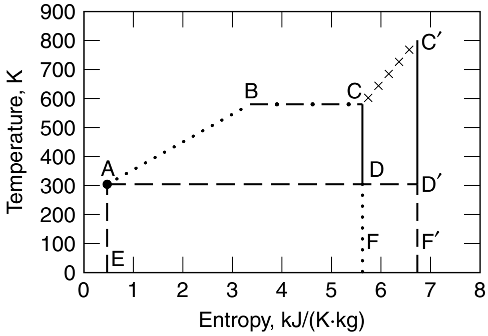

Fig. 28. Rankine cycle for superheat, where (•) represents adiabatic (isentropic) compression; (· · · ·), isobaric heating; (–·–), vaporization; (× × × ×), superheating; (—), turbine expansion; and (– – –), heat rejection. To convert kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184.

where h is the enthalpy at the points A, C, and D. Graphically, in Figure 27**b**, the efficiency is the ratio of the area of the region ABCDA to region EABCFE. The efficiency equation (eq. 5) emphasizes the importance of Mollier charts, where the ideal work is simply the distance along the vertical axis. On the Mollier chart, Figure 27**c**, the reversible work in the cycle is described as the length of the vertical line CD. The efficiency is the length of CD divided by the length of Ca, where point a is simply the projection of A to the same entropy as the turbine expansion.

Superheat and Reheat. One way to increase the area of the work regions on the T–S diagrams is to superheat the steam (Fig. 28). The pressure for the cycle defined by ABCC′D′A is again 10 MPa. The primed letters correspond to points in Figure 27**b**, but the points are not identical. The saturated steam at point C [311°C (592°F)] is heated to 536°C (998°F) at point C′. The superheated steam is expanded to point D′. The increase in work is area CC′D′D. The increase in rejected heat is area DD′F′F. The ratio of these two areas is greater than the ratio of the areas in the simple Rankine cycle, so the efficiency of the total cycle is improved. Similar improvement can be achieved by reheating the steam. After the steam has expanded to ~25% of its original pressure in the high pressure turbine, it can be returned to the boiler and reheated to approximately the same temperature as the inlet steam. This high temperature steam can then be expanded through the intermediate and low pressure turbines to the condenser.

Regenerative Rankine Cycle. A primary inefficiency in the Rankine cycle is caused by the heat added to the cycle to heat the water from the condensate temperature to the boiling point. Regenerative heating addresses this loss. In regenerative heating, some of the steam is removed from the expansion in the turbine and used to heat the water (39). In essence, regeneration uses some of the latent heat of the steam vaporization to heat feedwater, rather than rejecting this heat to the condenser. Figure 29 shows the effect of this process in the theoretical limit of an infinite number of regenerative heating steps. The area ABD is removed from the cycle, the heat rejected as area EADF is eliminated, and the increase in efficiency is substantial. In practice, a maximum of eight feedwater

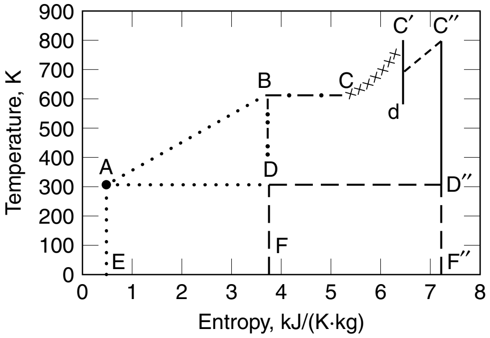

Fig. 29. Theoretical regenerative cycle at 16.5 MPa (165 bar, 2400 psi), showing reheat and efficiency improvement resulting from regeneration, where (· · · ·) is the region removed from cycle; (—·—), vaporization; (× × ×), superheating; (—), turbine expansion; (– – –), heat rejection; (- - -), reheating; and (—··—), regeneration. To convert kPa to psi, multiply by 0.145. To convert kJ to kcal, divide by 4.184.

heaters is economical, and line DB is no longer straight. When a cycle includes regeneration, the amount of work generated by each kilogram of steam at the turbine inlet is reduced because some of the potentially available work is used to heat the feedwater. When power capacity is temporarily more important than efficiency, cycles may be operated with one or more heaters out of service, provided that total steam flow does not exceed the turbine capacity at any stage.

Real Conventional Fossil Fuel Cycles. Modern fossil fuel cycles start at 16.5 MPa (2415 psia; 2400 psig) or supercritical 24 MPa (3515 psia; 3500 psig). Usually throttle pressures are given in gauge pressures. In a typical subcritical fossil fuel cycle (Fig. 25), the boiler feed pump suction comes from the deaerating heater. The more feedwater heaters, the more efficient is the cycle, but eight is usually the economically practical limit. Some cycles have as few as three feedwater heaters. The boiler feed pump turbine for large units is usually driven by the steam from the low pressure crossover and is thus a low pressure turbine. However, at low loads, it is driven by high pressure steam. Some cycles have a motor-driven boiler feed pump, so the boiler feed pump turbine is omitted from the diagram and the steam normally used to drive it goes into the main turbine. There is a transition from dry to wet steam. In Figure 25, the last (lowest pressure) extraction is essentially at the saturation line, which is the typical situation. In some units, there is a small amount of superheat at the last extraction; in others there may be a small amount of moisture.

Nuclear Steam Cycles. A cycle diagram for a nuclear power plant is shown in Figure 30. Although most nuclear power plant cycles begin with saturated steam, this diagram is for a unit with a once-through nuclear steam generator. The throttle steam has 17.2°C (31°F) of superheat. This steam is expanded through the high pressure turbine. In the middle of this expansion, steam is extracted for the highest pressure feedwater heater. After heating the feedwater, the water in the shell side of the heater is drained to the shell side of the second highest pressure heater. Because the inlet steam has such low enthalpy, the steam becomes moist in the high pressure turbine, typically 7–13% moisture at the HP exhaust. Moisture reduces the efficiency of the turbine

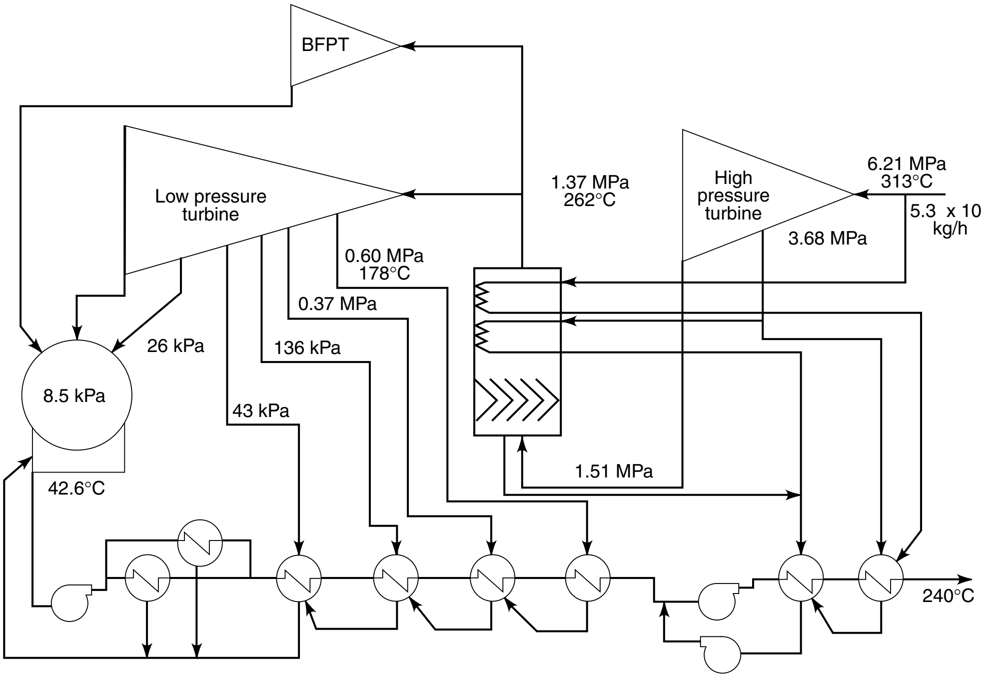

Fig. 30. Schematic of nuclear steam cycle where BFPT = boiler feed pump turbine. To convert MPa to psi, multiply by 145.

because the droplets do not follow the steam flow. They impinge on the turbine and must be accelerated. Typically, 10% efficiency is lost in wet steam. In addition, the droplets erode the turbine. After the high pressure turbine, the steam is dried and superheated in a moisture separator reheater (MSR). The moisture separation is thermodynamically equivalent to isothermal reheating. The two-phase fluid with a typical enthalpy of 2680 kJ/kg (1153 Btu/lb) is separated into steam at 2790 kJ/kg (1200 Btu/lb) and water at 846 kJ/kg (364 Btu/lb). The water goes to the second highest pressure heater, where it is merged with steam from the outlet of the first-stage reheater. The water from the second heater shell is then pumped into the feedwater. This arrangement creates a high pressure recirculating loop. The heat source for reheating is the main steam or a combination of the main steam and steam extracted from the high pressure turbine. The superheat is typically 28°C (50°F), which usually keeps three to five stages of the low pressure turbine dry.

Nuclear Cycle Water Treatment Issues. Relatively volatile components, such as amines and organic acids, can appear at rather high concentrations in the high pressure loop of nuclear power steam cycles. Because of the variation in distribution between water and steam phases with temperature and the generation of significant moisture, the chemical relationships can be quite complex. A full model of the equilibria occurring in the turbine is required to understand the chemical effects (40). Feedwater pH is not a good indicator of the pH of the liquid phase in the turbine. The pH of the turbine liquid depends on feedwater pH, the amines present, and the acids present. The equilibria can be such that an increase in the boric acid concentration in the feedwater raises the pH of the liquid phase at the end of the high pressure turbine. This apparent chemical inconsistency occurs because increased boric acid requires additional amine to maintain the feedwater pH.

Combined Cycle. In the last decade, the majority of new fossil fuel plants using steam have been combined cycle. Combined cycles use a steam turbine system as a bottoming cycle for a combustion turbine. Exhaust gases leave the combustion turbine at 510–593°C (950–1100°F). This heat is wasted in the simple combustion turbine cycle. However, it can be used to boil water in a heat recovery steam generator (HRSG). This process lowers the temperature of much of the rejected heat to that leaving the steam turbine. However, to prevent HRSG corrosion by sulfuric acid, the stack gas temperature is nominally 150°C (302°F), causing additional heat rejection to the environment. Because the combustion turbine does not need preheated air, there is no air heater in combined cycles. The condensate preheater (economizer) of the HRSG can extract sufficient heat as possible from the combustion gas to reach the inlet temperature for the low pressure HRSG section. Thus the feedwater heating of conventional utility cycles is not needed. There may be a single direct-contact heater to remove oxygen from the feedwater, but the deaeration function is often moved to the condenser. Combined cycle power plants have achieved 58% thermal efficiency and have been designed to achieve 60% (41).

The HRSG may be designed with two or three stages to efficiently convert the exhaust heat of the combustion turbine to steam. Each stage consists of an economizer (which heats feedwater to the boiling point), an evaporator, and a superheater. In the high pressure HRSG stage, the water is boiled in the evaporator and the gas turbine exhaust is cooled to ~350°C (662°F). The exhaust cannot boil more water at the high pressure, but it still contains enough energy to boil additional water at a lower pressure. No more than three stages are curently economical. Cycle diagrams and thermodynamics are available (41).

Many older conventional steam plants have been converted to combined cycle. The old boiler is removed and replaced by a combustion turbine and heat recovery steam generator. Although the cycle efficiency is not as high as completely new plants, substantial capital cost is avoided by the modification and reuse of existing steam turbine and auxiliary equipment. In many combined cycle power plants, steam is injected into the combustors of the combustion turbine to lower peak flame temperatures and consequently lower NO_x. Steam (or rarely water) may also be injected to increase the power output of the combustion turbine (power augmentation).

Cogeneration. Cogeneration is another modification of the Rankine cycle used when steam is required to heat a process. It is common in pulp and paper mills, chemical plants, and municipal or district heating systems. The steam is produced at higher pressure and temperature than would be required for the process. The steam is expanded through a turbine and steam at the desired pressure is extracted. The turbine may be used to drive a generator or other machinery (Fig. 31), a schematic diagram of the steam system of a pulp and paper mill, shows drive turbines, turbine-generators, and multiple boilers. One of the boilers is a heat recovery boiler, another is fueled by bark. There are pressure manifolds at 6.2 MPa (913 psig) and 538°C (1000°F);

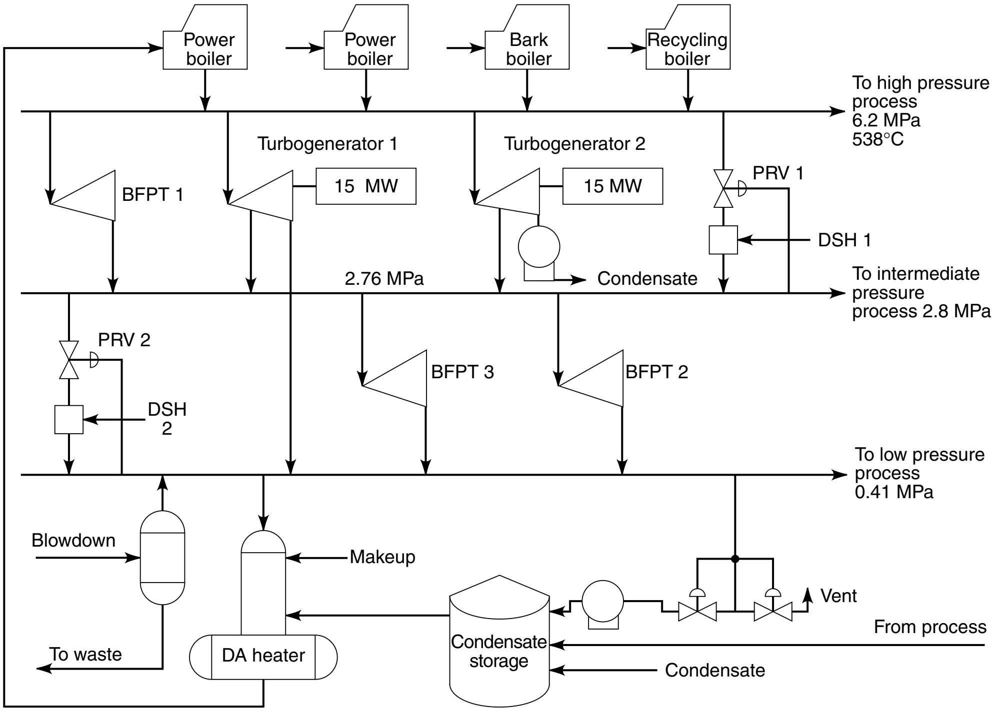

Fig. 31. Steam system of a pulp and paper mill where PRV = pressure reducing valve, DSH = desuperheater, and DA = deaerating. To convert MPa to psi, multiply by 145 (42).

2.8 MPa (420 psig) and 229°C (445°F); and 0.41 MPa (74 psig) and 145°C (292°F). Turbogenerator 2 exhausts to condensate, but turbogenerator 1 exhausts to the 0.41-MPa header, where the entire exhaust is used for heating. This steam would be generated in a low pressure boiler if it did not come from the turbine. For turbogenerator 1, the thermal efficiency of the electrical generation process approaches the mechanical efficiency of the turbogenerator (90 + %), because there is no heat rejected by this cycle.

5.2. Mechanical Drives. Steam turbines are very efficient at high load ratings and, depending on the steam balance in a plant, are normally considered as drive units if >37 kW (50 hp) is required, unless the steam source is intermittant. If many small loads are to be handled separately in a plant, it may be preferable to generate electric power by passing the steam through a back-pressure (no condenser) turbine connected to an electric generator. The generated electricity in turn can be fed into the motors throughout the plant. Steam turbines operate very effectively at high speeds (3000–10,000 rpm) and thus lend themselves well to large power output, high speed drives for gas compressors, multistage high pressure pumps (eg, boiler feed pumps), and other high speed rotating equipment. In such installations, the steam can be fed to the turbine and extracted at various stages of its expansion corresponding to the desired process operating pressures. Steam turbine drives having rpm reduction are used in large commercial ships and navy vessels for propulsion.

5.3. Steam Heating. Wet and saturated steam has a definite pressure for each fixed boiling or condensing temperature. Therefore, the control of the desired temperature for any process heating requirement may be fixed by choosing the steam pressure. It is customary for steam to be generated under slightly superheated conditions if the steam generator is to be located at a considerable distance from the various users.

When higher temperatures are needed, the higher corresponding pressure becomes important in the design of equipment. Steam pressure rises quite rapidly with temperature and is of significant concern for heating conditions at temperatures $>180°C$. The use of steam for heating is normally limited to pressures <2.2 MPa (330 psig) because the cost of the heat-transfer equipment becomes too high for sizable heating units as higher pressures are required. When temperatures in excess of 180–205°C are required, other heating media are usually preferred.

Evaporators. Steam heating systems have often been installed in a cascade system, as in multiple-effect evaporators. This arrangement makes possible the recovery of heat at several successive levels merely by reducing the pressure at each of the stages. Condensing all the steam vaporized in one stage by heating and vaporizing the material present in the succeeding stage at lower operating pressure produces good economy of heat. This system of heating operates best in the low pressure range because at higher pressures the equilibrium temperature changes more slowly with the pressure.

Control. When close temperature control is required in order to prevent overheating of material being processed or to ensure a high heating density, steam is the medium normally used. A pressure regulator controlling the steam pressure of a heating unit maintains temperatures usually within degrees of the design conditions on the process side.

5.4. Industrial Processes. *Steam Reforming Processes.* In the steam reforming process, light hydrocarbon feedstocks, eg, natural gas, liquefied petroleum gas, and naphtha, or in some cases heavier distillate oils are purified of sulfur compounds. These then react with steam in the presence of a nickel-containing catalyst to produce a mixture of hydrogen, methane, and carbon oxides. Essentially total decomposition of compounds containing more than one carbon atom per molecule is obtained.

Steam reforming in industrial practice falls into two main classes according to catalyst type and reactor equipment use: hydrogen production by high (generally $>700°C$, 1292°F) temperature reforming, and methane manufacture by low ($<550°C$, 122°F) temperature reforming. The amount of steam consumed by reaction in the overall process depends on the choice of product gas. A general hydrocarbon, C_xH_{2x+2}, reacting with steam gives in the low temperature case the following:

$$4\,C_xH_{2x+2} + 2x\,H_2O \rightarrow 3x\,CH_4 + x\,CO_2 + 4\,H_2$$

and in the high temperature case:

$$C_xH_{2x+2} + 2x\,H_2O \rightarrow (3x+1)\,H_2 + x\,CO_2$$

In practice, two competing reactions combine to limit the process.

$$CH_4 + H_2O \rightleftarrows CO + 3\,H_2$$

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The equilibrium composition of the product gas can be altered by choice of suitable temperature, pressure, and steam to feedstock ratio to produce a gas mixture consisting largely of methane or largely of hydrogen having varying proportions of carbon monoxide. In each case, some carbon dioxide is produced, which can be removed. It is often convenient to use more than one reaction stage to modify the gas mixture produced from the primary gasification step toward the desired composition.

Synthetic Ammonia. Steam-methane reforming is used to produce hydrogen for the production of ammonia, which is synthesized by using nitrogen from the air at high pressure and temperature over a suitable catalyst. In this process, ~0.75 kg of steam is required to produce 1 kg of ammonia. A very large synthetic ammonia plant uses a single-train process employing centrifugal compressors driven by steam turbines. The exhaust steam is used for the gas reforming reaction. The high pressure steam thus generated from waste heat is the heart of the energy system for the process, which in turn is the key to the process economics (43).

Coal Gasification. Coal gasification processes involve the reaction of coal at high temperature with steam and air or oxygen to produce a mixture of gases, typically carbon monoxide, carbon dioxide, hydrogen, and methane. Producer gas, a mixture of carbon monoxide and hydrogen, has been made by this method since early in the twentieth century. Sulfur in the coal reacts to form hydrogen sulfide. The gases from the gasifier can be further upgraded in several steps. By reaction with steam, the carbon monoxide in the gas is converted to hydrogen and carbon dioxide. Hydrogen sulfide and carbon dioxide can be removed in a purification system and the hydrogen converted to methane by reaction with carbon monoxide. There are numerous variations on the basic process. Because the gas produced in a coal gasification process can serve as a fuel for combustion turbines, coal gasification is becoming increasingly important. The combustion turbines used in the high efficiency combined-cycle power generation systems require gas or liquid fuel. Several integrated gasification combined cycle (IGCC) power plants have been built recently and more are expected as the price of natural gas for combustion turbines rises compared to coal prices. The IGCC thermal efficiencies are projected to be in the 45–50% range by 2010 (44). Since the carbon dioxide in the IGCC is more concentrated in the fuel stream than in combustion turbine exhaust gases, it is easier to sequester the carbon dioxide in the IGCC process than in conventional hydrocarbon burning plants.

Coal Liquefaction. Steam is used to produce hydrogen for the liquefaction of coal. In the liquefaction process, coal is crushed, dried, pulverized, and then added to a solvent to produce a slurry. The slurry is heated, usually in the presence of hydrogen to dissolve the coal. The extract is cooled to remove hydrogen, hydrocarbon gases, and hydrogen sulfide. The liquid is then flashed at low pressure to separate condensable vapors from the extract. Mineral matter and organic solids are separated and used to produce hydrogen for the process. The extract may be desulfurized. The solvent is separated from the products. There are at least six different liquefaction processes.

Petroleum Recovery. Steam is injected into oil wells for tertiary petroleum recovery. Steam pumped into the partly depleted oil reservoirs through injection wells decreases the viscosity of crude oil trapped in the porous rock of a reservoir, displaces the crude, and maintains the pressure needed to push the oil toward the production well. Steam is also used in hot-water extraction of oil from tar sands in the caustic conditioning before the separation in a flotation tank (45).

Evaporation and Distillation. Steam is used to supply heat to most evaporation and distillation processes, eg, in sugar-juice processing and alcohol distillation. In evaporation, pure solvent is removed and a low volatility solute is concentrated. Distillation transfers lower boiling components from the liquid to the vapor phase. The vapors are then condensed to recover the desired components. In steam distillation, the steam is admitted into direct contact with the solution to be evaporated and the flow of steam to the condenser is used to transport distillates of low volatility. In evaporation of concentrated solutions, there may be substantial boiling point elevation. For example, the boiling point of an 80% NaOH solution at atmospheric pressure is 226°C.

Desalination. A special case of distillation is water desalination. In places where energy is abundant but fresh water is not, eg, the Arabian Peninsula, water may be produced from seawater in flash evaporators. Low pressure turbine steam is extracted to provide heat for the evaporators. Condensed steam is returned to the cycle. Such units may be particularly prone to corrosion by salts. Sizes vary, but Shoaiba Desalination Plant completed in 2003 had six units and a total capacity of 150 million m^3/year. Steam comes from a local power plant (46).

Steam Cleaning. High pressure steam can be used to produce a high velocity jet with some superheating by expansion through a suitable nozzle to atmospheric pressure. The high velocity is effective in removing dirt and loose scale from solid surfaces. The high temperature encourages the melting or vaporization of oil and grease deposits, thus releasing the solid deposits for mechanical blast removal. Some condensation of steam on the initially cold surfaces also takes place, which may help to dissolve and release dirt and scale.

5.5. Hydrothermal Treatment of Wastes. Hydrothermal processing of materials appears to be a promising method of disposal for many noxious materials and of conversion of some wastes to valuable by-products. Most hydrothermal processing is oxidation, and has been called supercritical water oxidation. This method consists of mixing reactants and water; pressurizing, heating to reaction temperatures, and cooling the products; and then carrying out secondary processing of the products. For efficient oxidation, oxygen is added to the water. Typical pressures and temperatures are 22 MPa (3191 psia) and 550°C (1022°F) for destruction of wastes. Somewhat lower pressures and temperatures are used for conversions. Contact times are on the order of a few minutes. Organic chemicals are oxidized to carbon dioxide and water. Because the processes are $<1000°C$, nitrogen is usually reduced to the elemental state. Other common heteroatoms are converted to corresponding acids, eg, HCl and H_2SO_4. Reaction at high temperatures and pressures is an active field of research. There is consensus that the hydrothermal oxidation processes proceed by free-radical mechanisms.

Along the saturation line the dielectric constant of water declines with temperature (see Fig. 10), largely due to the decline in density. In the last 24°C below the critical point, the dielectric constant drops precipitously from 13.05 to 5.35. Continuing along the critical isobar [22.06 MPa (3205 psia)] in the next 5°C, it further declines to 2.61; and by 400°C it has declined to 1.98. In the region of the critical point, the dielectric constant of water becomes similar to the dielectric constants of typical organic solvents (Table 7). The solubility of organic materials increases markedly in the region near the critical point, and the solubility of salts tends to decline as the temperature increases toward the critical temperature.

At temperatures near the critical temperature, many organic degradation reactions are rapid. Halogenated hydrocarbons lose the halogen in minutes at 375°C (48). At temperatures typical of nuclear steam generators [271°C (520°F)], the decomposition of amines to alcohols and acids is well known (49). The pressure limits for the treatment of boiler waters using organic polymers reflect the rate of decomposition.

An important advantage of hydrothermal processing over incineration is that the former system is fully contained. If a process must be shut down, there is no discharge of material to the environment. Furthermore, the products may be analyzed or further processed before being discharged. The possibility of further processing makes hydrothermal processing an important candidate for reduction of wastes containing both organic molecules and radionuclides. Radionuclides can be recovered. Another advantage is that the input waste stream need not be highly characterized. The oxygen demand and the approximate amount of acid produced are the only principal environmental parameters to be considered.

The formation of acids from heteroatoms creates a corrosion problem. At the working temperatures, stainless steels are easily corroded by the acids. Even platinum and gold are not immune to corrosion. One solution is to add sodium hydroxide to the reactant mixture to neutralize the acids as they form. However, because the dielectric constant of water is low at the temperatures

Table 7. **Dielectric Constants of Solvents**[a]

Substance	Dielectric constant at 20–25°C
n-pentane	1.844
cyclohexane	2.22
benzene	2.284
chloroform	4.8
acetone	20.7
ethanol	24.3
methanol	32.63
water	78.45

[a] Ref. 47.

and pressure in use, the salts formed have low solubility at the supercritical temperatures and tend to precipitate and plug reaction tubes.

There are two general goals in hydrothermal processing of wastes. First is the total destruction of organic material. Pilot plants for destruction of chemical warfare agents and explosives have been constructed and are operating. In benchtop experiments, destruction and removal of these agents may exceed 99.9999%. Between 1996 and 2005, the size of operating units has increased from a small commercial system to dispose of 0.019 m^3/day (5 gal/day) of wastes from pilot plants is in use at one chemical company (50) to 8890 dry kg/day (9.8 dry tons/day) of municipal sludge at the Harlingen, Texas sewage treatment plant (51).

The second goal of hydrothermal processing is the conversion of waste materials into useful chemicals. This goal is usually pursued at lower temperatures and pressures. Glucose and cellulose can be pyrolysed in supercritical steam, yielding carbon dioxide and hydrogen. At room temperature and atmospheric pressure, the process produces char, hydrogen, and hydrocarbons. At intermediate temperatures, supercritical and hot water dissolve hemicellulose and lignin from wood. Ether linkages can also be cleaved.

Alcohols undergo dehydration in supercritical and hot water (52). Tertiary alcohols require no catalyst, but secondary and primary alcohols require an acid catalyst. With 0.01 M H_2SO_4 as a catalyst, ethanol eliminates water at 385°C and 34.5 MPa to form ethene. Reaction occurs in tens of seconds. Only a small amount of diethyl ether forms as a side reaction.

The use of supercritical and hot water as a solvent is still largely experimental. Because supercritical technology is well known in the power industry, this use of water is likely to increase in the future. Corrosion control may be an important limiting consideration. General process economics are the second potential limit.

6. Corrosion in Steam

Use of metals in hot steam is limited by oxidation rate, mechanical strength, and creep resistance. Temperature and stress limits and corrosion allowances are specified in national standards and pressure vessel codes (53,54). General corrosion rates in pure steam (Table 8) are about the same as in high purity deoxygenated water, except for gray iron, nickel, lead, and zirconium, which corrode faster in steam. There is evidence that some nickel alloys corrode faster in steam than in air. Iron-base alloys, including the austenitic and ferritic stainless steels, are used extensively in contact with steam. These oxidize to form a protective film of the spinel oxide, Fe_3O_4 (magnetite), or, in the case of stainless steels, M_3O_4, where M is iron, chromium, or nickel. Gamma-Fe_2O_3 has also been found on ferrous alloys in degassed high temperature water and steam. Its physical properties are very similar to those of Fe_3O_4. It is magnetic and has an almost identical crystal structure.

Only Fe_3O_4 and γ-Fe_2O_3 are considered to be protective films. Both are adherent and good electronic conductors. Alpha-Fe_2O_3, hematite, which forms in water and steam containing oxygen, is not adherent, is less protective,

Table 8. **Corrosion Rates of Metals in Steam**[a]

Material	Temperature, °C	Corrosion rate, mm/year	Comments
cast irons			
gray	25–112	<0.5	
nickel	25–350	<0.05	
silicon	25–300	<0.05	
mild steel	25–510	<0.05	
austenitic stainless steel alloys			
302, 304, 321, 347	25–790	<0.05	intergranular crack
316, 317	25–350	<0.05	
copper	25–250	<0.05	
copper alloys			
brass			
70–80 Cu+Zn, Sn, or Pb	25–212	<0.05	
57–93 Cu+Al, Zn, or As	25–212	<0.05	
cupro-nickel 66–88:11–13	25–300	<0.05	no Zn
nickel 99	25–425	0.5–1.3	
Ni–Cu 66–32	25–350	<0.05	
Ni–Cr–Fe T6–16–7	25–815	0.5–1.3	stress cracks
Ni–Mo 62–28+Fe, V	25–350	<0.05	
Ni–Cr–Mo 54–15–16+Fe, W	25–350	<0.05	
aluminum	50–250	0.5–1.3	
aluminum alloys			
gold	25–350	<0.05	
lead	25–150	0.5–1.3	
	300	>1.3	
platinum	25–350	<0.05	
silver	25–350	<0.05	
tantalum	25–250	<0.05	
titanium	25–350	0.0	aerated steam
zirconium	25–350	>1.3	

[a] Extracted from Ref. 55.

and is an insulator. FeO, which does not form at temperatures <570°C, is nonprotective. Under slightly oxidizing conditions in high pure water a mixture of magnetite and hematite forms. This mixture is generally more protective that magnetite. This mixed oxide forms the basis for oxidizing water treatments.

A good summary of the behavior of steels in high temperature steam is available (55,56). Calculated scale thickness for 10 years of exposure of ferritic steels in 593°C and 13.8 MPa (2000 psi) superheated steam is ~0.64 mm for 5 Cr–0.5 Mo steels, and 1 mm for 2.25 Cr–1 Mo steels. Steam pressure does not seem to have much influence. The steels form duplex layer scales of a uniform thickness. Scales on austenitic steels in the same test also form two layers, but were irregular. Generally, the higher the alloy content, the thinner the oxide scale. Excessively thick oxide scale can exfoliate and can lead to concentration of corrodents and corrosion under-the-scale. Exfoliated scale can cause solid particle erosion of the downstream equipment and clogging. Thick scale on boiler tubes impairs heat transfer and causes an increase in metal temperature.

Where corrosive impurities from steam or water concentrate on metal surfaces, corrosion can be severe (57–59). Concentration occurs in boilers in the waterwalls, where boiling occurs. General and pitting corrosion, stress–corrosion cracking, corrosion fatigue, corrosion–erosion, caustic gouging, and hydrogen embrittlement and cracking have been observed. Concentration occurs in turbines near the saturation line, where the ability of salts to elevate the boiling point of water creates a salt solution zone (60). In the salt solution zone, a 35% NaCl solution is produced from steam containing a few parts per billion NaCl. Turbines exhibit general corrosion, stress corrosion cracking and corrosion fatigue. Nuclear turbines may exhibit erosion–corrosion in regions where the steam is wet. Stress corrosion cracking and corrosion fatigue can lead to sudden failures of materials. Corrosion is not usually caused by the steam, but by the concentrated steam impurities, eg, chlorides, caustic, inorganic and organic acids, carbonates, sulfates, hydrogen sulfide, and their mixtures. Oxygen and oxides of copper, lead, and nickel can aggravate the corrosion.

7. Economic Aspects

Increasing fuel costs and sizes of industrial and utility installations have forced the emphasis in economical considerations to shift to high thermal efficiency, reliability, and availability. The investment, operating, maintenance, transmission, insurance, and other costs as well as depreciation must also be considered, but these are often less important.

Thermal efficiency and heat rate (an inverse of efficiency calculated as the heat input divided by the power output) directly influence the fuel cost. Increasing cycle pressure and temperature and using superheat, reheat, and condensing cycles result in a significant increase of efficiency and lower heat rate. In the process industry, this can be best achieved by cogeneration; in the electric utility industry, by combined gas–steam turbine cycles and further increase of cycle parameters. Using advanced power cycles currently available, a 1000-MWe (1.34×10^6hp) unit can save coal at a rate of 4 million metric tons/year, or $4 million/year at $30/ton, if the cycle parameters can be increased from 24.1 MPa (3500 psi)/540°C inlet/540°C reheat to 28.9 MPa/580°C/580°C/580°C (4292 psia/1076°F/1076°F/1076°F) double reheat. This change would result in an average gross plant efficiency improvement from 39.6 to 40.9% and in a heat rate improvement from 9077 to 8789 kJ/kWh (8610 to 8336 btu/kWh). Research efforts are underway for plants at 38.5 MPa/760°C/760°C/760°C (5584 psia/1400°F/1400°F/1400°F) with an efficiency of 48% and a heat rate of 7489 kJ/kWh (7103 btu/kWh).

BIBLIOGRAPHY

"Steam" in *ECT* 1st ed., Vol. 12, pp. 778–793, by H. N. La Croix, Foster Wheeler Corp.; in *ECT* 2nd ed., Vol. 18, pp. 692–715, by J. K. Rice, Cyrus Wm. Rice and Co.; in *ECT* 3rd ed., Vol. 21, pp. 507–551, by O. Jonas, Westinghouse Electric Corp.; in *ECT* 4th ed., Vol. 22, pp. 719–764, by James Bellows, Westinghouse Electric Corp.; "Steam" in *ECT* (online), posting date: December 4, 2000, by James Bellows, Westinghouse Electric Corp.

CITED PUBLICATIONS

1. V. Regnault, *Mém. l'Inst. France* **21**, 465 (1847).
2. W. T. Parry and co-workers, *ASME International Steam Tables for Industrial Use*, ASME, New York, 2000.
3. NIST Database 10, Standard Reference Data Program, Gaithersburg, Md., 1996.
4. P. R. Tremaine and co-workers, *Proceedings of the 13th International Conference on the Properties of Water and Steam, Toronto, 1999*, NRC Research Press, 2000.
5. Available at www.iapws.org.
6. IAPWS, Guideline on the Use of Fundamental Physical Constants and Basic Constants of Water, available at Ref. 5.
7. L. A. Curtis, D. J. Frurip, and M. Blander, in J. Straub and K. Schaffler, *Proceedings of the 9th International Conference on the Properties of Steam*, Pergamon Press, Oxford, U.K., 1980, p. 521.
8. A. H. Harvey and J. C. Bellows, "Evaluation and Correlation of Steam Solubility Data for Salts and Minerals of Interest in the Power Industry", NIST Technical Note 1387, 1997.
9. R. B. Dooley and co-workers, in D. A. Palmer and co-workers, *Aqueous Systems at Elevated Temperatures and Pressures*, Elsevier, 2004, Chapt. 17.
10. D. A. Palmer, J. M. Simonson, and Jorgen P. Jensen, in D. A. Palmer and co-workers, *Aqueous Systems at Elevated Temperatures and Pressures*, Elsevier, 2004, Chapt. 12.
11. K. Daucik and J. P. Jensen, in M. Nakahara and co-workers, *Proceedings of the 14th International Conference on the Properties of Water and Steam*, Kyoto, 2004, Maruzen, 2005, pp. 618–621 and references cited therein.
12. S. L. Goodstine, *Proc. Am. Power Conf.* **36**, 784 (1974).
13. O. I. Martynova, *Russ. J. Phys. Chem.* **38**, 587 (1964).
14. O. Jonas, *Combustion* **50**, 11 (1978).
15. J. M. Simonson and D. A. Palmer, *Proceedings of the 52nd International Water Conference*, Pittsburgh, Pa., Oct. 21–23, 1991, p. 253.
16. M. Nakahara and co-workers, *Proceedings of the 14th International Conference on the Properties of Water and Steam*, Kyoto, 2004, Maruzen, 2005.
17. J. W. Cobble and S. W. Lin, in P. Cohen, *ASME Handbook on Water Technology for Thermal Power Systems*, ASME, New York, 1989, Chapt. 8.
18. D. J. Wesolowski and co-workers, in D. A. Palmer and co-workers, *Aqueous Systems at Elevated Temperatures and Pressures*, Elsevier, 2004, Chapt. 14.
19. F. J. Pocock, in J. Straub and K. Schaffler, *Proceedings of the 9th International Conference on the Properties of Steam*, Pergamon Press, Oxford, U.K., 1980, p. 521.
20. M. W. Chase and co-workers, *JANAF Thermochemical Tables*, 3rd ed., American Chemical Society, Washington, D.C., 1986.
21. *Steam: Its Generation and Use*, 39th ed., Babcock and Wilcox Co., New York, 1978.

22. J. G. Singer, ed., *Combustion: Fossil Power Systems*, Combustion Engineering, Inc., Windsor, Conn., 1981.
23. F. N. Kemmer, ed., *NALCO Water Handbook*, McGraw-Hill Book Co., Inc., New York, 1979.
24. *Betz Handbook of Industrial Water Conditions*, Betz, Trevose, Pa., 1962.
25. A. R. Cantafio, ed., *Principles of Industrial Water Treatment*, Drew Industrial Division, Ashland Chemical Co., Boonton, N.J., 1994.
26. J. C. Bellows, in Ref. 16, pp. 612–617 and references cited therein.
27. A. F. Aschoff and co-workers, *Interim Consensus Guidelines on Fossil Plant Cycle Chemistry*, Electric Power Research Institute, CS-4629, 1986.
28. J. C. Bellows, *Proceedings of the 56th International Water Conference*, Pittsburgh, Pa., 1995, p. 155.
29. *Boiler-Water Limits and Steam Purity Recommendations for Watertube Boilers*, American Boiler Manufacturers Association, Arlington, Va., 1981.
30. B. Dooley and co-workers, *Proceedings of the 53rd International Water Conference*, Pittsburgh, Pa., 1992, p. 154.
31. F. J. Pocock, J. A. Lux, and R. V. Seibel, *Proc. Am. Power Conf.* **24**, 758 (1966).
32. E. P. Partridge and R. E. Hall, *Trans. ASME* **61**, 597 (1939).
33. J. Stodola, *Proceedings of the 47th International Water Conference*, Pittsburgh, Pa., 1986, p. 234.
34. R. K. Freier, in Hamburg Power Works, *Chemistry and Physics*, HEW, Hamburg, Germany, 1972.
35. ASME Power Test Code, PTC 19.11, ASME, New York, 1997 (revision in press).
36. Available at http://www.eia.doe.gov, Table 8.12 Electric Noncoincident Peak Load and Capacity Margin, 1986–2004, compiling data from the North American Electric Reliability Council, Princeton, N.J., 1995.
37. P. Schofield, in P. Cohen, *ASME Handbook on Water Technology for Thermal Power Systems*, ASME, New York, 1989, Chapt. 3.
38. G. J. Silvestri, Jr., *Steam Cycle Performance*, Power Division, ASME, New York.
39. G. J. Silvestri, Jr., in P. Cohen, *ASME Handbook on Water Technology for Thermal Power Systems*, ASME, New York, 1989, Chapt. 1.
40. J. C. Bellows, *Proceedings of the 54th International Water Conference*, Pittsburgh, Pa., 1993, p. 127.
41. H. Termuehlen, *100 Year of Power Plant Development*, ASME Press, 2001, Chapt. 6.
42. C. H. Cho, *Efficient Allocation of Steam*, MIT Press, Cambridge, Mass., 1982, p. 3.
43. *Chem. Eng.* **74**, 112 (1967).
44. G. Parkinson, *Turbomach. Inter.* 6 (May/June 2004).
45. R. Loftness, *Energy Handbook*, Van Nostrand Reinhold Co., Inc., New York, 1978.
46. Available at http://www.water-technology.net/projects/shuaiba/.
47. D. R. Lide, ed., *Handbook of Chemistry and Physics*, 75th ed., CRC Press, Ann Arbor, Mich., 1994.
48. V. A. Korovin and co-workers, *Energetik* (5), 24 (1980).
49. R. Gilbert, C. Lamarre, and Y. Dundar, *Proceedings of the 10th Annual Canadian Nuclear Society Conference*, 1989.
50. R. N. McBrayer and J. W. Griffith, *Proceedings of the 56th International Water Conference*, Pittsburgh, Pa., 1995, p. 499.
51. J. W. Griffith and D. H. Raymond, *Waste Manag.* **22**(4), 453 (2002).
52. M. J. Antal, in H. J. White and co-workers, *Proceedings of the 12th International Conference on the Properties of Water and Steam, Orlando, Fla., 1994*, Begell House, New York, 1995, p. 24.
53. *Bri. Stand.* BS749, **1113**, 2790.
54. *ASME Boiler and Pressure Vessel Code*, ASME, New York, 1977.

55. N. E. Hammer, *Metals Section Corrosion Data Survey*, 5th ed., National Association of Corrosion Engineers, Houston, Tex., 1974, pp. 174–175.
56. G. E. Lien, ed., *Behavior of Superheater Alloys in High Temperature, High Pressure Steam*, ASME, New York, 1971.
57. O. Jonas, *Identification and Behavior of Turbine Steam Impurities, Corrosion 77*, National Association of Corrosion Engineers, San Francisco, Calif., 1977.
58. O. Jonas, W. T. Lindsay, Jr., and N. A. Evans, in J. Straub and K. Schaffler, *Proceedings of the 9th International Conference on the Properties of Steam*, Pergamon Press, Oxford, U.K., 1980, p. 595.
59. R. J. Lindinger and R. M. Curran, *Experience with Stress Corrosion Cracking in Large Steam Turbines, Corrosion 81*, National Association of Corrosion Engineers, Toronto, Ontario, Canada, 1981.
60. W. T. Lindsay, Jr., *Proceedings of the Westinghouse Steam Turbine-Generator Symposium*, Charlotte, N.C., 1978.

JAMES BELLOWS
Siemens Power Generation, Inc.