Chapter 6

Steel Plant Fuels and Water Requirements

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6.1 Fuels, Combustion and Heat Flow

Any substance capable of producing heat by combustion may be termed a fuel. However, it is customary to rank as fuels only those which include carbon and hydrogen and their compounds. Wood was the earliest fuel used by man. Coal was known to exist in the fourth century B.C., and petroleum was used by the Persians in the days of Alexander. Prehistoric records of China and Japan are said to contain references to the use of natural gas for lighting and heating.

Heat generated by the combustion of fuel is utilized in industry directly as heat or is converted into mechanical or electrical energy. Fuel has become the major source of energy for manufacturing enterprises.

Fuel enters significantly into manufacturing costs, and in some industries represents one of the largest items of expense. The steel industry is one of the major consumers of metallurgical coal and also consumes large quantities of electricity, natural gas and petroleum.

Energy conservation efforts and technological improvements have combined to decrease domestic steel industry energy consumption from 34.40 gigajoules per net tonne (29.58 million Btu/ton) of shipments in 1980 to 24.44 gigajoules per net tonne (21.02 million Btu/ton) of shipments in 1995 per AISI survey data. The actual total steel industry average has dropped to an even lower value because most of the non-surveyed companies are electric arc furnace based, which inherently consume fewer gigajoules per net tonne (Btu/ton).

6.1.1 Classification of Fuels

There are four general classes of fuels; namely, fossil, byproduct, chemical and nuclear. Of these classes, the first three listed achieve energy release by combustion of carbon and/or hydrogen with an oxidant, usually oxygen; the process involves electron exchange to form products of a lower energy state and results in an energy release in an exothermic reaction. The fourth class liberates energy by fission of the nucleus of the atom and converting mass into energy.

Fossil fuels are hydrocarbon or polynuclear aromatic compounds composed principally of carbon and hydrogen and are derived from fossil remains of plant and animal life. These fossil remains have been transformed by biochemical and geological metamorphoses into such fuels as coal, natural gas, petroleum, etc.

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Byproduct and waste fuels are derived from a main product and are of a secondary nature. Examples of these fuels are coke breeze, coke-oven gas, blast-furnace gas, wood wastes, etc.

Chemical fuels are primarily of an exotic nature and normally are not used in conventional processes. Examples of these fuels are ammonium nitrate and fluorine.

Nuclear fuels are obtained from fissionable materials. The three basic fissionable materials are uranium–235, uranium–233 and plutonium–239.

Fossil and byproduct fuels currently used in the steel industry are classified further into three general divisions; namely, solid, liquid and gaseous fuels. Fuels in each general division can be classified further as natural, manufactured or byproduct. Fuels found in nature sometimes are called primary fuels; those manufactured for a specific purpose or market, together with those that are the unavoidable byproduct of some regular manufacturing process, are called secondary fuels. The primary fuels serve as the principal raw materials for the secondary fuels. Table 6.1 gives a classified list of the important fossil fuels. It also lists some interesting byproduct fuels, many of which have been utilized by industry to conserve primary fuel.

6.1.1.1 Importance of Each Class

Coal is the major fuel of public utilities for the generation of power and is essential to the steel industry for the manufacture of coke.

Coal has been supplanted almost entirely by liquid fuels for the generation of motive power by railroads in North America. However, coal continues as a major raw material for many chemical plants as a source of carbon, hydrogen, and their compounds.

The growth of petroleum consumption has resumed after the price shocks of the past two decades due to the increasing demand for its distillation products. Gasoline, the most important product, is used as a motor fuel. Diesel engine fuel is a distillate of crude oil. Distillate and residual fuel oils, and some crude petroleums of too low commercial value for distillation are used for industrial and domestic heating. Crude and refined petroleum of various grades are used for lubrication of all types of machinery and prime movers. Petroleum and natural gas are raw materials for the petrochemical industry.

Natural gas has replaced coal to a considerable extent for domestic and industrial heating due to the installation of very large pipelines from producing to consuming centers, the relative level in the price of natural gas over the intervening time, and its convenience, cleanliness, controllability and versatility as a fuel. The byproduct gaseous fuels—coke-oven gas and blast furnace gas—are major integrated steel industry fuels.

The nuclear energy industry has fallen on hard times. The development of a practical method for fission of the atom and the release of nuclear energy in controlled chain reactions had given rise to a different type of power generation system. Many large reactors were built throughout the country and are still in operation. However, no new units are under construction or are being designed. Nuclear power will contribute an ever decreasing share of power to the electric grid as units are taken out of service unless some major breakthrough in design and operation occurs.

6.1.2 Principles of Combustion

Fossil and byproduct fuels consist essentially of one, or a mixture of two or more, or of four combustible constituents: (1) solid carbon, (2) hydrocarbons, (3) carbon monoxide, and (4) hydrogen. In addition to these combustible constituents, nearly all commercial fuels contain inert material, such as ash, nitrogen, carbon dioxide, and water. Bituminous coal is an example of a fuel which contains all four of the combustible constituents named above, and coke is an example of a fuel containing only one (solid carbon). The constituents which make up liquid fuels and many coals are quite complex, but because these complex constituents decompose or volatilize into the four

Table 6.1 Classification of Fuels [a]

| | Primary Fuels | Secondary Fuels | |
	Natural	Manufactured	Byproduct
Solid	Anthracite coal Bituminous coal Lignite Peat Wood	Semi-coke (low-temperature carbonization residue) Coke Charcoal Briquettes { Coal slack and culm Lignite Peat Sawdust Petroleum-refining residue Pulverized coal	Charcoal—low-temperature distillation of wood Wood refuse—chips, shavings, trimmings, tan bark, sawdust, etc. Bagasse—refuse sugar cane Anthracite culm—silt refuse of anthracite screening Coke breeze { Byproduct coke—screenings Petroleum coke— petroleum-refining residue Waste materials { Corn from grain Barley Wheat Buckwheat Sorghum
Liquid	Petroleum	Gasoline Kerosene Alcohol Colloidal fuels Fuel oil { Residual oils Distillate oils Crude petroleum Naphtha Vegetable oils { Palm Cottonseed	Coal distillates { Tar Napthalene }—coke Pitch } manu- Benzol } facture Acid sludge—petroleum-defining residue Pulp-mill waste
Gaseous	Natural gas	Producer gas Water gas Carburetted water gas Coal gas Oil gas Reformed natural gas Butane[b] Propane[b] Acetylene Hydrogen	Blast-furnace gas—pig-iron manufacture Coke-oven gas[c]—coke manufacture Oil-refinery gas Sewage gas—sewage sludge Basic oxygen furnace gas—steel manufacture

[a]Excluding chemical and nuclear fuels.
[b]Liquefiable heavier constituents of natural gas.
[c]Considered byproduct of coke manufacture in steel industry but a manufactured fuel in the gas industry.

simpler constituents named above before actual combustion takes place, a knowledge of the combustion characteristics of these constituents is sufficient for nearly all practical applications. All of these four constituents of fuels except carbon are gases at the temperatures where combustion occurs. Combustion takes place by combining oxygen, a gas present in air, with the combustible constituents of a fuel. The complete combustion of all fuels generates gases. It is apparent, therefore, that a review of the properties, thermal values and chemical reactions of gases is necessary for an understanding of any class of fuel.

Because fuels are used to develop heat, a knowledge of heat terms and the principles of heat flow are also essential for the efficient utilization of this heat. The combustion of fuels involves, besides combustion reactions, the factors and principles which influence speed of combustion, ignition temperature, flame luminosity, flame development, flame temperature and limits of flammability. The ensuing divisions of this section deal generally with these subjects. Sections 6.2, 6.3 and 6.4, respectively, deal specifically with the combustion of solid, liquid and gaseous fuels.

6.1.2.1 Units for Measuring Heat

Heat is a form of energy and is measured in absolute joules in SI units.

In the centimetre-gram-second (cgs) the unit for measuring heat was the calorie (abbreviated cal), defined as the amount of heat required to raise the temperature of one gram of pure, air-free water 1°C in the temperature interval of 3.5° to 4.5°C at normal atmospheric pressure: this unit was the gram-calorie or small calorie, identified in the Table 6.2 as $cal_{4°C}$. The temperature interval chosen for this definition was selected because the density and, therefore, the heat capacity of water varies slightly with temperature and the temperature of maximum density of water is very nearly 4°C. A larger heat unit in the cgs system was the kilocalorie (kilogram-calorie or large calorie), equal to 1000 gram-calories and abbreviated kcal.

Other values for the calorie were obtained by selecting other temperature intervals, resulting, for example, in the $cal_{15°C}$ and the $cal_{20°C}$ listed in Table 6.2. Yet another variation was the mean calorie (abbreviated cal_{mean}), defined as 1/100 of the amount of heat required to raise the temperature of one gram of water from 0°C (the ice point) to 100°C (the boiling point).

None of the foregoing definitions of the calorie were completely satisfactory because of the variation of the heat capacity of water with temperature. Consequently, on the recommendation of the Ninth International Conference of Weights and Measures (Paris, 1948), the calorie came to be defined in energy units in ways that made its value independent of temperature. The thermochemical calorie (abbreviated $cal_{thermochem}$) was defined first in international electrical-energy units and later (1948) in terms of mechanical-energy units. The calorie used in the present International Tables, identified as cal_{IT} was adopted in 1956 at the International Conference on Properties of Steam in Paris, and is expressed in mechanical-energy units.

As stated above, the SI unit used to define the calorie in terms of mechanical-energy units is the absolute joule: the word "absolute" differentiates the SI joule based on mechanical-energy units from the international joule formerly used which was based on international electrical units.

The presently accepted values in absolute joules of the various calories discussed above are presented in Table 6.2 here.

Table 6.2 cgs/SI Equivalent Values for Measuring Heat

1 $cal_{4°C}$	=	4.2045 joules
1 $cal_{15°C}$	=	4.18190 joules
1 cal_{mean}	=	4.19002 joules
1 cal_{IT}	=	4.1868 joules (exactly)
1 $cal_{thermochem}$	=	4.184 joules (exactly)

In the foot-pound-second (fps) system, the principal unit adopted for measuring heat was the British thermal unit (Btu). Defined as the amount of heat required to raise by 1°F the temperature of one pound of pure, air-free water, its value depended upon the temperature interval chosen for its complete definition. As in the case of the calorie, several values came into use, notably the $Btu_{39°F}$ based on a 1°F rise in temperature at or near the temperature of maximum density of water (39.2°F), the $Btu_{59°F}$ based on the temperature interval of 58.5°F to 59.5°F corresponding nearly to the 14.5°C to 15.5°C interval of the $cal_{15°C}$, the $Btu_{60°F}$ based on the temperature interval from 60°F to 61°F, and the mean Btu (Btu_{mean}) that represented 1/180 of the heat required to raise the temperature of a pound of water from 32°F (the freezing point) to 212°F (the boiling point). Other values for the Btu were adopted, based on definitions that made the unit independent of the properties of water: these included the Btu of the International Tables referred to above (abbreviated Btu_{IT}, and the thermochemical Btu (designated $Btu_{thermochem}$). Following the recommendations of the 1948 International Conference on Weights and Measures, all of the foregoing values for the Btu came eventually to be expressed in SI mechanical-energy units, and now have been assigned the values presented in Table 6.3 in absolute joules.

Table 6.3 fps/SI Equivalent Values for Measuring Heat

$Btu_{39°F}$	=	1059.67 joules
$Btu_{59°F}$	=	1054.80 joules
$Btu_{60°F}$	=	1054.68 joules
Btu_{mean}	=	1055.87 joules
Btu_{IT}	=	1055.056 joules
$Btu_{thermochem}$	=	1054.350 joules

When both are determined for the same temperature interval, 1 Btu equals very nearly 252 calories, and 1 kilocalorie (1000 cal) very nearly equals 3.9683 Btu.

6.1.2.2 Calorific Value of Fuel

The heat given up or absorbed by a body between two temperatures, provided no change of state or of allotropic form is involved, is known as sensible heat. The heat given up or absorbed by a body when a change of state or of allotropic form takes place and no temperature change is involved is known as latent heat. For example, 1 kilogram of water absorbs 418.68 kilojoules of sensible heat when being heated from 0°C to 100°C, and absorbs 2257.1 kilojoules of latent heat when converted to steam at 100°C. Likewise, 1 pound of water absorbs 189.9 kilojoules (180 Btu) of sensible heat on being heated from 32°F to 212°F, and absorbs 1023.8 kilojoules (970.4 Btu) of latent heat when converted to steam at 212°F.

Sensible heat and latent heat are used frequently in combustion calculations, particularly in problems dealing with heat losses in flue gases. Their significance is indicated in describing gross and net heating values.

The gross heating value of a fuel is the total heat developed by the combustion of a fuel at constant pressure after the products of combustion are cooled back to the starting temperature, assuming that all of the water vapor produced is condensed; that is, the gross heating value includes both sensible and latent heat. The net heating value of a fuel is defined as the heat developed by the combustion of a fuel at constant pressure after the products of combustion are cooled back to the starting temperature, assuming that all of the water vapor remains uncondensed. Accordingly, the net heating value includes only the sensible heat.

Where combustion calculations in this chapter are in SI the starting point is 273.15K (0°C) at 101.325 kPa (760 mm Hg) absolute pressure. Where the calculations are in cgs units, the starting

point is 0°C at 760 mm absolute pressure. The starting point for calculations in the fps system in this chapter has been taken as 60°F at 30 in. of Hg absolute pressure; this has generally been the base for combustion calculations in the American steel industry.

When a fuel contains neither hydrogen nor hydrocarbons, no water vapor is produced by combustion and the gross and net heating value will be the same, as in the case of burning carbon or carbon monoxide. The heating value or calorific value of a fuel may be determined on a dry or wet basis. The determination may be made by laboratory tests employing calorimeters, or by calculation. The process of determining the calorific value of solid and liquid fuels by a calorimeter consists in completely oxidizing the fuel in a space enclosed by a metal jacket (called the bomb) so immersed that the heat evolved is absorbed by a weighed portion of water contained in an insulated vessel. From the rise in temperature of the water, the heat liberated by one gram of the fuel is calculated. The best types of calorimeters for solid and liquid fuels are those called oxygen-bomb calorimeters in which the fuel is burned in the presence of compressed oxygen. Gas calorimeters are of different construction to permit volumetric measurement of the gas and its complete combustion under non-explosive conditions, as well as absorption of the heat produced in a water jacket.

A saturated gas is one which contains the maximum amount of water vapor it can hold without any condensation of water taking place. The usual basis for reporting the calorific value of a saturated fuel gas in SI units is in gross kilojoules per cubic metre measured at 273K and 101 kPa absolute pressure. In the cgs system, calorific value usually has been reported in gross kilocalories per cubic metre measured at 0°C and 760 mm Hg absolute pressure. In fps units in the American steel industry, calorific value usually has been reported in gross Btu per cubic foot of saturated gas measured at 60°F and 30 in. Hg absolute pressure.

The heating value of a given fuel can be obtained by multiplying the calorific value of each gas by its percentage of the total fuel volume, and then totaling the individual values of the separate constituents. The heat of combustion for various dry elementary gases may be found in Table 6.4. For instance, the gross heating value of dry blast-furnace gas is 3633 kilojoules per cubic metre (92.5 Btu per cubic foot) for the composition used in the following calculations.

In the calculation of the heating value of gases saturated with water vapor, the volume of water vapor must be deducted from the unit volume of the gas. For instance, a cubic metre of dry carbon monoxide gas has a heating value of 12,623 kilojoules, but when saturated with water vapor at 273K (0°C) and 101 kPa (760 mm Hg), a cubic metre has a heating value of only 12,405 kilojoules (see Table 6.4). Likewise, a cubic foot of dry carbon monoxide gas has a heating value of 321.4 Btu, but when saturated with water vapor at 60°F and 30 in. Hg absolute pressure, a cubic foot has a heating value of only 315.8 Btu. The amount of water vapor present in saturated mixtures can be calculated from data in Table 6.5, as discussed in Section 6.1.2.4.

6.1.2.3 Thermal Capacity, Heat Capacity and Specific Heat

The thermal capacity or heat capacity of a substance is expressed as the amount of heat required to raise the temperature of a unit weight of the substance one degree in temperature. In SI, it is expressed in joules per kilogram Kelvin (J/kg K). The fps system has used Btu per pound per degree Fahrenheit (Btu/lbm °F), while the cgs system has used calories per gram per degree Celsius (cal/g °C). The specific heat is always a ratio, expressed as a number; for example, the specific heat of wrought iron is 0.115. There is no further designation, as this means that if it takes a certain number of joules to heat a certain number of kilograms of water a certain number of Kelvins, it will take only 0.115 times as many joules to heat the same number of kilograms of wrought iron the same number of Kelvins, and the same figure, 0.115, obviously applies if the centimetre-gram-second or foot-pound-second system were used.

The amount of heat required to raise the temperature of equal masses of different substances to the same temperature level varies greatly; that is to say, the specific heat varies greatly; also the specific heat of the same substance varies at different temperatures. Usually, it is necessary to know

Table 6.4 Essential Gas Combustion Constants [a]

Gas	Formula	Molecular Weight	Specific Gravity (Air = 1)	Heat of Combustion [b] Btu per ft³ [c] Gross	Net	Btu per lb [c] Gross	Net	kJ per m³ [d] Gross	Net	kJ per kg [d] Gross	Net	Required for Combustion O₂	N₂ [e]	Air	Flue Products CO₂	H₂O	N₂
Carbon (Graphite)	C	12.01	—	—	—	14,093	14,093	—	—	32,780	32,780	—	—	—	—	—	—
Hydrogen	H₂	2.016	0.06959	325.02	274.58	60,991	51,605	12,767	10,786	141,865	120,033	0.5	1.882	2.382	—	1.0	1.882
Oxygen	O₂	32.00	1.1053	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Nitrogen	N₂	28.016	0.9718	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Carbon monoxide	CO	28.01	0.9672	321.37	321.37	4347	4347	12,623	12,623	10,111	10,111	0.5	1.882	2.382	1.0	—	1.882
Carbon dioxide	CO₂	44.01	1.5282	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Methane	CH₄	16.042	0.5543	1012.32	911.45	23,875	21,495	39,764	35,802	55,533	49,997	2.0	7.528	9.528	1.0	2.0	7.528
Ethane	C₂H₆	30.068	1.0488	1773.42	1622.10	22,323	20,418	69,660	63,716	51,923	47,492	3.5	13.175	16.175	2.0	3.0	13.175
Ethylene	C₂H₄	28.052	0.9740	1603.75	1502.87	21,636	20,275	62,995	59,033	50,325	47,160	3.0	11.293	14.293	2.0	3.0	11.293
Propylene	C₃H₆	42.078	1.4504	2339.70	2188.40	21,048	19,687	91,903	85,960	48,958	45,792	4.5	16.939	21.439	3.0	3.0	16.939
Acetylene	C₂H₂	26.036	0.9107	1476.55	1426.17	21,502	20,769	57,999	56,020	50,014	48,309	2.4	9.411	11.911	2.0	1.0	9.411
Benzene	C₆H₆	78.108	2.6920	3751.68	3600.52	18,184	17,451	147,366	141,428	42,296	40,591	7.5	28.232	35.732	6.0	3.0	28.232
Hydrogen sulfide	H₂S	34.076	1.1898	646	595	7097	6537	25,375	23,372	16,508	15,205	1.5	5.646	7.146	SO₂ = 1.0	1.0	5.646
Sulfur dioxide	SO₂	64.06	2.264	—	—	—	—	—	—	—	—	—	—	—	—	—	—

(a)Adapted from "Gas Engineers Handbook" (See Segeler listing in bibliography at end of chapter)
(b)Based on perfect combustion
(c)Based on dry gases at 60°F and 30 in. Hg. For gases saturated with water, 1.74% of the heating value must be deducted.
(d)Based on dry gases at 273K (0°C) and approx. 101 kPa (760 mm Hg). For gases saturated with water at 273K (0°C), 0.60% of the the heating value must be deducted. (To convert kJ to kcal, multiply by 0.239.)
(e)N₂ in air accompanies O₂ (N₂ not required for combustion).
Note: Conversion Factors: Btu/ft³ to kJ/m³ = 39.28; Btu/lb to kJ/kg = 2.326

Table 6.5 Water Vapor Pressure [a]

Temp. (°C)	Pressure mm Hg	Pressure Pa[b]	Temp. (°F)	Pressure (in. Hg)	Pressure Pa[c]	Temp. (°C)	Pressure mm Hg	Pressure Pa[b]	Temp. (°F)	Pressure (in. Hg)	Pressure Pa[c]
0	4.579	610.5	32	0.1803	608.8	50	92.51	12,334	125	3.956	13,360
2	5.294	705.8	35	0.2035	687.2	52	102.09	13,611			
4	6.101	813.4	40	0.2478	836.8	54	112.51	15,000	130	4.525	15,280
6	7.013	935.0				56	123.80	16,505			
8	8.045	1072.6	45	0.3004	1014	58	136.08	18,143	135	5.165	17,440
10	9.209	1227.8				60	149.38	19,916	140	5.881	19,860
12	10.518	1402.3	50	0.3626	1224	62	163.77	21,834	145	6.682	22,560
14	11.987	1598.1	55	0.4359	1472	64	179.31	23,906	150	7.572	25,570
16	13.634	1817.7	60	0.5218	1762	66	196.09	26,143			
18	15.477	2063.4	65	0.6222	2101	68	214.17	28,554	155	8.556	28,890
20	17.535	2337.8	70	0.7393	2497	70	233.7	31,160	160	9.649	32,580
22	19.827	2643.4				72	254.6	33,940			
24	22.377	2983.4	75	0.8750	2955	74	277.2	39,960	165	10.86	36,670
26	25.209	3360.9	80	1.032	3485	76	301.4	40,180	170	12.20	41,200
28	28.349	3779.6				78	327.3	43,640			
30	31.824	4242.9	85	1.213	4096	80	355.1	47,340	175	13.67	46,160
32	35.663	4754.7	90	1.422	4802	82	384.9	51,320	180	15.29	51,630
34	39.898	5319.3	95	1.660	5606	84	416.8	55,570	185	17.07	57,640
36	44.563	5941.2				86	450.9	60,120			
38	49.692	6625.1	100	1.933	6527	88	487.1	64,940	190	19.02	64,230
40	55.324	7375.9	105	2.243	7574	90	525.76	70,100	195	21.15	71,420
42	61.50	8199	110	2.596	8766	92	566.99	75,590	200	23.46	79,220
44	68.26	9101				94	610.90	81,450			
46	75.65	10,086	115	2.995	10,110	96	657.62	87,680	205	25.99	87,760
48	83.71	11,160	120	3.446	11,640	98	707.27	94,290	210	28.75	97,080
						100	760.00	101,325	212	29.92	101,035

[a] Values for °C and mm Hg from "International Critical Tables" (E. W. Washburn, ed. in chief), published for National Research Council by McGraw-Hill Book Company, New York, 1928. Values for °F and in. Hg from "Gas Engineers Handbook (see Segeler listing in bibliography at end of chapter).
[b] Calculated, using factor 133.3224 to convert mm Hg (0°C) to Pa.
[c] Calculated, using factor 3376.85 to convert in. Hg (60°F) to Pa. Factor for converting in. Hg (32°F) to Pa is 3386.38.

the amount of heat required to raise the temperature of a substance some appreciable amount. For that purpose, formulae and tables are usually accessible in handbooks for supplying the mean specific heat between various temperature levels. Two values of specific heat for gases are usually given: (1) specific heat at constant pressure, and (2) specific heat at constant volume. The difference is due to the heat equivalent of the work of expansion caused by an increase of volume resulting from a temperature rise. Normal combustion practice with gases in steel plants deals with a constant pressure condition (or nearly so), and for this reason specific heat at constant pressure is used. The mean specific heat is the average value of the specific heat between two temperature levels. It is obtained by integrating the equations for instantaneous specific heat over the temperature limits desired, and dividing this quantity by the difference between the temperature limits.

The heat content is the heat contained at a specified temperature above some fixed temperature. It is calculated by multiplying the weight of a substance by the mean specific heat times the temperature difference, or H_t = weight × mean specific heat × ($T_2 - T_1$). For convenience in calculations with gases, the unit weight of the volume of a cubic metre or a cubic foot of gas is often used.

6.1.2.4 Gas Laws

Calculations based on the gas laws to be discussed involve the concepts of absolute zero and absolute temperature. Absolute zero in SI is 0K, in the cgs system it is –273.15°C and in the fps system it is –459.67°F: for practical purposes to facilitate calculations, –273°C and –460°F can be taken as absolute zero in the cgs and fps systems, respectively.

Absolute temperature in SI is the temperature expressed in Kelvins above 0K at an absolute pressure of 101.325 kPa (one standard atmosphere). In the cgs system, absolute temperature (°C$_{abs}$) has been the temperature in degrees Celsius (formerly called degrees centigrade) above –273.15°C at 760 mm Hg (millimetres of mercury) at one standard atmosphere absolute pressure. Absolute temperature in the cgs system also has been expressed according to the Kelvin scale of temperature, using K instead of °C, (1°C = 1K). Absolute zero on the Kelvin scale is 0K, and on the Celsius scale absolute zero, as stated above, is –273.15°C. Temperatures on the Kelvin and Celsius scales have the following relation:

$$T_K = T_{°C} + 273.15$$

or, to facilitate calculations,

$$T_K = T_{°C} + 273 \qquad (6.1.1)$$

Absolute temperature in the fps system is the temperature in degrees Fahrenheit (°F$_{abs}$) above 459.67°F at 29.921 inches of mercury (one standard atmosphere) absolute pressure. Also in the fps system, absolute temperatures have been expressed according to the Rankine temperature scale, using degrees Rankine (°R) instead of degrees Fahrenheit (°F), (1°R = 1°F). Absolute zero on the Rankine scale is 0°R, and on the Fahrenheit scale absolute zero, as stated above, is –459.67°F. Temperatures on these two scales have the following relation:

$$T_{°R} = T_{°F} + 459.67$$

or, to facilitate calculations,

$$T_{°R} = T_{°F} + 460 \qquad (6.1.2)$$

Again to facilitate calculations, rounded values for an absolute pressure of one atmosphere (101 kPA in SI and 30 in. Hg in the fps system) can be used instead of the more precise values in the definitions.

The volume of an ideal gas varies in direct proportion to its absolute temperature (Charles' Law) and inversely as its absolute pressure (Boyle's Law).

For example, in SI units, the volume of 1000 m^3 of a gas measured at 288K (15°C) and 101 kPa absolute pressure, when heated to 1253K (980°C) and 101 kPa absolute pressure, is equal to:

$$1000 × 1253/288 = 4351 \text{ m}^3$$

and the volume of 1000 m^3 of fuel gas measured at 288K(15°C) and 101 kPa absolute pressure is equal to 802 m^3 when compressed to 25 kPa gauge pressure at 288K, calculated as follows:

$$1000 × 101/(101+25) = 802 \text{ m}^3$$

Similarly, in the fps system, the volume of 40,000 ft^3 of gas measured at 60°F and 30 in. Hg absolute pressure, when heated to 1800°F and 30 in. Hg absolute pressure, is equal to:

$$40,000 × (460 + 1800)/(460+60) = 174,000 \text{ ft}^3$$

and the volume of 40,000 ft^3 of fuel gas measured at 60°F and 30 in. Hg (standard conditions) is equal to 31,579 ft^3 when compressed to 8 in. Hg gauge pressure at 60°F, calculated as follows:

$$40,000 \times 30/(30+8) = 31,579 \text{ ft}^3$$

The total pressure of any gas mixture is equal to the sum of the pressures of each component. Each component produces a partial pressure proportional to its concentration in the mixture. Therefore, in a mixture of water vapor and any other gas, each exerts a pressure proportional to its percentage by volume, and since water has a definite vapor pressure at various temperatures, as shown in Table 6.5, the concentration of water vapor in a gas is limited. When this limit of water vapor is reached, the gas is said to be saturated. Any drop in temperature or increase in pressure from that point will cause condensation of some of the water vapor; for instance, the water vapor in 1000 m^3 of saturated fuel gas at 293K (20°C) and 101 kPa would equal:

$$1000 \times 2.3378/100 = 23.1 \text{ m}^3$$

(2.3378 kPa is the partial pressure of water vapor in a saturated mixture at 293K (20°C) and 101 kPa as shown in Table 6.5.) In fps units, water vapor in 1000 ft^3 of saturated fuel gas measured at 60°F and 30 in. Hg is calculated as follows:

$$1000 \times 0.522/30 = 17.40 \text{ ft}^3$$

(0.522 is the partial pressure of water vapor in a saturated mixture at 60°F and 30 in. Hg, from Table 6.5.) The amount of water vapor which will condense at various temperatures may be ascertained by the use of Table 6.6.

In some combustion calculations, it is necessary to convert volumes to weights and vice versa. Such conversions can be made very conveniently by using molar units; namely, the mole (abbreviated mol and expressed in kilograms) in SI; the gram-mole (abbreviated g-mol and expressed in grams) in the cgs system; and the pound-mole (abbreviated lb-mol and expressed in pounds) in the fps system. A mol, g-mol or lb-mol of a substance is that quantity whose mass expressed in the proper units stated above is the same number as the number of the molecular weight. Thus, the molecular weight of oxygen is 32, so that the mol in SI is 32 kg of oxygen, the g-mol in the cgs system is 32 grams of oxygen, and the lb-mol in the fps system is 32 lb of oxygen.

In SI, a mol of any gas (its molecular weight in kilograms) theoretically occupies 22.414 m^3 at 273.15K and 101.325 kPa absolute pressure. (Values of 22.4 m^3, 273K and 101 kPa are close enough for most calculations.) In the cgs system, a g-mol of any gas (its molecular weight in grams) theoretically occupies 22.414 dm^3 at 0°C and 760 mm Hg absolute pressure. In the fps system, a lb-mol of any gas (its molecular weight in pounds) theoretically occupies 359 ft^3 at 32°F and 29.921 in. Hg absolute pressure; or, at 60°F and 30 in. Hg absolute pressure (the usual reference points for combustion problems in the steel industry) a lb-mol occupies 378.4 ft^3. The simplicity of using molar units in combustion calculations is shown by the following examples: The weight of a cubic metre of dry air is calculated in SI as follows:

$$0.21 \ (\% \text{ vol. of } O_2 \text{ in air}) \times 32 \ (\text{mol. wt. of } 0_2) = 6.72$$
$$0.79 \ (\% \text{ vol. of } N_2 \text{ in air}) \times 28 \ (\text{mol. wt. of } N_2) = 22.12$$
$$\text{Weight in kg of a mol of dry air} = 28.84.$$

$$28.84/22.4 = 1.29 \text{ kg (weight per m}^3 \text{ of dry air at 273K and 101 kPa absolute pressure)}$$

The volume of 1 kg of dry air at 273K and 101 kPa absolute pressure is equal to:

$$22.4/28.84 = 0.78 \text{ m}^3$$

In the cgs system, the calculations would be similar to those in SI, except that the weight of a gram-mol of dry air would be determined to be 28.84 grams, and the weight of a cubic decimetre (liter) of dry air would be found to be 1.29 grams: the volume of 1 gram of dry air at 0°C and 760 mm Hg would be found to be 0.78 dm^3.

Table 6.6 Properties of Dry Air [a]

SI Units[b]				fps Units[d]			
Temp. (°C)	Volume of 1 kg (m³)	Mass of 1 m³ (kg)	Mass of Water Vapor to Saturate 100 kg of Dry Air at 100% Humidity[c] (kg)	Temp. (°F)	Volume of 1 lbm (ft³)	Mass of 1 ft³ (lbm)	Mass of Water Vapor to Saturate 100 lbm of Dry Air at 100% Humidity[c] (lbm)
0	0.7735	1.2928	0.3774	32	12.360	0.080906	0.3767
5	0.7874	1.2700	0.5403	40	12.561	0.079612	0.5155
10	0.8019	1.2471	0.7638	50	12.812	0.078050	0.7613
15	0.8160	1.2255	1.0649	60	13.063	0.076550	1.1022
20	0.8302	1.2046	1.4702	70	13.315	0.075103	1.5726
25	0.8443	1.1844	2.0082	80	13.567	0.073710	2.2184
30	0.8584	1.1649	2.7194	90	13.818	0.072370	3.0998
35	0.8726	1.1460	3.6586	100	14.069	0.071077	4.2979
40	0.8868	1.1277	4.8872	110	14.321	0.069829	5.0913
45	0.9010	1.1099	6.5279	120	14.571	0.068627	8.0981
50	0.9151	1.0928	8.6686	130	14.823	0.067463	11.0935
55	0.9293	1.0761	11.5070	140	15.074	0.066338	15.2441
60	0.9434	1.0600	15.3233	150	15.327	0.065244	21.1155
65	0.9576	1.0443	20.5315	175	15.954	0.062679	52.6416
70	0.9717	1.0291	27.8395	200	16.584	0.060298	226.384
75	0.9859	1.0143	38.5230				
80	1.0001	0.9999	55.1492				
85	1.0142	0.9860	83.6207				
90	1.0284	0.9724	141.5052				
95	1.0425	0.9592	312.9940				

[a]At an absolute pressure of 101.325 kPa (760 mm Hg) in SI units, and 30 in. of Hg in fps units.

[b]Calculated on basis of density of dry air at 273.15K (0°C) and 101.325 kPa (760 mm Hg) equal to 1.2928 kg per m³.

[c]Mass of water vapor at lower humidities is approximately proportional to the humidity; e.g., at 50% humidity, the mass will be one-half that at 100% humidity for a given temperature.

[d]From "Gas Engineers Handbook" (see Segeler listing in bibliography at end of chapter).

In the fps system, the weight of a lb-mol of dry air would be determined to be 28.84 lbm, (lbm denotes pounds-mass and replaces the previous designation lb) and the weight of 1 ft³ of dry air at 60°F and 30 in Hg would be:

28.84/378.4 = 0.076 lbm (weight per ft³ of dry air at 60°F and 30 in. Hg absolute pressure)

Also, the volume of 1 lbm of dry air at 60°F and 30 in. Hg would be

$$378.4/28.84 = 13.1 \text{ ft}^3$$

The relation of an ideal gas to its volume and pressure is expressed by the formula:

$$PV = nRT \tag{6.1.3}$$

where:

R = gas constant
P = absolute pressure
V = volume
n = number of mols
T = absolute temperature of gas

The numerical value of R in the above equation depends upon what units (SI, cgs or fps) are used to measure P, V, n and T. Values of R for various combinations of units for measuring the other quantities are as follows:

SI units $R = 8.3144$ kJ/mol K

CGS units $R = 8.3144$ J/g-mol K
            $R = 62.37$ mm Hg-dm^3/g-mol K
            $R = .08206$ dm^3-atm/g-mol K

FPS units $R = 10.703$ lbf ft^3 in^2/lb-mol °R
            $R = 21.83$ in. Hg-ft^3/lb-mol °R

In SI units, an example of the use of the foregoing formula would be to calculate the volume occupied by 100 kg of natural gas having a composition of 80% CH_4, 18% C_2H_6 and 2% N_2 by volume at a gauge pressure of 27 kPa and a temperature of 38°C (using the data from Table 6.4).

The weight of a mol of the gas is:

$CH_4 = 0.80 \times 16 = 12.8$
$C_2H_6 = 0.18 \times 30 = 5.4$
$N_2 = 0.02 \times 28 = \underline{0.56}$ kg
                        18.76 kg

P $= 27 + 101 = 128$ kPa absolute
n $= 100/18.76 = 5.33$
R $= 8.3144$
T $= 273 + 38 = 311$

Substituting these values into the equation 6.1.3 for a perfect gas:

$$128V = 5.33 \times 8.3144 \times 311$$
$$V = 107.7 \text{ m}^3$$

In fps units, a similar application of the formula would be to calculate the volume occupied by 100 lbm of natural gas of the same composition as above at 8 in. Hg gauge pressure and a temperature of 100°F.

P $= 30 + 8 \quad = 38$ in. Hg absolute
n $= 100/18.75 = 5.33$ lb-mols
R $= 21.83$
T $= 460 + 100 = 560$°R

$$38V = 5.33 \times 21.83 \times 560$$
$$V = 1715 \text{ ft}^3$$

6.1.2.5 Combustion Calculations

The combustion of fuels is carried out by chemical reaction with air, and occasionally with air enriched with oxygen, or with pure oxygen. Dry air is a mixture of the following gas volumes under average conditions:

$N_2 = 78.03\%$
$O_2 = 20.99\%$
Ar $= 0.94\%$
$CO_2 = 0.03\%$
$H_2 = \underline{0.01\%}$
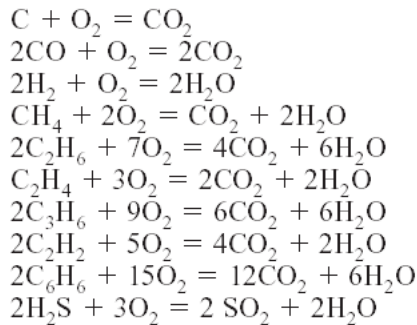Total $= 100.00\%$

In combustion calculations it is customary to include all elements in dry air (other than oxygen) with the nitrogen, as shown below:

	% by Volume	% by Weight
Oxygen	20.99	23.11
Nitrogen	79.01	76.89

Only the oxygen in the air reacts with a fuel in combustion processes. The nitrogen acts as a diluent which must be heated up by the heat of the reaction between the oxygen and the fuel. It, therefore, reduces, the temperature of the flame and reduces the velocity of combustion.

Water vapor which is present in air also acts as a diluent. The amount of moisture present in air is generally stated in terms of humidity. Air is capable of being saturated with water vapor the same as other gases as described in Section 6.1.2.4. Air which is saturated completely with water vapor has a humidity of 100%; if only 50% saturated, it has a humidity of 50% (Table 6.6).

The principal combustion reactions are:

$$C + O_2 = CO_2$$
$$2CO + O_2 = 2CO_2$$
$$2H_2 + O_2 = 2H_2O$$
$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$2C_2H_6 + 7O_2 = 4CO_2 + 6H_2O$$
$$C_2H_4 + 3O_2 = 2CO_2 + 2H_2O$$
$$2C_3H_6 + 9O_2 = 6CO_2 + 6H_2O$$
$$2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$$
$$2C_6H_6 + 15O_2 = 12CO_2 + 6H_2O$$
$$2H_2S + 3O_2 = 2 SO_2 + 2H_2O$$

The amount of oxygen required and consequently air, together with the amount of the resultant products of combustion, may be calculated in SI by the use of mols and the proper chemical reaction. For instance, it will require $(32 \div 12)$ or 2.667 kg of O_2 to burn 1 kg of C, and as dry air contains 23.11% by weight O_2, the weight of dry air required to burn one kilogram of carbon will be (2.667×0.2311) or 11.540 kg. The product of combustion, CO_2, will amount to $[(12 + 32) \div 12] = 3.667$ kg.

Combustion calculations using gases are more conveniently made in volumetric units. For instance, to burn a cubic metre of CO completely to CO_2 requires $^1/_2 m^3$ of O_2 in accordance with the molecular relationship in the reaction. The dry air required would be $(0.5 \div 0.209)$ or 2.382 m^3. For burning a cubic metre of methane, CH_4, to CO_2 and H_2O, the air required would be $(2.0 \div 0.209)$ or 9.528 m^3.

The foregoing calculations may be performed with fps units by substituting pounds-mass (lbm) for kilograms and cubic feet for cubic metres.

Combustion calculations are necessary to determine the air requirements and the products of combustion for burning fuels of various compositions. The percent of air used above theoretical requirements is called percent excess air; the percent below, the percent deficiency of air. Typical combustion data on a dry basis for burning gaseous fuels of the compositions stated are shown in Table 6.7. In making calculations to include the water vapor which may be present in a saturated or partially saturated gas and in air, the same general method may be used by adding water vapor to the fuel gas composition, and by adding the volume of water vapor which is introduced through air in the products of combustion column, headed H_2O.

In order to maintain combustion, a fuel must, after it has been ignited, be able to impart sufficient heat to its air-gas mixture so that it will not drop below ignition temperature, the minimum point of self-ignition. Too lean or too rich a mixture of a fuel with air is unable to support combustion. An upper and lower limit of flammability exists for all gases. The limits of flammability, as well as ignition temperatures, for a number of gases are shown in Table 6.8.

In the design of burners or in the selection of fuel for a specific purpose, consideration of velocity of combustion is of major importance. Because gaseous fuels are composed usually of a mixture of combustible gases, a knowledge of the relative combustion speed of each elementary gas will provide means for evaluating this factor in any gaseous mixture. The velocity of combustion, or rate of flame propagation, of a given fuel, is influenced by three factors: (1) degree to which the air and gas are mixed, (2) temperature of the air-gas mixture, and (3) contact of the air- gas mixture with a hot surface (catalyst). By intimately mixing air and gas, combustion may be accelerated

Table 6.7 Combustion Data [a] for Blast Furnace, Coke Oven and Natural Gas

Blast Furnace Gas (all volumes at 0°C and 101.325 kPa).

Gas Comp.	% by Volume	Air Per m³	Air Each Component	No Excess Air CO₂	H₂O	SO₂	O₂	N₂	10% Excess Air CO₂	H₂O	SO₂	O₂	N₂	50% Excess Air CO₂	H₂O	SO₂	O₂	N₂
CO_2	11.5	…	…	.115	…	…	…	…	.115	…	…	…	…	.115	…	…	…	…
N_2	60.0	…	…	…	…	…	…	.600	…	…	…	…	.600	…	…	…	…	.600
CO	27.5	2.382	.655	.275	…	…	…	.517	.275	…	…	…	.517	.275	…	…	…	.517
H_2	1.0	2.382	.0238	…	.010	…	…	.019	…	.010	…	…	.019	…	.010	…	…	.019
(from excess air)												.014[b]	.054[b]				.071[b]	.269[b]
Total	100.0	…	.679	.390	.010	…	…	1.136	.390	.010	…	.014	1.190	.390	.101	…	.071	1.405

Coke Oven Gas (all volumes at 0°C and 101.325 kPa).

Gas Comp.	% by Volume	Air Per m³	Air Each Component	No Excess Air CO₂	H₂O	SO₂	O₂	N₂	10% Excess Air CO₂	H₂O	SO₂	O₂	N₂	50% Excess Air CO₂	H₂O	SO₂	O₂	N₂
CO_2	1.4	…	…	.014	…	…	…	…	.014	…	…	…	…	.014	…	…	…	…
H_2S	0.6	7.146	.0429	…	.006	.006	…	.034	…	.006	.006	…	.034	…	.006	.006	…	.034
O_2	0.4	…	−.0190	…	…	…	…	−.015	…	…	…	…	−.015	…	…	…	…	−.015
N_2	4.3	…	…	…	…	…	…	.043	…	…	…	…	.043	…	…	…	…	.043
CO	5.6	2.382	.1334	.056	…	…	…	.105	.056	…	…	…	.105	.056	…	…	…	.105
H_2	55.4	2.382	1.3196	…	.554	…	…	1.042	…	.554	…	…	1.042	…	.554	…	…	1.042
CH_4	28.4	9.528	2.7060	.284	.568	…	…	2.138	.284	.568	…	…	2.138	.284	.568	…	…	2.138
C_2H_4	2.5	14.293	.3573	.050	.050	…	…	.282	.050	.050	…	…	.282	.050	.050	…	…	.282
C_2H_6	0.8	16.675	.1334	.016	.024	…	…	.105	.016	.024	…	…	.105	.016	.024	…	…	.105
Illuminants	0.6	26.208	.1572	.018	.018	…	…	.124	.018	.018	…	…	.124	.018	.018	…	…	.124
(from excess air)												.101[b]	.382[b]				.507[b]	1.909[b]
Total	100.0	…	4.831	.438	1.220	.006	…	3.858	.438	1.220	.006	.101	4.240	.438	1.220	.006	.507	5.767

Natural Gas (all volumes at 0°C and 101.325 kPa).

Gas Comp.	% by Volume	Air Per m³	Air Each Component	No Excess Air CO₂	H₂O	SO₂	O₂	N₂	10% Excess Air CO₂	H₂O	SO₂	O₂	N₂	50% Excess Air CO₂	H₂O	SO₂	O₂	N₂
CO_2	0.08	…	…	.001	…	…	…	…	.001	…	…	…	…	.001	…	…	…	…
O_2	0.17	…	−.002	…	…	…	…	−.002	…	…	…	…	−.002	…	…	…	…	−.002
N_2	1.02	…	…	…	…	…	…	.010	…	…	…	…	.010	…	…	…	…	.010
CH_4	81.88	9.528	7.802	.819	1.638	…	…	6.164	.819	1.638	…	…	6.164	.819	1.638	…	…	6.164
C_2H_6	16.85	16.675	2.810	.337	.506	…	…	2.220	.337	.506	…	…	2.220	.337	.506	…	…	2.220
(from excess air)												.223	.838[b]				1.114[b]	4.191[b]
Total	100.00	…	10.610	1.157	2.144	…	…	8.392	1.157	2.144	…	.223	9.230	1.157	2.144	…	1.114	12.583

[a]The same numerical values apply if all volumes are expressed in cubic feet at 60°F and 30 in. Hg absolute pressure.
[b]From excess air.

Table 6.8 Limits of Flammability and Ignition Temperature for Simple Gases and Compounds [a]

Simple Gases and Compounds	Limits of Flammability		Ignition Temperature (In Air)	
	Lower % by Volume Gas in Air	Upper % by Volume Gas in Air	(°C)	(°F)
H	4.0	75	520	968
CO	12.5	74	644–658	1191–1216
CH_4	5.0	15.0	705	1301
C_2H_6	3.0	12.5	520–630	968–1166
C_3H_8	2.1	10.1	466	871
C_2H_4	2.75	28.6	542–548	1008–1018
C_3H_6	2.00	11.1	458	856
C_4H_8	1.98	9.65	443	829
C_2H_2	2.50	81	406–440	763–824
C_6H_6	1.35	6.75	562	1044
C_7H_8	1.27	6.75	536	997

[a] From U.S. Bureau of Mines Bulletin 503 (1952); see also U.S. Bureau of Mines Bulletin 627 (1965); also "Gas Engineers Handbook" under Segeler listing at end of chapter.

and a shorter, sharper flame developed. In the case of a gas containing large amounts of hydrogen, intimate mixing will provide a combustion reaction of explosive velocity relative to that of a gas containing large amounts of methane. Inert gases, such as carbon dioxide and nitrogen, present in fuel gases or in a gas-air mixture, reduce combustion velocity. The proportion of nitrogen in a fuel gas-air mixture may be reduced by oxygen enrichment of air for combustion, and combustion speed may, by this means, be accelerated many fold. Such measures also will raise the flame temperature. The use of preheated air for combustion also accelerates combustion of gases. In order to burn large volumes of fuel in a small space, a mixture of air and gas is sometimes directed against a hot, incandescent surface. By increasing the velocity of combustion, higher temperatures are localized close to the burner point. This condition is desirable for some processes and highly undesirable for others. For instance, the scarfing process requires a highly intensive localized heat, while the heating of steel for rolling requires a lower intensity distribution of heat over the full surface of the pieces being heated. In order to reduce combustion speed of a gaseous fuel, the air and gas streams may be stratified to produce slow mixing. Such a method creates a diffusion flame, a long flame of relatively uniform temperature with a relative higher degree of cracking of the hydrocarbon components.

Theoretical flame temperature is the temperature which would be attained by the products of combustion if the combustion of a fuel took place instantaneously, and there were no loss of heat to the surroundings. Such a condition never exists, but theoretical flame temperature represents another measure for comparing fuels. Fuels which develop a high flame temperature by combustion are more capable of producing a higher thermal efficiency in practice than those which develop low flame temperatures. The efficiency of heat utilization is the relation of the total heat absorbed by a substance to the heat supplied. Because the temperature level at which waste gases leave a furnace is usually fixed within a relatively narrow range, the higher the flame temperature the higher the potentiality for heat absorption by the substance to be heated. The theoretical flame temperature of a fuel may be calculated by balancing the sum of the net heating value of a given quantity of fuel and the sensible heat of the air-gas mixture against the heat content of the products of combustion.

Theoretical flame temperature so calculated should be corrected for dissociation of CO_2 and H_2O at temperatures in excess of 1650°C (3000°F). The theoretical flame temperatures for a number of important gaseous fuels are given in Table 6.23 in Section 6.4.5. The reader is referred to the *Gas Engineers Handbook* and the books by Lewis and von Elbe, by Hougen et al., and Trinks and Mawhinney and others listed in the bibliography at the end of this chapter for a full explanation of combustion stoichiometry, fuel economy calculations and the calculation of theoretical flame temperatures, and the dissociation of gases at elevated temperatures.

There are a number of factors which determine the character, size and shape of a gas flame. Gases burned at very high combustion velocity will produce very little or no luminosity regardless of the kind of gas. The velocity and volume with which the air-gas stream leaves a burner or furnace port, the fuel-air ratio, and the amount of non-combustible material in the fuel will influence the length and shape of a flame. The kind of gas to be burned has a very great effect upon the character of the flame. Carbon monoxide and hydrogen burn with an invisible to a clear blue flame, while the hydrocarbon gases, methane, ethane, etc. are capable of developing highly luminous flames. The principal reason that these gases burn with a luminous flame is due to the thermal breakdown of the hydrocarbons into carbon and hydrogen, and under combustion conditions which permit this, the carbon particles are heated to incandescence thereby giving the flame its luminous appearance. The luminosity of a flame may be decreased or increased by varying the supply of air. A deficiency of air below theoretical requirements will increase luminosity and it also usually will lengthen the flame. An excess of air will decrease luminosity and shorten the flame with most burners or furnace ports. Increasing the temperature of preheat of the air for combustion will reduce luminosity, as is also the case when water vapor (steam), which may be introduced with the gas, air, or for atomization of liquid fuels, is increased. A luminous flame has a number of desirable qualities, the principal one being its greater ability to transfer heat by radiation from a fixed temperature level. However, it should be noted that a luminous flame is obtained usually at a lower temperature level than when the same fuel is burned with a lower degree of luminosity.

6.1.3 Heat Flow

Heat flow is caused by a difference in temperature, and heat is transmitted in three ways, namely, by conduction, by convection, and by radiation

6.1.3.1 Conduction

Conduction is the transmission of heat through a solid body without visible motion of the body, as through a steel bar. The amount of heat transferred through a homogeneous solid by conduction is expressed by the formula:

$$q = (k \, A \, \Delta T)/ \, x \qquad\qquad (6.1.4)$$

where, in SI, the quantities are expressed in the following units:

q = watts transmitted (1 W = 1 J/s)
k = conductivity factor in W/m K
A = area in m^2
ΔT = temperature difference in K
x = length of heat-transfer path in metres

and, in fps units:

q = Btu transmitted per hour
k = conductivity factor in Btu in. / ft^2 h °F
A = area in square feet
ΔT = temperature difference in °F
x = length of heat-transfer path in inches

The flow of heat through a non-homogeneous solid body by conduction is expressed by the formula:

$$q = \frac{\Delta T}{\left(\dfrac{x_1}{k_1 A_1}\right) + \left(\dfrac{x_2}{k_2 A_2}\right) + L \left(\dfrac{x_n}{k_n A_n}\right)} \quad (6.1.5)$$

where, in SI units,

x_1, x_2 and x_n = the respective lengths of heat-transfer path through the various resistances in metres

k_1, k_2 and k_n = the corresponding conductivity factors of the various resistances expressed in W/m K

A_1, A_2 and A_n = the corresponding areas expressed in m^2

6.1.3.2 Convection

When heat is transmitted by the mechanical motion of gas or water currents in contact with a solid, or by gas currents in contact with a liquid, the transfer of heat is by convection. In the transfer of heat by convection, it is necessary to conduct heat through the relatively stationary film between the moving and stationary bodies. This film becomes thinner as the velocity of the currents parallel to its surface increases. The transfer of heat by convection is expressed by the formula:

$$q = U A \Delta t \quad (6.1.6)$$

where, in SI, the quantities are expressed in the following units:

q = watts transmitted

U = film coefficient, expressed in W/m^2 K, dependent upon the velocity, specific gravity and viscosity of the moving fluid and the conductivity of the film

A = area in m^2

Δt = temperature difference in K

and, in fps units,

q = Btu transmitted per hour

U = film coefficient (Btu per ft^2 per °F per h) dependent upon the velocity, specific gravity and viscosity of the moving fluid and the conductivity of the film

A = area in ft^2

Δt = temperature difference in °F

6.1.3.3 Radiation

Radiation refers to the transmission of heat through space without the help or intervention of matter. This is the means by which the heat of the sun reaches the earth, and by which much of the heat of combustion of fuels is utilized in high-temperature processes in the steel industry. When radiant energy strikes any body a certain proportion of the total is reflected, while that absorbed is reconverted to heat energy. A perfect black body is one that will not reflect radiation falling upon it but absorbs all of it. The coefficient of reflectivity of a body receiving radiation is equal to one minus its black body coefficient. Emissivity refers to the rate at which a body radiates heat in relation to a black body of equal area, and this rate depends upon the temperature of the body and the nature of its surface. Kirchoff's Law shows that the absorptivity and emissivity of a given surface are numerically equal at the same temperature. The Stefan-Boltzmann Law states that the total energy of a black body is proportional to the fourth power of its absolute temperature, that is:

$$W = \sigma T^4 \quad (6.1.7)$$

where, in SI units, W equals the total emissive power of a black body, expressed in watts per square metre (W/m^2), σ is the Stefan-Boltzmann constant equal to 5.71×10^{-5} ergs/cm^2 s K^4 or 5.71×10^{-8} watts per m^2 K^4 and T is the absolute temperature in Kelvins (K).

In fps units, W is expressed in Btu/ft^2 h °R^4 and σ equals 0.173×10^{-8} Btu/ft^2 h °R^4 with T representing the absolute temperature in °R.

The net effect of heat transfer between two bodies, neither of which can be considered a black body, must take into account the emissivity factor ε, which is the ratio of the emissive power of an actual surface to that of a black body; this results in the following equation in SI units:

$$q = 5.71\varepsilon A \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right] \tag{6.1.8}$$

where

$$
\begin{aligned}
q &= \text{watts transmitted} \\
5.71 &= \text{Stefan-Boltzmann constant expressed in W/m}^2\text{K}^4 \\
\varepsilon &= \text{emissivity factor} \\
A &= \text{surface area in m}^2 \\
T_1 &= \text{absolute temperature of body giving off heat, in Kelvins (K)} \\
T_2 &= \text{absolute temperature of body receiving heat, in Kelvins (K)}
\end{aligned}
$$

In fps units, equation 6.1.8 becomes:

$$q = 0.173\varepsilon A \left[\left(\frac{T_1}{100} \right)^4 - \left(\frac{T_2}{100} \right)^4 \right] \tag{6.1.9}$$

where

$$
\begin{aligned}
q &= \text{Btu transmitted per hour} \\
0.173 &= \text{Stefan-Boltzmann constant expressed in Btu/ft}^2 \text{ °R}^4 \\
\varepsilon &= \text{emissivity factor} \\
A &= \text{surface area in ft}^2 \\
T1 &= \text{absolute temperature of body giving off heat, in °R} \\
T2 &= \text{absolute temperature of body receiving heat, in °R}
\end{aligned}
$$

The emissivity factors for various materials at specified temperatures are presented in Table 6.9. Emissivities vary from almost zero to slightly less than one, depending on the nature of the mate-

Table 6.9 Emissivity Factors (a perfect absorber or radiator 5 1)

Material	ε
Polished aluminum at 230°C (445°F)	0.039
Polished aluminum at 580°C (1075°F)	0.056
Polished brass at 300°C (570°F)	0.031
Polished nickel at 380°C (715°F)	0.086
Polished nickel-plated steel at 22°C (72°F)	0.052
Bright tinned steel plate at 24°C (75°F)	0.071
Polished mild steel	0.288
Cast iron—machined—at 22°C (72°F)	0.437
Cast iron—liquid—at 1330°C (2425°F)	0.282
Cast iron—rough oxidized	0.97
Mild steel—dull oxidized—from 26° to 355°C (79° to 672°F)	0.96
Firebrick glazed through use at 1000°C (1830°F)	0.75
Silica brick (rough)	0.81

rial, its surfaces face finish, and its temperature. Polished metal surfaces have low emissivities, whereas those of oxidized surfaces and non-metals generally approach a value of one. In the generation of heat from fuels, the character of the flame and its proximity to the receptor of heat is particularly significant in the transfer of heat by radiation. The amount of heat transferred from a flame varies widely and in proportion to its degree of luminosity. The transfer of heat by radiation varies inversely with the square of the distance between the transmitter and receptor of radiant energy. For that reason, flames should be kept close to the substance to be heated where high heat transfer rates are desirable.

6.2 Solid Fuels and Their Utilization

Solid fuels have played a significant role in the evolution of our modern, industrial civilization. Coal in particular has been of far-reaching importance in that it has provided the prodigious amount of energy essential to the development of the iron and steel industries. Vast quantities of this energy source remain to be exploited, but the rate of utilization far exceeds the rate at which coal is being formed. It follows that the efficient use of the remaining supply is desirable. Toward this end, modern coal research is directed.

Geologically, the earliest-formed coal thus far encountered occurs in the Silurian strata of Bohemia. It is not until Lower Carboniferous time, see Table 6.10, however, that the source materials

Table 6.10 Geologic Time Divisions

Era	Period		Epoch	Millions of Years
Cenozoic	Quaternary		Recent / Pleistocene	70
	Tertiary		Pliocene / Miocene / Oligocene / Eocene	200
Mesozoic	Cretaceous / Jurassic / Triassic			500
Paleozoic	Carboniferous	Permian		3000 +
		Pennsylvanian (Upper Carboniferous)		
		Mississippian (Lower Carboniferous)		
	Devonian / Silurian / Ordovician / Cambrian			
Proterozoic	Algonkian	Keweenawan		
		Huronian		
Archeozoic	Archean	Timiskamian		
		Keewatin		

of coal began to accumulate in significant quantities. Every continent, including Antarctica, contains some coal and no system of rocks younger than the Silurian is devoid of this important substance. In North America major concentrations of source materials were accumulated during the Carboniferous, Cretaceous and Tertiary periods. A similar statement can be made for Europe but, in contrast, some of the most important Asiatic coals occur in Triassic and Jurassic rocks of the Mesozoic Era.

6.2.1 Coal Resources

The known coal deposits in the U.S. are greater than those of any other country. Based on 1995 International Energy Annual data, the U.S. identified recoverable coal reserves of all ranks were estimated to be 246 billion metric tons (272 billion short tons) which is approximately 24% of the known world reserves. This figure represents coal of all ranks in the ground at depths and bed thicknesses generally considered mineable under current economic conditions. This would be enough to supply requirements for a long period in the future if all present coal reserves were available economically and of acceptable quality. A considerable quantity of the reserves of better quality coking coal has been utilized in the past and it is apparent that in the future it will be necessary to use coals requiring efficient extraction, cleaning, and other processing to assure proper utilization.

For obvious reasons, the steel industry has been striving to use coals which would produce metallurgical coke of optimum quality with a minimum of processing. Concentrations of coals of this class are found chiefly in the Appalachian area, although isolated deposits also exist in some Central and Western states. The preponderance of total coal reserve in the U.S. is in the form of lower-rank coals in the Great Plains, the Rocky Mountains, the Pacific Coast states and the Gulf region, see Fig. 6.1. These western coals are taking a larger share of the electric utility market due to lower sulfur content and lower mining costs. As a result, the eastern share of national production fell to 53% in 1995 from the 93% level in 1970. Total domestic coal production is still increasing and reached 937 million metric tons (1,033 million short tons) in 1995.

6.2.1.1 Origin and Composition of Coal

Coal is known to be a complex mixture of plant substances which have been altered in varying degrees by physical and chemical processes. Ordinarily, plant material, upon death, completely decomposes because of the action of microorganisms. Under certain circumstances, notably those associated with forested fresh-water swamps, this action is inhibited by antibiotic solutions which are common in this type of environment. As a result, the rate of accumulation of the plant material exceeds that of its decomposition and dispersion. Under such conditions a brown fibrous deposit known as peat is formed. Peat is the first step in the formation of coal.

Peat deposits, formed millions of years ago, subsequently were submerged through vertical movements of the earth's crust, in which position they became covered by deposits of sedimentary rocks. Later movements of the earth's crust raised many of these deposits to various heights above sea level. In the meantime, the peat had been changed, through agencies of biological action, pressure, and heat, into coal. The better ranks of coal in this country were formed during the Carboniferous period, the geologic period when conditions were most favorable for plant accumulation and decomposition. Included in the present deposits that originated in that period are the coal fields of the Appalachian and Central states.

The rate at which peat forms depends upon the rapidity of plant growth and the manner in which tissue increment is related to the rate of decomposition. It has been estimated that approximately one century is required to form a deposit of mature, compacted peat about one-third metre (one foot) in thickness. Certain studies of volatile matter relationships suggest that about a one-metre thick (a three-foot-thick) deposit of mature peat is required to produce a one-third-metre thick (one-foot-thick) layer of bituminous coal. These and other data indicate that a coal seam which is
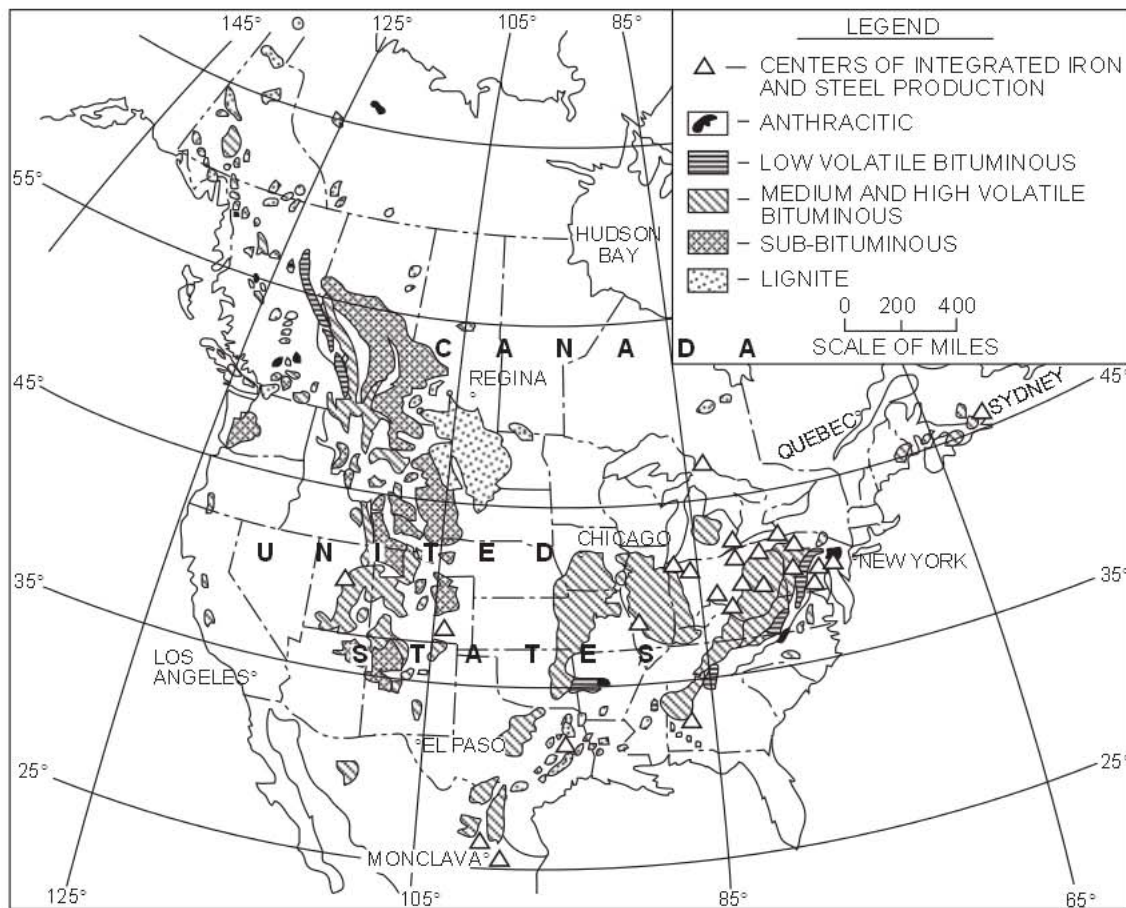
Fig. 6.1 Map showing general location and extent of the important coal fields of North America and centers of integrated iron and steel production. (Map prepared by the Canadian Department of Energy, Mines and Resources, Ottawa, Canada.)

a metre or more (several feet) thick may require a time span of thousands of years for its formation. If, in the course of time, the peat is subjected to the necessary conditions it becomes modified to brown coal and, when adequately consolidated, to lignite. From the lignitic stage, the material passes progressively through the sub-bituminous, bituminous, semi-anthracite and anthracite stages with a gradual change in the composition of the individual components of the complex mass. The proximate and ultimate compositions of coal, defined later in Section 6.2.3 and shown in Tables 6.11, 6.12 and 6.13 illustrate the gradual concentration of carbon and loss of oxygen in the various stages of coal formation.

Peat varies in appearance from a light, brown-colored, fibrous material to a very black and dense, muck-like sediment. Lignite is usually brown in color and commonly shows a woody texture. It contains a large amount of moisture and usually disintegrates, or slacks, into small pieces as it dries on exposure to air. Sub-bituminous coal varies in color from very dark brown to black and fractures irregularly. Bituminous coal is black in color and usually exhibits a banded structure due to the alternate dull and vitreous layers of varying thickness. Coals of the high-volatile bituminous rank commonly burn with a smoky, yellow flame. Anthracite is black, hard and brittle and has a high luster. It ignites less easily than bituminous coal and burns with a short, bluish, yellow-tipped flame producing very little or no smoke. The characteristics of semi-anthracite coal are intermediate between those of bituminous coal and anthracite.

All of the solid natural fuels contain both combustible and non-combustible materials. The combustible material is composed mainly of carbon, hydrogen and, to a lesser extent, sulfur. The non-

Table 6.11 Typical Moisture and Ash Content of Raw Solid Fuels [a]

Fuel	Moisture Content (%)	Ash Content (%)
Peat	65–90	[b]
Lignite (North Dakota)	35–40	7.6
Sub-Bituminous (Wyoming)	15–25	3.3
Bituminous (Low-Volatile B)	2.5	11.4
Anthracite (Northeastern Pa.)	5.5	9.6

[a] For additional coal analyses, see Bureau of Mines R.I. 7104 (1968), "Analyses of Tipple and Delivered Samples of Coal" and previous reports in the same series; also "Combustion Engineering" and "Steam, Its Generation And Use" published by Combustion Engineering, Inc. and the Babcock & Wilcox Co., respectively, cited in the references.

[b] Highly variable, from 2–15% or higher.

combustible constituents are water, nitrogen and oxygen, and a variety of mineral materials usually referred to as ash.

The bituminous coals are of greatest interest to the steel industry in view of the fact that essentially all coking coals fall in this category. The lustrous black bands which are conspicuous in a lump of bituminous coal are generally referred to as vitrain although some American coal petrographers employ the term anthraxylon in preference. Following U.S. Bureau of Mines terminology, the anthraxylon is derived from woody plant tissues and is surrounded by a dull ground mass made up of translucent attritus, opaque attritus and fusain. The attrital portion is composed of finely comminuted fragments of altered plant materials. Fusain is a friable, charcoal-like substance derived from woody tissues and is a term used universally without modification.

In addition to the readily recognizable bands of vitrain and fusain, European and Asiatic coal investigators have found it useful to identify silky, minutely striated layers within a coal as clarain. Layers of dull, compact coal are called durain. Thus, coal seams can be thought of as being composed, usually, of various mixtures of vitrain, fusain, clarain and durain, each occurring in the form of layers which are visually observable. Coals made up largely of vitrain and clarain are spoken of as bright coals whereas coals containing a high percentage of durain are called splint coals. Bright coals are generally better coking coals than splint coals, vitrain apparently playing an important part in the carbonization process. Fusain will not coke, but in small percentages it may actually increase coke strength provided the particle size is fine enough. The fixed carbon content is higher and the volatile matter content is lower in fusain than in the other banded ingredients.

Microscopic study has shown the banded components to be composed of identifiable plant entities called phyterals, but of greater significance is the fact that the vitrain, fusain, clarain and durain are made up of numerous components or macerals which can be defined by their physical and chemical properties. Durain, for example, may include several macerals (vitrinite, semi-fusinite, micrinite, cutinite, etc.) which are easily distinguished by their differing optical properties. Additional information regarding the nature and variability of these individual coal components and their contribution to the effective and efficient utilization of all types of coal appears in references on applied coal petrography at the end of this chapter.

Table 6.12 Typical Compositions of Peat and Coals of Different Ranks (Dry Basis)

Group (ASTM Designation D 388)	Proximate Analyses (%)			Ultimate Analyses (%)						Gross Heating Value	
	Volatile Matter	Fixed Carbon	Ash	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen		kJ/kg[a] (dry)	BTU/lbm[b] (dry)
Meta anthracite	1.2	90.7	8.1	86.8	1.6	0.6	0.9	2.0		31,797	13,682
Anthracite	3.4	87.2	9.4	84.2	2.8	0.8	0.6	2.2		32,094	13,810
Semianthracite	13.0	74.6	12.4	78.3	3.6	1.4	2.0	2.3		31,560	13,580
Bituminous											
Low-Volatile	16.0	79.1	4.9	85.4	4.8	1.5	0.8	2.6		34,860	15,000
Medium-Volatile	22.2	74.9	2.9	86.4	4.9	1.6	0.6	3.6		35,274	15,178
High-Volatile A	34.3	59.2	6.5	79.5	5.2	1.4	1.3	6.1		33,456	14,396
High-Volatile B	39.2	55.4	5.4	78.3	5.2	1.5	1.4	8.2		32,787	14,108
High-Volatile C	36.4	54.5	9.1	73.1	4.8	1.5	2.6	8.9		31,302	13,469
Subbituminous											
A	38.9	56.4	4.7	75.1	5.0	1.4	1.0	12.8		31,595	13,595
B	42.8	54.4	2.8	75.0	4.9	1.3	0.5	15.5		30,788	13,248
C	39.4	47.4	13.2	64.2	4.4	1.2	0.4	16.6		25,796	11,100
Lignite A and B	41.8	49.4	8.8	64.4	4.2	1.1	0.8	20.7		25,643	11,034
Peat	67.3	22.7	10.0	52.2	5.3	1.8	0.4	30.3		21,048	9,057

(a) To convert to kilocalories per kilogram, multiply by 0.2390.
(b) To convert to kJ/kg from Btu/lbm, multiply by 2.326.

Table 6.13 Approximate Range of Moisture Contents for Peat and for Coals of Different Ranks (ASTM Designation D 388)

Fuel	Moisture Content (%)
Meta anthracite	3–10
Anthracite	1–8
Semianthracite	1–10
Low-Volatile Bituminous	2–4
Medium-Volatile Bituminous	1–4
High-Volatile A Bituminous	2–11
High-Volatile B Bituminous	4–15
High-Volatile C Bituminous	7–17
Subbituminous A	10–20
Subbituminous B	14–25
Subbituminous C	16–34
Lignite A and B	23–60
Peat	55–90

6.2.1.2 Chemical Composition and Coal Classification

There are two methods commonly employed to determine the chemical composition of coal; namely ultimate analysis and proximate analysis (Table 6.12). An ultimate analysis determines the quantities of carbon, hydrogen, oxygen, nitrogen, sulfur, chlorine and ash in dry coal; a proximate analysis determines the fixed carbon, volatile matter, moisture and ash contents. The proximate analysis is used most commonly because it furnishes most of the data required for normal commercial evaluations.

The analysis of coal can be made in the laboratory on an 'air-dry' basis. The coal sample is delivered to the laboratory in sealed containers. In the laboratory, the coal is weighed and then exposed to the air of the laboratory for a period of time and then weighed again. The percent loss in weight is the 'air-dry' loss. However, since the air-dry analysis is of little value to the user, the analysis is converted to the 'as-received' basis by combining air-dry loss and final moisture content.

$$1.0 - \frac{\% \, air\text{-}dry \, loss}{100} \qquad (6.2.1)$$

The heating value of coal is reported on as-received basis and dry basis. To convert the analysis to dry basis from the as-received basis, each constituent value (except the moisture because that is being eliminated) is divided by the factor

$$1.0 - \frac{\% \, moisture \, in \, as\text{-}received \, analysis}{100} \qquad (6.2.2)$$

Typical ranges of moisture are listed for various coals in Table 6.11 and Table 6.13.

Using data provided by chemical, physical or petrographic analyses, coals are classified according to rank, grade, and type. Classification according to rank is based upon the degree of metamorphism within the coal series from the level of lignite to that of anthracite coal. The American Society for Testing and Materials ranks coals according to their fixed-carbon content on a dry basis, and the lower rank coals according to Btu content on a moist basis. The classification of coals by rank adopted by the American Society for Testing and Materials (ASTM Specification D388), is shown in Table 6.14.

Table 6.14 Classification of Coals by Rank (a)(f)

Class	Group	Fixed Carbon Limits, per cent (Dry, Mineral-Matter-Free Basis)		Volatile Matter Limits, per cent (Dry, Mineral-Matter-Free Basis)		Calorific Value Limits (Moist,(b) Mineral-Matter-Free Basis)(g)				Agglomerating Character
		Equal or Greater Than	Less Than	Greater Than	Equal or Less Than	Equal or Greater Than Btu/lb	kJ/kg	Less Than Btu/lb	kJ/kg	
I. Anthracitic	1. Meta-anthracite	98	...	...	2	...	...	...	...	
	2. Anthracite	92	98	2	8	...	...	...	...	Nonagglomerating
	3. Semianthracite(c)	86	92	8	14	...	...	...	...	
II. Bituminous	1. Low volatile bituminous coal	78	86	14	22	...	...	...	...	
	2. Medium volatile bituminous coal	69	78	22	31	...	...	...	...	
	3. High volatile A bituminous coal	...	69	31	...	14,000(d)	32,500(d)	...	...	Commonly agglomerating(e)
	4. High volatile B bituminous coal	...	...	...	...	13,000(d)	30,200	14,000	32,500	
	5. High volatile C bituminous coal	...	...	...	...	11,500	26,700	13,000	30,200	Agglomerating
						10,500	24,400	11,500	26,700	
III. Subbituminous	1. Subbituminous A coal	...	...	...	...	10,500	24,400	11,500	26,700	
	2. Subbituminous B coal	...	...	...	...	9,500	22,100	10,500	24,400	Nonagglomerating
	3. Subbituminous C coal	...	...	...	...	8,300	19,300	9,500	22,100	
IV. Lignitic	1. Lignite A	...	...	...	...	6,300	14,600	8,300	19,300	
	2. Lignite B	...	...	...	...	...	...	6,300	14,600	

(a) This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48% dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound (36,100 kJ per kg).

(b) Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

(c) If agglomerating, classify in low-volatile group of the bituminous class.

(d) Coals having 69% or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

(e) It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high volatile C bituminous group.

(f) From ASTM Designation D-388-66 in "ASTM Standards 1975," Part 26, page 215, to which reference may be made for method of calculation to mineral-matter-free basis and other information. Reproduced by permission of the American Society for Testing and Materials. The complete specification is obtainable from the society.

(g) Rounded values for kJ/kg, obtained by calculation, are not part of the original specification.

In the U.S., coals are also classified into types and such terms as bright, semi-splint, splint, cannel and boghead coal are applied. The data required are obtained from microscopic studies. The U.S. Bureau of Mines defines bright coal as containing less than 20% opaque matter; semi-splint must have between 20 and 30%, and splint coal must be made up of more than 30% of this ingredient. Cannel and boghead coals are non-banded and are characterized by a small percentage of anthraxylon (vitrain). Boghead possesses a high percentage of volatile oils and gases, and contains an abundance of algal material. Cannel, or candle, coal is so named because it can be ignited with a match or a candle flame and it burns with unusual brilliance. Cannel coal is non-coking, often contains large quantities of spore and pollen materials, and like boghead, has a high content of volatile oil and gas.

Coals are classified to grade by their ash and sulfur contents. The mineral constituents of the ash are also important because they influence fouling and slagging in the furnace.

6.2.2 Mining of Coal

It is found that seams of coals vary in thickness throughout the world from a few millimetres to over 75 metres (a fraction of an inch to over 250 feet). In this country the thickest seams are found in the sub-bituminous coals of the West, one of which approaches about 30 metres (100 feet). In the East, the Mammoth bed in the anthracite fields of Pennsylvania attains a thickness of 15 to 18 metres (50 to 60 feet) but is found to be quite variable when traced laterally. The Pittsburgh seam at the base of the Monongahela series in the Appalachian area is noteworthy because of its exceptionally uniform thickness (approximately 2 metres or 7 feet) over thousands of square miles. Fig. 6.2 shows the western portion of Pennsylvania in such a manner as to make clear the areal extent as well as the sub-surface relations of the coal-bearing formations of this region. Data are provided in Table 6.15 as to thickness of seams and distance between coals.

Coal seams may dip gently as shown in Fig. 6.2, or they may be horizontal, or they may exist almost vertical with respect to the Earth's surface. Mining problems are often complicated by the fact that seams seldom remain in the same plane throughout their extent. Under present conditions, a coal bed must be at least 0.75 to 0.90 metres (30 inches to 36 inches) thick to be profitable for
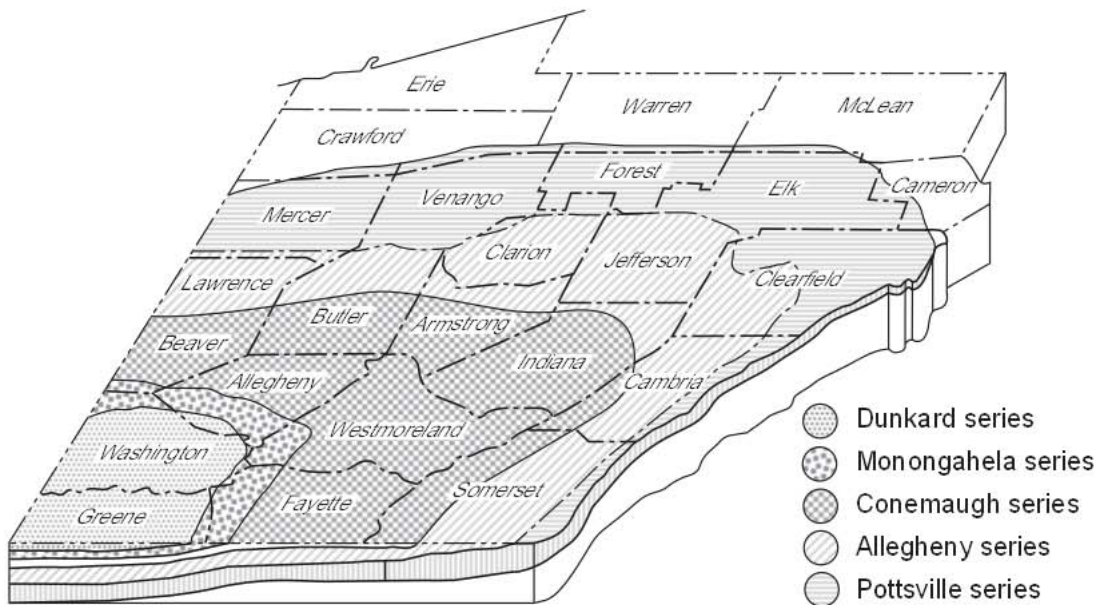

Fig. 6.2   Distribution of coal-bearing strata in Western Pennsylvania.

Table 6.15 Important Coals of the Northern Portion of the Appalachian Coal Region

Series	Strata	Thickness		Totals From Top	
		m	ft	m	ft
Dunkard	Proctor Sandstone	12.2–12.2	40-40	12.2	40
	Windy Gap Coal	0.15–0.30	$^1/_2$–1	54.9	180
	Gilmore Coal	0.15–0.30	$^1/_2$–1	88.4	290
	Nineveh "A" Coal	0.076–0.30	$^1/_4$–1	138.7	455
	Nineveh Coal	0.15–0.30	$^1/_2$–1	153.9	505
	Hostetter Coal	0.15–0.30	$^1/_2$–1	176.8	580
	Fish Creek Coal	0.15–0.30	$^1/_2$–1	205.7	675
	Dunkard Coal	01.5–03.0	$^1/_2$–1	225.6	740
	Jollytown Coal	0.15–0.30	$^1/_2$–1	240.8	790
	Hundred Coal	0.076–0.30	$^1/_4$–1	254.5	835
	Washington "A" Coal	0.15–0.30	$^1/_2$–1	280.4	920
	Washington Coal	0.61–1.52	2–5	313.9	1030
	Little Washington Coal	0.38–0.61	$1^1/_4$–2	321.3	1054
Monongahela	Waynesburg Coal	0.91–1.52	3–5	374.6	1229
	Uniontown Coal	0.30–0.91	1–3	391.7	1285
	Lower Uniontown Coal	0–0.30	0–1	413.0	1355
	Sewickley Coal	0.91–1.52	3–5	452.6	1485
	Redstone Coal	0.91–1.52	3–5	470.9	1545
Conemaugh	Pittsburgh Coal	1.52-2.43	5-8	484.6	1590
	Morgantown Coal	0.30–1.52	1–5	490.7	1610
	Little Pittsburgh Coal	0.30–1.83	1–6	507.5	1665
	Little Clarksburg Coal	0.61–2.13	2–7	530.4	1740
	Normantown Coal	0–0.30	0–1	545.6	1790
	Clarysville Coal	0–0.30	0–1	560.8	1840
	Elk Lick Coal	0.61–1.22	2–4	591.3	1940
	Harlem Coal	0.15–0.61	$^1/_2$–2	621.8	2040
	Upper Bakerstown Coal	0.15–0.30	$^1/_2$–1	650.7	2135
	Bakerstown Coal	0.61–1.52	2–5	652.3	2140
	Brush Creek Coal	0–1.83	0–6	714.8	2345
	Mahoning Coal	0.30–1.83	1–6	722.1	2369
Allegheny	Upper Freeport Coal	0.61–1.52	2–5	730.0	2395
	Lower Freeport Coal	0.61–0.91	1–3	751.3	2465
	Upper Kittanning Coal	0–0.30	0–1	768.1	2520
	Middle Kittanning Coal	0.91–1.52	3–5	775.7	2545
	Lower Kittanning Coal	0–2.74	0–9	797.1	2615
	Clarion Coal	0.30–1.22	1–4	829.1	2720
Pottsville	Brookville Coal	0.30–0.91	1–3	836.7	2745
	Mercer Coal	0–0.61	0–2	853.4	2800

mining. Table 6.15 also shows that coal seams vary in their distance below the Earth's surface. U. S. Geological Survey estimates of coal reserves do not include coal seams deeper than about 910 metres (3000 feet) from the surface, although in Great Britain and Europe coal seams at greater depth are being mined.

The mining of coal is performed by either one of two methods: (1) open pit or stripping, also called contour mining, or (2) underground or deep mine. The first method involves removing the formation (over-burden) above the seam by stripping with scrapers, bulldozers, or mechanically operated shovels, followed by removing the exposed coal. Stripping is applied to coal seams which are relatively close to the surface, particularly to thick seams underlying overburden about 25 to 50 metres (80 to 150 feet) deep, although the development or larger equipment and improved techniques in recent years has justified removal of layers of overburden thicker than this. Auger mining is being used extensively to recover coal where the overburden is too great for strip-mining practices to be employed. A large-diameter auger or drill with cutting bits on its end is propelled into the exposed edge of a coal seam. As the auger progresses into and along the seam, the broken coal is conveyed away from the face through the tube to the outside for transport away from the auger. Production by strip mining has increased greatly since World War I due to reduced labor and material costs and a quicker return on capital investment compared to underground mining. In the U.S., surface mining accounted for slightly over 25% of the coal produced in 1957. By 1995, surface mining has climbed to about 62% of the total coal mined.

6.2.2.1 Underground Mining

Underground mining is performed by either the room-and-pillar or the longwall method. The room-and-pillar method is in more common use in the U.S. The longwall method is particularly adaptable to mining seams up to about 4.6 metres (15 feet) thick under conditions where the roof may be permitted to cave. It is used more extensively in the mines of the eastern U.S. There are a number of modifications applicable to each method. The room-and-pillar system consists essentially of working out rooms, chambers, or breasts in the coal seam from passages (entries) driven from the mine entrance. Entrance to an underground mine is by drift, shaft or slope. The rooms vary in width from about 3.5 to 12 metres (12 feet to 40 feet), 6.1 metres (20 ft.) being the most common, and from about 45 to 90 metres (150 feet to 300 feet) in length, depending on such factors as weight and character of the overlying and underlying structure and thickness of seam. Pillars separating the rooms vary in width from about 2 to 30 metres (6 feet to 100 feet), depending on conditions and mining practice. These pillars are sometimes removed by retreat mining and the coal recovered.

In the longwall method, a continuous mining face is maintained in the coal seam. After mining, the roof is permitted to cave, about 5 to 9 metres (15 or 30 feet) from the mine working face.

Prior to the advent of mechanical mining, undercutting of the coal seam preparatory to blasting was done manually. Production per man was low by this method and required a number of working faces in the mine to produce high mine tonnage. Hand loading of coal into mule-drawn cars was the prevailing practice for many years until development of machinery for cutting, loading and haulage. Electric trolley-type locomotives capable of hauling longer underground trains of cars of increased capacity displaced mule-drawn trains as mine capacity increased.

In some modern underground mines, the coal is carried out of the mine by a system of conveyor belts to a shipping station or cleaning plant. In other mines, the coal is carried in mine cars to a rotary dumper. From the dumper the coal is fed by way of a conveyor or elevator to a shipping station or cleaning plant.

6.2.2.2 Continuous Mining

The cutting machines and loading machines characteristic of mechanical mining in the past were single-purpose units, and each performed essentially a single function of mining at the working face. After either unit completed its work it was withdrawn from the face to allow other units of the production setup to move up to the face to carry out succeeding functions. To keep all operating units working at full efficiency, it was necessary to have additional working places near at hand so that the single-purpose machines could enter the places in rotation and carry out their functions without interference.

To eliminate some of the difficulties attendant upon the addition of extra working places, multi-purpose machines known as continuous miners have been developed and the operation carried out by such machines has been given the name continuous mining. Continuous miners combine in a single unit the actions of dislodging the coal from the solid seam and loading it into some unit of a transportation system. Such machines, therefore, combine in one operation the separate steps of cutting, drilling, blasting and loading common to earlier mechanical mining methods. Coal planers and shearers with long-wall mining achieve these combined objectives.

There are several types of continuous miners in operation, one of which is a ripper-type miner that has cutting bits mounted in the rims of multiple wheels that are rotated to rip the coal out of the seam while the ripper wheels are propelled into and up or down in the coal seam. The coal that is ripped loose from the seam falls into the gathering head of the loader, which has dual gathering arms that sweep the broken coal into the conveyor section of the machine for loading into shuttle cars or other suitable conveying equipment.

Continuous miners of some other types employ auger-type cutters that bore into the face, the cut coal in both cases being carried by a conveyor on the machine to a shuttle car or other means of transportation.

6.2.3 Coal Preparation

As one phase of coal preparation, the objective of coal cleaning (often called washing) is removal of solid foreign matter, such as rock and slate, from the coal prior to its use. Reduction of ash and sulfur contents; control of ash fusibility; increase of heating (calorific) value; and improvement of coking properties of the coal can be achieved by this practice. From a coal-cleaning standpoint, the impurities in coal are of two types; namely, those which cannot be separated from the coal, usually called fixed or inherent impurities; and those which can be removed, herein referred to as free impurities. Altogether, these impurities are of eight types, named as follows: (1) residual inorganic matter of the coal-forming plants from which the coal was derived; (2) mineral matter washed or blown into the coal-forming mass during the periods of its formation; (3) pyrites (FeS_2) formed by bacterial reaction of iron and sulfur in the coal-forming matter; (4) sedimentary deposits during the coal-forming periods which appear as partings, sometimes called "bone," that usually must be mined with the coal; (5) massive deposits formed through deposition on bedding planes; (6) saline deposits, somewhat rare in coal beds of the U.S.; (7) slate, shale, clay, etc. from the underlying and overlying strata accidentally included in mining; and (8) water or moisture, which includes that naturally carried by the coal in air-dry condition, and excess moisture producing a condition of wetness. Items (1) (2) and, for the most part (3) form fixed ash, while (4), (5), (6), and (7) are partly free ash-forming materials that can be removed by hand-picking and suitable mechanical cleaning treatments. Item (8) involves drying operations differing from those required to separate mineral impurities, which is the primary objective of cleaning. Mechanical cleaning is possible because of the difference in specific gravity between the major impurities and the coal, the density of the former being 1.7 to 4.9, while pure coal has a density of about 1.3. Sulfur is present as pyrites, organic compounds, and sulfates, and only part of the pyrites can be removed by cleaning. Phosphorus is usually associated more with bony and impure coal than with clean coal and is, therefore, reduced by washing. Salts, particularly the alkali chlorides, lower the fusion point of the ash, affect coke-oven linings and are troublesome in waste liquors from coking operations.

The advent of full-seam mechanical coal mining and the increasing need for metallurgical coke of low and uniform ash and sulfur contents has focused attention on the needs for the most efficient types of washers.

The preparation of coal starts at the production face in the mine. If loading is done by hand, the miner is required to discard all rock and slate over 75 mm (3 in.) size. As practically all loading is done mechanically in the U.S. little attempt is made to prepare the coal at the face other than to control the tonnage from various sections of the mine if sulfur content of the coal is high or variable.

The cleaning qualities of a particular coal are determined by the float and sink test, commonly referred to as a washability test. Fundamentally, this test effects a fractionation of the coal by size and specific gravity. This test consists in crushing coal to proper size and floating individual sizes of it on liquids having specific gravities of 1.30, 1.40, 1.50, 1.60, etc., to determine the weight and character of the material that floats and sinks in each liquid. The proportion of coal, and the ash and sulfur content of the different fractions, provides reasonably complete data on the washability characteristics of a tested coal. Extreme fines may be evaluated by froth flotation.

Coal preparation is accomplished by a combination of crushing, sizing, cleaning, and dewatering operations:

1. Crushing
   a) Mine breakers
   b) Bradford breakers
   c) Roll crushers
   d) Impact crushers

2. Sizing
   a) Grizzlies
   b) Vibrating screens
   c) Classifiers
   d) Cyclones

3. Cleaning
   a) Jigs
   b) Dense media processes
   c) Cyclone processes
   d) Tables
   e) Froth flotation

4. Dewatering
   a) Screens
   b) Centrifuges
   c) Vacuum filters
   d) Thermal dryers

By far the largest percentage of coal is cleaned by wet methods.

A complete description of each of the foregoing processes would be too lengthy for inclusion herein; hence only a brief review will be given of the principles of some of the more important types of cleaning processes in use at present. A reference list for further study of this subject is appended to this chapter.

Jigs were probably the earliest type of machine used in the mineral industry to separate materials of different densities. They consist essentially of a box with a perforated base into which the material is placed, and by alternate surges of water upward and downward through the perforations, materials of different specific gravities stratify. Materials having the highest specific gravities remain at the bottom while the lighter material rises. With proper mechanical facilities, a continuous separation is achieved. While jigs are not very efficient in cleaning a mixture of various sizes, they are capable of satisfying some market requirements, and capacities up to about 450 metric tons (500 net tons) per hour have been obtained.

In dense-media processes, only a part of the power for separating coal and refuse is supplied by an upward flow of liquid, this separating power being supplemented by using a liquid medium which is heavier than water. The medium employed is a mixture of water and some finely divided solid material, such as sand, magnetite, or barite, which can be separated readily from the washed coal and reused. In the high-density suspension process, the upward flow is discarded entirely, the liquid medium consisting of a mixture which is just dense enough so that the coal floats in it, and the impurities sink. The size of coal has less significance in the efficiency of this process than of those

previously described, and material ranging from 1.6 to 254 mm (1/16 inch to 10 inches) can be cleaned in one operation. However, difficulty is encountered in separating the solid material from coal of fine size. Capacities up to about 545 metric tons (600 net tons) per hour have been obtained with bituminous coal. The Chance cone method, which uses a mixture of sand and water, is also widely used in the U.S. The Tromp and Barvoys processes, using magnetite and barite respectively as the solid material in the mixture, are used extensively in Europe and in the U.S. In these processes, the specific gravity of the mixture of solid material and water can be varied by changing their proportions to suit the optimum conditions in cleaning. Agitation in the separating cone is supplied by an upward current of water and by mechanical stirring.

Cyclones, which have an inverted conical shape and are fed tangentially at the widest part of the cone, are used with the dense medium process to increase the separating rate of particles in the medium. This device is particularly effective on sizes between $3/_4$ inch (17 mm) and 100–mesh (0.15 mm). Cyclones can also be used in the absence of a specific medium, but the efficiency is lower and they must often be combined in stages. In this practice they are referred to as hydro-clones or water-only cyclones.

Coal is also cleaned on table concentrators. Essentially these tables consist of a slightly inclined rectangular surface having a series of parallel grooves or cleats. The tables are mechanically agitated to permit stratification of the light and heavy material and to cause the heavy material to move with the long axis of the table. A current of water is introduced at the top edge of the table to wash the coal which has settled above the refuse to the discharge edge of the table. The refuse which settles underneath the coal moves longitudinally down the table and is discharged at the end. Tables have been used principally for cleaning coal of the smaller sizes, from about 0.3 to 12.7 mm (48–mesh up to about $^1/_2$ in.).

Froth flotation of coal involves agitating fine coal with a mixture of water and a relatively small quantity of some frothing agent. In this process, coal is buoyed to the surface by the froth and removed while refuse settles. It is widely used to recover coal finer than 100–mesh (150 mm).

With practically all wet-washing systems the water is recirculated. When the water passes through the dewatering screens it contains a considerable amount of small-size coal solids which must be recovered for efficiency reasons. Also, the circulating water and effluent from flotation must be clarified before it is returned to the cleaning unit. This clarification is accomplished in various ways, the most important being by the use of hydraulic cyclones followed by a Dorr-type thickener. Settling cones and settling tanks are also used for this purpose. Where the Dorr-type thickener and settling tanks are used, it is customary to draw off the settlings in the form of a slurry containing 40% to 60% solids and to further separate the slurry in a vacuum-type filter. The filters deliver a product with approximately 25% moisture. For a more complete discussion of dewatering and waste disposal, the reader is referred to a standard book on coal preparation.

6.2.4 Carbonization of Coal

The most important use of coal in the modern steel industry is in the manufacture of metallurgical coke, which is discussed in detail in Chapter 7 in the Ironmaking Volume.

The carbonization of coal in byproduct ovens entails the production of large amounts of coke-oven gas and tar, important fuels in the steel industry, as well as light oils and various coal chemicals. The yields of gas and tar are largely a matter of the type of coal used and the temperatures employed in coke manufacture.

6.2.5 Combustion of Solid Fuels

The principal combustion reactions of solid fuels have been given in Section 6.1.2, and this present discussion will deal with operating factors pertinent to the combustion of solid fuels in steel plants.

The combustion of coke in blast furnaces has been studied by a number of investigators, each of whom has found that combustion takes place in a relatively small space directly in front of each tuyere.

Coke breeze, produced by screening coke at both the coke plant and blast furnaces, is utilized as a fuel in steel plant boiler houses to generate steam and in ore-agglomerating plants. When used as boiler fuel, coke breeze is burned on chain-grate stokers. Of importance in the combustion of coke breeze on chain-grate stokers is the maintenance of a relatively uniform fuel bed on the grate, approximately 200 to 300 mm (8 to 12 in.) thick, to prevent blowholes, and a balanced or slight positive pressure in the furnace at fuel-bed level. The operation of the grate should permit the normal combustion of approximately 146 kilograms per square metre (30 pounds of coke breeze per square foot) of effective grate area per hour. Chain-grate stokers are particularly adaptable to solid fuels with an ash of low fusion point. The design of front and back arches must take into consideration the fuel to be burned on chain-grate stokers. The arches are utilized to reflect heat and thereby aid ignition on the fuel bed.

Stokers for firing coal were generally used in steel plant boilers on units whose capacity is under approximately 45,000 kilograms (100,000 pounds) of steam per hour and for units using exclusively a solid fuel. They were often used on boilers to provide flexibility for the adjustment of boiler output to the steam load in plants where there is an insufficient or fluctuating supply of gaseous byproduct fuels. When coal is used as a boiler fuel today, pulverized boilers dominate the field. The advantage of stokers lies in their ability to control easily the rate of combustion of a solid fuel with efficient use of air. The combustion process on stoker-fired boilers consists essentially in first driving the volatile matter from a continuous supply of fuel, and then oxidizing the carbon in the residue on the stoker. The combustion of the coke-like residue on the grate produces CO_2 and CO. The CO and volatile matter are burned over the grate by secondary air admitted over the fuel bed. The temperature of the fuel bed is affected by the rate of firing and, at the top or hottest part of the bed, varies from about 1230°C (2250°F) at low to 1510°C (2750°F) at high rates. The amount of primary air supplied determines the capacity of stoker-fired furnaces and the effective use of secondary air determines the efficiency of combustion. In well operated and carefully sealed boilers, approximately 20 to 30% excess air will permit combustion of the gases within seven or eight feet above the grate.

Stokers are classified in general according to the travel of the fuel. In an overfired stoker the fuel is fed on top of the bed, and in an underfired or a retort stoker the fuel is fed at the bottom or side of the bed. A traveling-grate or chain-grate stoker carries the bed horizontally on the flat upper surface of a conveyor as in a chain-grate stoker. There are a number of modifications of these stoker types. The spreader stoker projects the coal into the furnace above the fuel bed and the fuel is burned both in suspension and on the fuel bed. While the fuel bed of a stoker-fired boiler is relatively thin, usually from 100 to 300 mm (4 to 12 in.), compared to a gas-producer bed, similar zones of reaction occur. In overfired stokers the ash zone is immediately above the grate, followed by the oxidation, reduction and distillation zones. In underfired or retort stokers the distillation of the volatile matter takes place in an oxidizing atmosphere and the volatile products pass through the incandescent residue from combustion rather than through green coal, as in the case of overfired stokers. The normal combustion rates on coal-fired stokers amounts to approximately 150 to 300 kilograms of coal per square metre (30 to 60 pounds per square foot) of effective grate area per hour.

6.2.5.1 Pulverized Coal

The cement industry was the first to use pulverized (powdered) coal extensively as a fuel. Public utilities and the steel industry began applying pulverized coal on an experimental basis as a boiler fuel around 1917, and by 1935 practically all large boilers (above about 45,000 kilograms or 100,000 pounds of steam per hour) in public utility power stations used this fuel, except for those stations located in the vicinity of oil and natural gas fields where local fuels were more competitive than coal. Large modern boiler installations in integrated steel plants generally use pulverized

coal if coal is utilized, either as a standby or as an auxiliary fuel, in conjunction with blast-furnace gas for steam or power generation. Although pulverized coal has been used as a fuel for metallurgical purposes in steel plants, such as in open-hearth, reheating, forge and annealing furnaces, today it is employed as an injectant in the blast-furnace tuyere to increase furnace performance and efficiency.

Pulverized-coal firing offers important combustion advantages over grate firing and an economic advantage over gaseous and liquid fuels in most sections of the country. Boiler capacities are not limited as is the case with boilers equipped with stokers. Fine particles of coal burned in suspension are capable of developing a highly luminous high-temperature flame. Coal in this form may be burned normally with less excess of air above theoretical requirements than with a solid fuel, and the rate of heat release from the combustion of pulverized coal is greater than that accomplished with the solid fuel. Coal, when pulverized to the degree common for boiler uses (70% through a 0.074 mm or 200–mesh screen), has the control flexibility of gaseous and liquid fuels. Practically all ranks of coal, from anthracite to lignite, can be pulverized for combustion and each possesses specific combustion characteristics which largely influence the extent of pulverization. Pulverized-coal firing in modern boilers has certain inherent problems. Excessive fly-ash discharge from the stack, high operating power consumption rates, excessive pulverizer maintenance cost, erosion of induced-draft fan blades and other boiler components, and requirements for large furnace volumes impose practical limitations in selecting this type of firing for low-capacity boilers. Dust collectors are required to control stack particulate emissions, while scrubbers are required to remove the sulfur from the waste gas stream.

The ash-disposal problem has been one of the principal deterrents to a more extended use of pulverized coal. In the cement kiln, coal ash is no problem as it is absorbed by the cement in the kiln without adverse effect on the final product. In boilers, the principal difficulty of clogged boiler tubes and deterioration of furnace walls has been overcome by the use of slagging-type furnaces in which the ash in molten form is granulated by water jets at the bottom of the furnace well. The introduction of the cyclone furnace, which offered the removal of the ash as liquid slag, further increased the application of pulverized-coal firing for steam and power generation. This equipment was developed to solve two major problems that beset the power engineer: (1) the increasing necessity to use low quality, high-ash fuels for steam generation; and (2) the requirement that as much of the coal ash as possible be kept in the furnace and not permitted to go through the furnace and out of the stack. However, the removal of ash as a liquid slag requires the use of coal having ash of low fusion point and such special coal is sometimes difficult to obtain.

The problem of ash contamination resulting from burning fine particles of coal in suspension above a metallic liquid bath or mass of hot steel, damage to refractories from the chemical or physical action of ash, and the clogging of furnace checkers or recuperators from ash accumulation, as well as the normal availability of other fuels, has prevented widespread use of the fuel for metallurgical purposes in steel plants.

Pulverized coal offers high boiler efficiency, and means for quick regulation of boiler load. The rank of coal pulverized and the extent of pulverization particularly determine the speed of combustion. A high-volatile coal will burn faster than anthracite coal, also one with a lower ash content will burn faster. The process of combustion with pulverized coal is similar to that of lump coal but is of much higher velocity due to the introduction of the particle in suspension in a high-temperature chamber, and the greater surface exposure relative to weight. The release of volatile matter in pulverized coal is practically instantaneous when blown into the furnace, and the speed of combustion of the resulting carbonized particle and volatile gases depends upon the thoroughness with which the pulverized coal has been mixed with air. High combustion temperatures, low ash losses, and low excess air needs (10–20%), with resultant high boiler efficiencies (85–90% with good practice), make pulverized coal an ideal boiler fuel.

Air for combustion of pulverized fuel is generally preheated, with 10–50% of that required introduced ahead of the pulverizer and the balance made up at a point near the burner. This method of

introducing the air helps dry the coal and maintains a nonexplosive mix in the pulverized coal transmission system.

The combustion chamber size for pulverized coal is generally proportioned for a heat-release range of from approximately 207,000–1,035,000 watts per cubic metre or 745,000–3,725,000 kilojoules per cubic metre per hour (20,000–100,000 Btu per cubic foot per hour) of combustion space. However, the cyclone furnace has heat-release rates of approximately 5,175,000–9,315,000 watts per cubic metre or 18,625,000–33,525,000 kilojoules per cubic metre per hour (500,000–900,000 Btu per cubic foot per hour) within the cyclone chamber and the boiler furnace is used only for extracting heat from the flue gases. The difference in requirements is dependent upon whether pulverized coal is the sole fuel to be used in the chamber, the size of the coal particles, the rank of coal to be pulverized, the ash-slagging temperature of the coal, and the desired temperature for the combustion chamber. Spreader-stoker installations offer low first cost for smaller-size boilers, and the fly-ash emission from the boiler is not as severe as with the pulverized-fuel boilers.

Another technology is fluidized bed combustion which has been used to provide emission control for high sulfur coals. In this type of firing, the fuel limestone sorbent particles are kept suspended and bubbling or fluidized in the lower section of the furnace through the action of air under pressure through a series of orifices in a lower distribution plate. The fluidization promotes the turbulent mixing required for good combustion, which in turn promotes the three required parameters for efficient combustion; time, turbulence, and temperature. The limestone captures the freed sulfur from the coal products of combustion to form calcium sulfate. The mixture of ash and sulfated limestone sorbent discharged is a relatively inert material, disposal of which presents little hazard. This type firing also achieves a measure of NO_x control in that it burns at a lower temperature, somewhat below maximum NO_x formation.

6.3 Liquid Fuels and Their Utilization

Liquid fuels are essential to practically all parts of the American transportation system. The movement of passengers and freight by highway and air is dependent upon gasoline and other products of petroleum. The railways of the country have nearly all been equipped with diesel locomotives powered by fuel oil. Nearly all ocean-going ships are driven by oil, as are the majority of lake and river craft. Liquid fuels have also become of major importance as a source of heat and power in manufacturing plants. The particular advantages of petroleum as a source of energy and the available supplies have brought about a phenomenal growth in the petroleum industry.

The oil industry has recovered from the traumatic price increases of the 1970s and early 1980s which temporarily reduced the demand for oil products. The U.S. domestic demand for all oil products reached its low point in 1983 at 2.42 million cubic metres (15.23 million barrels) per day and returned to its highest level since 1979 in 1994 at 2.82 million cubic metres (17.72 million barrels) per day. During this period, the share of crude oil produced by the domestic oil industry has continued a steady decline to 1.06 million cubic metres (6.66 million barrels) per day in 1994 since reaching a peak of 1.53 million cubic metres (9.64 million barrels) per day in 1970. Unless a major new field is discovered, this decline in production and reserves will continue indefinitely.

Worldwide crude oil production in 1994 was also back to its highest levels since 1979 with a production rate of 9.63 million cubic metres (60.58 million barrels) per day with OPEC countries accounting for 41.1% of the total. This is still well below the 48.9% share OPEC held in 1979. Fortunately, as consumption of oil products has risen over the last decade, so has the known worldwide reserves. These reserves have stood at nearly 159 billion cubic metres (1,000 billion barrels) since the beginning of the 1990s. This is over 30% above the levels of the 1970s with the OPEC countries accounting for the majority of the increase.

Fuel oil is the principal liquid fuel used in the steel industry. Tar and pitch consumption has over the years decreased considerably. Fuel oil is utilized predominantly in the blast furnace as an injec-

tant for coke replacement, in reheating furnaces as a substitute for gaseous fuels and in boilers as a backup fuel for other byproduct fuels.

Tar and pitch are byproducts of the manufacture of coke. The virgin tar as it comes from the ovens contains valuable tar-liquor oils which can be extracted and the residue pitch used as a fuel. It is customary to mix virgin tar with this highly viscous residue to provide fluidity for facilitating handling and burning, or to utilize tar in which only the lighter products have been removed by a topping process by which sufficient fluidity is retained. Pitch-tar mixtures and topped tar make available for use as a fuel 78 to 83% of the heat in the crude tar recovered in the distillation process.

6.3.1 Origin, Composition and Distribution of Petroleum

Classified according to their origins, three main types of rocks make up the outer crust of the earth: igneous, sedimentary and metamorphic rocks. Igneous rocks are formed from magma, a molten (liquid or pasty) rock material originating at high pressures and temperatures within the earth. Lava is magma that reaches the surface in the liquid or pasty state. Very commonly, the magma cools and solidifies before reaching the surface. In any case, when the molten material cools sufficiently to become solid, igneous rocks are the result. If cooling is slow, the rocks will be crystalline (granite, for example); but if the cooling is rapid, the rocks will not be crystalline but glassy in nature (obsidian, for example). Because of the nature of their origin and their usually dense, nonporous structures, igneous rocks are never hosts to petroleum deposits.

Sedimentary rocks are formed from eroded particles of rocks and soil, carried away by wind or water (and sometimes glacial action) and deposited in seas, lakes, valleys and deltas in relatively even, sometimes very thick, beds or strata (sandstones and shales are formed from deposits of this type). Other types of stratified deposits may be formed by evaporation of land-locked seas (beds of rock salt), by accumulation of the mineral remains of animals (composed chiefly of calcium carbonate, which is the principal constituent of limestone), or by chemical precipitation (gypsum and some limestones originate in this manner). The beds of sand, silt, clay, calcium carbonate or whatever eventually are covered by other sedimentary deposits, sometimes to very great depths. With the passage of long periods of time, pressure of the overlying strata, heat, cementation by chemical means, earth movements, or a combination of these or other agencies, the strata are consolidated into sedimentary rocks, typified by the few mentioned parenthetically earlier. Petroleum occurs almost entirely in sedimentary rock formations, principally sandstones and limestones, under certain ideal conditions to be described later.

Metamorphic rocks originally were sedimentary or igneous rocks. Their composition, constitution or structure have been changed through the single or combined action of natural forces such as heat, pressure, or other agencies. Marble, for example, is metamorphosed limestone.

The organic theory of the origin of petroleum, generally accepted by geologists, is that petroleum has been derived from either animal or vegetable matter, or both, by a process of slow distillation, after its burial under beds of sediments. There is evidence to indicate that the animal and vegetable matter was of marine origin; such evidence includes the association of brines with oil, the visible oily coating on seaweed found in certain localities, and the optical phenomenon of light polarization by oils similar to that of substances found in certain plants and animals and which is not shown by inorganically synthesized petroleum. The accumulation of the matter from which petroleum has been derived, its burial by sedimentary material, and the action of pressure and heat to cause distillation, has resulted in petroleum formation in many parts of the world. Geological studies indicate that petroleum was not formed in the pools in which it is found, but that the action of water pressing against oil formations caused the petroleum to flow, over a period of many years, through porous beds or strata to points of accumulation. Pools of oil occur in traps in sedimentary rocks such as sandstone or limestone. Essentially, such traps are formed by an impervious layer which prevents upward migration of the petroleum to any further extent. The oil is obtained by drilling wells into these zones of accumulation. The well is encased in a steel pipe through which it is often customary to run a number of smaller pipes to bring the product to the surface. These traps may be
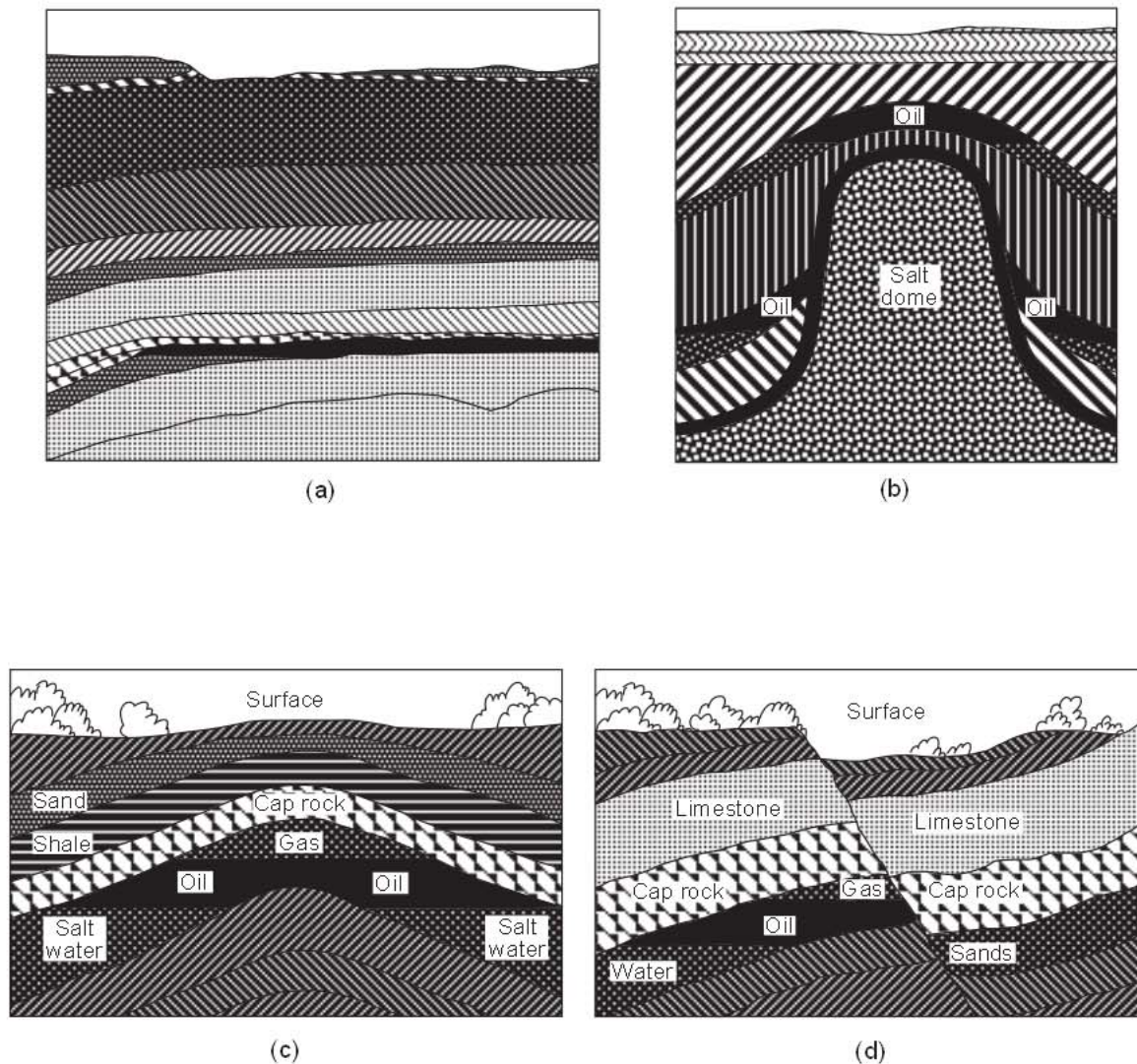
Fig. 6.3 Schematic representation of four geologic structures associated with the underground accumulation of petroleum through natural agencies: (a) stratigraphic trap, (b) salt domes, (c) anticlines, (d) faults. *From Fundamentals of Petroleum, NAVPERS 10883, Superintendent of Documents, U.S. Government Printing Office, Washington, DC.*

formed in various ways, a few of which are illustrated schematically in Fig. 6.3. In the stratigraphic trap, the producing formation gradually pinches out and disappears up the structure. An impervious layer is deposited on top of the sand, thus forming a cap rock. The solid black section in Fig. 6.3(a) represents petroleum accumulated below the cap rock. The salt dome is believed to be the result of intrusion of large masses of salt into the sediments where they are found. This intrusion creates an upward pressure and results in the doming of the overlying sedimentary rocks. In this type of structure, petroleum accumulates within the upturned porous beds about the summit and flanks of the salt core, as indicated by the solid black sections in Fig. 6.3(b). In an anticlinal structure, Fig. 6.3(c), the rocks comprising the crust of the earth are folded upward. The oil and gas are usually found on the crest of an anticlinal structure. An impervious cap rock must be present to seal the reservoir and prevent the escape of the gas and oil into higher layers. This cap rock, in one form or another, must be present in all reservoirs to contain the oil and gas within the structure. A fault, Fig. 6.3(d) is a structural closure caused by the fracturing of the crustal rocks during earth movements. In the process of folding, a reservoir for oil may be formed when a porous rock is brought into contact with an impervious layer, thus forming a trap.

Crude petroleum is a liquid containing a complex mixture of solid, liquid and gaseous hydrocarbons. The solid hydrocarbons are in solution and the liquid is at least partly saturated with gases (methane, ethane, etc.). The elementary composition of American crude oils from representative fields covers the following ranges: carbon 84–87%, hydrogen 11.5–14.0%, sulfur 0.05–3.0%, and nitrogen 0.01–1.70%

Ordinary crude petroleum is brownish-green to black in color with a specific gravity from approximately 0.810 to 0.981, and an ash content of 0.01 to 0.05%.

The principal constituents in crude oil are the paraffin (C_nH_{2n+2}), naphthene (C_nH_{2n}), and aromatic (C_nH_{2n-x}) series of hydrocarbons, and asphaltic compounds. In paraffin-base crudes, such as found in Pennsylvania, the asphaltic content is low, only traces of sulfur and nitrogen are found, and the specific gravity averages approximately 0.810. In mixed-base crudes which have a lower content of paraffins and a higher content of naphthenes than the paraffin-base crudes, the content of asphaltic compounds is higher, the sulfur content usually is under 0.4% and the paraffin-wax content is generally high. Mixed-base crudes occur in the mid-continent region. The naphthene-base crudes contain a high percentage of naphthenes and very little paraffin wax. They occur in the central, south-central and south-western areas of the U.S. Light naphthene-base crudes contain a low proportion of asphalt, compared to reverse proportions in heavy naphthene-base crudes. The sulfur content varies widely. The aromatic crudes, which occur chiefly in California, generally have a high asphaltic-compound content, sulfur content varying from 0.1 to 4.13% and a relatively high nitrogen content. The presence of wax is often widespread, although some crudes of this class are free of wax.

Crude oil is delivered by rail, ocean tankers, inland and intercoastal waterways, in specially constructed tanks, and by pipelines, including the Alaskan pipeline.

6.3.2 Grades of Petroleum Used as Fuels

Fuel oils may be classified generally as: (1) raw or natural crude petroleums, (2) distillate fuel oils, (3) residual fuel oils, and (4) blended oils. By the older methods of refining, the products from many of the oil refineries west of the Mississippi River were gasoline, naphtha, kerosene and fuel oil, while eastern refineries usually carried the fractionation of oil much further, their output being such products as gasoline, benzene, naphtha, kerosene, light machine oil, automobile oils, cylinder oils, paraffin wax and tar, pitch, or coke. Recent improvements in thermal cracking at both high and low pressure and the use of catalytic conversion processes have enabled refiners to convert more of the petroleum to gasoline and to produce lubricants from western petroleum relatively high in asphalt.

Distillate fuel oils consist of the fractions distilled intermediate between kerosene and lubricating oils. Residual fuel oils are the viscous residual products remaining after the more volatile hydrocarbons have been driven off in the refining process. Blended oils are mixtures of any or all of the three classes of fuel oils. The distribution of products obtained from crude oil in a sample of eight refineries is listed in Table 6.16.

Table 6.16 Percentages of Yield of Refined Petroleum Products from Crude Oil [a]

Fuel Gas	2%
Propane + Butane	5%
Gasoline	55%
Low Sulfur Diesel/#2 Oil	7%
Jet Fuel/Kerosene	28%
Bunker/Asphalt	3%
Total	**100%**

[a] Based on the average yield from eight different refineries.

6.3.3 Properties and Specifications of Liquid Fuels

Before discussing the more important properties and specifications of fuel oil, some of the common terms will be reviewed. Further details may be found in the ASTM Standards for Petroleum, Section 5, cited in the references at the end of this chapter.

Specific gravity is the ratio of the weight of a volume of a body to the weight of an equal volume of some standard substance. In the case of liquids, the standard is water. Baumè gravity is an arbitrary scale for measuring the density of a liquid, the unit being called Baumè degree. Its relation to specific gravity is shown by the formula:

$$Be^\circ = \frac{140}{Sp.\ Gr.} - 130 \text{ (for liquids lighter than water)} \qquad (6.3.1)$$

For example, the Baumè hydrometer will read 10° Bè in pure water, when the specific gravity scale reads 1.00.

The American Petroleum Institute (API) Gravity is a modification of the Baumè scale for light liquids. API gravities are always reported at 15°C (60°F). The relation between API gravity and specific gravity is:

$$^\circ API = \frac{141.5}{Sp.\ Gr.} - 131.5 \qquad (6.3.2)$$

The greater the degrees Baumè or API, the lighter or lower in density the fluid. There are roughly 90 API degrees between the heaviest and lightest oils which, therefore, make this scale valuable for determining differences between the density of various oils.

Flash point is the lowest temperature at which, under specified conditions, a liquid fuel vaporizes rapidly enough to form above its surface an air and vapor mixture which gives a flash or slight explosion when ignited by a small flame. It is an indication of the ease of combustion or of the fire hazard in handling or using oil.

Pour point is the lowest temperature at which oil will pour or flow when chilled without disturbance under specified conditions.

Viscosity is the property of liquids that causes them to resist instantaneous change of shape or rearrangement of their parts due to internal friction. Since this property has a direct relation to resistance of flow in fuel-oil pipe systems and to atomization, it is an important specification.

Absolute viscosity is a measure of internal fluid friction. It is defined as the tangential force on unit area of either of two parallel planes a unit distance apart when the space between the two planes is filled with liquid and one of the planes moves relative to the other with unit velocity in its own plane, and is also referred to as dynamic viscosity.

The unit for expressing absolute viscosity in SI is the Pascal-second (Pa s). By definition the pascal equals one Newton per square metre (N/m^2) and the Newton has the formula kg m/s^2, thus the dimensions for the Pascal-second are kilograms per second per metre (kg/s/m). One Pascal-second is equal to 0.1 poise or 10 centipoises (the poise and centipoise are defined below).

The cgs unit of absolute viscosity is the poise, which has the dimensions, grams per centimetre per second (g/s/cm). The centipoise is 1/100 of a poise and is the unit of absolute viscosity most commonly used in cgs. One poise equals 10 Pa s (the SI unit) and one centipoise equals 0.1 Pa s.

Absolute viscosity in the fps system is expressed in pounds force per second per foot (lbf/s/ft) The absolute viscosity of water at 20°C (68°F) in SI equals 0.1 Pa s; in the cgs system it equals 1 centipoise; and in the fps system it equals 0.00209 lbf/s/ft.

Relative viscosity of a fluid is defined as the ratio of the absolute viscosity of the fluid to the absolute viscosity of water, with both the fluid and water at the same temperature and with their respective viscosity measured in the same units.

Kinematic viscosity relates to the time for a fixed amount of a fluid to flow through a capillary tube under the force of gravity; it may be defined as the quotient of the absolute viscosity in centipoises divided by the specific gravity of a fluid, both at the same temperature. The unit of kinematic viscosity is the stoke or centistoke (0.01 stoke), derived as follows:

$$\frac{\text{centipoises}}{\text{specific gravity}} = \text{centistokes} \qquad (6.3.3)$$

The viscosity of all liquids decreases with increasing temperature and ASTM viscosity determinations are made at oil temperatures of 37.8°, 50.0°, 54.4° and 99.2°C (100°, 122°, 130° and 210°F, respectively), and are often expressed as Saybolt Universal at 37.8°C (100°F) or Saybolt Furol at 50°C (122°F). The terms "Saybolt Universal" and "Saybolt Furol" represent the type of instrument used in making the viscosity determinations. Viscosity measurements made by either method may be converted by the use of tables.

Reid Vapor Pressure is a test for the vapor pressure of gasoline at 37.8°C (100°F). It shows the tendency of gasoline to generate vapor bubbles and is expressed in SI in kiloPascals, in the cgs system in kilograms per square centimetre, and in the fps system in pounds per square inch absolute.

Octane number is the anti-knock rating of gasoline. The rating is made by matching the fuel in a test engine with a mixture of normal heptane, which detonates very easily and has an octane rating of zero, and iso-octane, which has exceptionally high anti-knock characteristics and is rated at 100. A fuel knock that matches a mixture of say 60% octane and 40% heptane would have an octane rating or number of 60. Cetane number is used to show the ignition quality of diesel oils. The rating is based on a scale resembling those of octane numbers by matching the ignition delay of the fuel against blends of cetane, a fast-burning paraffin, and methyl naphthalene, a slow-burning aromatic material.

The ASTM has developed a table for grading fuel oils, consisting of six grades. According to this classification, heating oils generally used for domestic and small industrial heating furnaces comprise Grades 1, 2 and 3. Grades 5 and 6, formerly known as Bunker B and Bunker C fuel oils, respectively, are used extensively in the steel industry. Grade 5 fuel oil is usually cracking-still tar and Grade 6 fuel oil, a straight-run or cracked residual, or a mixture of residual and cracking-still tar blended to reduce the viscosity as required by the consumer.

All grades of fuel oil are normally sold to meet specifications mutually satisfactory to buyer and seller. A typical specification of Grade 6 fuel oil is given in Table 6.17. Some purchasers may also specify the desired calorific value of Grade 6 fuel oil (for example, 41,805 kilojoules per cubic decimetre or 150,000 Btu per gallon, minimum) and the fire point of the oil (for example, 205°C (400°F) minimum and 232°C (450°F) maximum).

Table 6.17 Typical Specification for Grade 6 Fuel Oil

	Minimum	Desired	Maximum
Gravity — API at 15.6°C (60°F)	10	12	14
Viscosity — SSF at 50°C (122°F)	280	300	310
Pour Point	—	0°C (32°F)	10°C (50°F)
Flash Point	107°C (225°F)	121°C (250°F)	149°C (300°F)
Sulfur (%)	0	0.6	1.0[a]
Sodium Chloride	0	0	0.719 kg/m³ (0.006 lb/gal)
Ash (%)	0	0	0.15
Bottom Sediment and Water (%)	0	0	2.0

[a] For blast-furnace use, 1.5% maximum.

The yield of tar produced in byproduct coke ovens by high-temperature distillation between 1000° and 1100°C (1832° and 2012°F) differs within very wide limits according to the kind of bituminous coal coked, and to the temperature, coking time, and design of oven employed in the process. Virgin tar as produced in the byproduct ovens consists essentially of tar acids, neutral oils which are principally aromatic hydrocarbons, and a residue pitch.

The residue pitch from the distillation of tar is highly viscous or brittle. Pitch contains a substantial percentage of free carbon and some high-boiling and complex organic chemicals. The composition and properties of a typical pitch-tar mix and Grade 6 fuel oil are shown in Table 6.18.

Table 6.18 Composition and Properties of Typical Liquid Fuels

Fuel	Ultimate Analysis of Fuel (%)						
	H$_2$O	C	H$_2$	N$_2$	O$_2$	S	Ash
Pitch-Tar (Dry)	. . .	90.78	5.35	1.39	1.65	0.61	0.22
Pitch-Tar (Natural Basis)	1.33	89.57	5.28	1.37	1.63	0.60	0.22
Grade 6 Fuel Oil (Dry)[a]	. . .	88.60	10.50	0.30	0.00	0.55	0.05

Fuel	Specific Gravity at 15.6°C (60°F)	Mass		Dry Air Required for Combustion		Theoretical Flame Temperature	
		kg/dm^3	lb/gal	m^3/kg	ft^3/lbm	°C	°F
Pitch-Tar (Dry)	—	—	—				
Pitch-Tar (Natural Basis)	1.199	1.196	9.9855	9.41	158.13	1924	3495
Grade 6 Fuel Oil (Dry)	0.9529	0.951	7.935	10.64	180	2093	3800

Fuel	Calorific Value			
	Gross		Net	
	kJ/kg	Btu/lbm	kJ/kg	Btu/lbm
Pitch-Tar (Dry)	—	—	—	—
Pitch-Tar (Natural Basis)	37,577	16,155	36,458	15,674
Grade 6 Fuel Oil (Dry)	43,938	18,890	41,449	17,820

[a] Courtesy of Sun Oil Co. — Typical composition.

The viscosity of liquid fuels such as virgin tar, pitch-tar mixtures and topped tar decreases with temperature increase as shown in Table 6.19.

Table 6.19 Effect of Temperature on Viscosity of Various Tars and Tar Mixtures

Fuel	Test Temperature		Viscosity in Saybolt Universal Seconds		
	(°C)	(°F)	Max.	Min.	Avg.
Virgin Tar	79.4	175	189.4	73.3	109.4
Pitch-Tar Mix	79.4	175	1940	181	946.1
Pitch-Tar Mix	98.9	210	687	97	561.7
Topped Tar	93.3	200	700	550	600

6.3.4 Combustion of Liquid Fuels

The combustion of liquid fuel usually is obtained by atomizing the fuel. Atomization breaks up the fuel into fine, mist-like globules, thus permitting an increased area for intimate contact between the air supplied for combustion and the fuel. The chemistry of combustion of liquid fuels is complex. The small particles of fuel either vaporize to form gaseous hydrocarbons which burn to CO_2 and H_2O through a chain of reactions, or the fuel cracks to form carbon (soot) and hydrogen which also burn with complete combustion to CO_2 and H_2O. Both of these conditions normally occur in the combustion of liquid fuels. The first condition predominates with good atomization and proper mixing with sufficient air. A deficiency of air or poor atomization will cause smoke. For large furnaces the atomizing agent is usually steam at a pressure anywhere between 415 and 860 kPa (60 and 125 pounds per square inch) gauge. The steam consumed in atomization varies from 0.3 to 0.7 kilograms per kilogram of fuel. When liquid fuels are used in smaller furnaces, atomization usually is achieved by compressed air or by mechanical action. The character of a liquid-fuel flame, that is, its shape, size and luminosity, may be altered with a fixed burner design by changing the degree of atomization which is controlled by the steam pressure. Liquid fuels normally are burned in steel plants to produce a highly luminous flame at an intensity of flame propagation intermediate between that generally secured with coke-oven gas and that with natural gas.

Liquid fuels are often preferred because they permit better control of flame direction and, because of their high calorific value, control of flame temperature and luminosity.

The amount of air required to burn liquid fuels depends upon the chemical composition of the particular fuel. Grade 6 fuel oil requires approximately 10.64 m^3 per kilogram (180 ft^3 per lbm) of dry air for perfect combustion, and tar-pitch approximately 9.34 m^3 (158 ft^3). From the ultimate analysis of a liquid fuel, the theoretical air requirements and products of combustion may be calculated, as explained in Section 6.1.2.5.

6.3.5 Liquid-Fuel Burners

There are many different designs of burners for liquid fuels. Burners designed for atomization by steam or air may be classified into two general types, the inside mixing and the outside mixing. In the inside-mixing type the fuel and atomizing agent are mixed inside the burner or burner system, while in the outside-mixing type the two fluids meet immediately outside the burner tip. In large reheating furnaces the inside-mixing type is used. The inside-mixing type is sometimes classified as an emulsion type or a nozzle-mix type of burner. In the emulsion type the mixing is performed at a point several feet from the burner tip, while in the nozzle-mix type the two fluids meet inside the burner but very close to the burner tip. In the latter type, mixing probably takes place both inside the burner and as the stream enters the furnace. Liquid-fuel burners used in reheating, forge and annealing furnaces seldom require water cooling.

The handling of liquid fuels at consuming plants requires a system for their transportation, storage and conditioning. Where liquid fuels are received by tank car, a system of receiving basins, unloading pumps, strainers and storage tanks generally is required. The storage tanks must be of ample size to meet fuel demands between deliveries and should be provided with heaters to maintain proper fluidity for flow through pipelines to the system pressure pumps. Pressure pumps are used to deliver the liquid fuel through a pipe system to the point of consumption. Where there are a number of consuming units being served from a common fuel-storage system, the pipe feeder line is designed in the form of a loop through which the fuel flows at constant pressure and temperature. The various units tap into this loop. The fuel-oil lines are lagged and provided with tracer steam lines to maintain uniform fluidity throughout the system and to provide fuel at the burners at the proper viscosity for atomization. The temperature at which liquid fuel is delivered to the burners varies with the character of the fuel and burner design. Where pitch is used, a temperature as high as 150°C (approximately 300°F) in the lines is sometimes required. A temperature level usually somewhere between 95° and 120°C (approximately 200° and 250°F) is maintained for pitch-tar mixtures, and 65° and 95°C (approximately 150° and 200°F) for Grade 6 fuel oil. Additional

details on burners and firing practices for liquid fuels appear in several references cited at the end of this chapter.

6.4 Gaseous Fuels and Their Utilization

The availability of natural gas in so many sections of this country has had a profound influence upon our industrial progress. It was first used as an illuminating gas at Fredonia, New York, in 1821. The discovery of new fields and the installation of pipelines to consuming centers led to increasing demands, as the convenience, cleanliness, and general utility of this form of fuel became better known. The initial use of natural gas for steel manufacture was at a rolling mill plant at Leechburg, Pa., in 1874. A well in this area permitted exclusive use of natural gas for puddling, heating, and steam generation for a period of six months. Since 1932 there has been an accelerated demand for natural gas, which peaked in 1972 at 0.626 trillion cubic metres (22.10 trillion cubic feet). The rapid price escalation which followed the oil shocks cut demand by 1986 to less than 75% of the previous peaks. As supplies have increased and prices have fallen, the consumption of natural gas has returned to 0.587 trillion cubic metres (20.73 trillion cubic feet) in 1994. Deregulation of the gas industry has been the main contributing factor in the resurgence of gas as the fuel of choice in the U.S.

Many industrial and some commercial gas users purchase their own gas from suppliers in the Gulf of Mexico and Southwestern states, arrange for transportation on the interstate pipeline system and if necessary pay the local utility to move the gas into the plant. In some cases, industrial users have bypassed the local utility completely and have built short pipelines from the interstate pipeline to their plant. End users have many options available to them with regards to the quality of service required. For example, a company could request firm or interruptible transportation services from the interstate and/or sign up for storage capacity with the local distribution company to hedge against winter curtailments on the interstate system.

As with oil, the U.S. natural gas reserves are shrinking while the worldwide reserves have risen substantially. For example, over the past two decades, U.S. natural reserves have fallen 30% to 4,599 billion cubic metres (162,415 billion cubic feet) and the world natural gas reserves have nearly doubled to 141,024 billion cubic metres (4,980,278 billion cubic feet). The majority of the world increase has come from the Middle East and the CIS (former Soviet Union Republics). The predominant domestic supply sources are the Gulf of Mexico, Southwestern states and Western Canada.

Producer gas was the first gaseous fuel successfully utilized by the iron and steel industry. This gas permitted the early experimentation in regeneration, and the utilization of this principle started a new era of steel manufacturing. The advantages of preheated gas and air were so clearly indicated in 1861 that producer gas rapidly became the major fuel utilized by open-hearth furnaces and maintained its position for almost sixty years, or until about 1920, when byproduct coke plants, supplying coke-oven gas and tar, began to challenge this leadership.

Blast-furnace gas utilization by the iron and steel industry probably should rank first historically, although its adoption by the industry was slower than in the case of producer gas. The sensible heat in the blast-furnace top gases was first utilized in 1832 to transfer heat to the cold blast. Originally, this heat exchanger was mounted on the furnace top. In 1845, the first attempts were made to make use of its heat of combustion, but history indicates that the burning of blast-furnace gas was not successful until 1857. It is probable that progress in the utilization of blast-furnace gas was delayed by its dust content, the problems of cleaning and handling, and the low cost of solid fuel. Increasing cost of other fuels and competition forced its use, and by the turn of this century, blast-furnace gas had become one of the major fuels of the iron and steel industry. In 1995, the steel industry used approximately 18 billion cubic metres (651 billion cubic feet) of blast-furnace gas (based on 3,535 kJ/m^3 or 90 Btu/ft^3) for blast-furnace stove heating, coke-oven underfiring, the raising of steam in boilers and heating steel in various types of furnaces. This quantity of blast-furnace gas would, in joules (Btu's), equal 1.6 billion cubic metres (57 billion cubic feet) of natural gas.

The initial use of byproduct coke-oven gas in the iron and steel industry was at the Cambria Steel Company, Johnstown, Pa., in 1894. This installation was followed by only a few byproduct coke-plant additions until a shortage of transportation facilities and the rising price of coal and natural gas during the first World War accelerated installations throughout the steel industry. The utilization of coke-oven gas has been very profitable as it reduced the purchase of outside fuels. It is estimated that plants operating steelmaking furnaces in the U.S. used approximately 11,794 million cubic metres (28,052 million cubic feet) of coke-oven gas as fuel in 1995 (based on 19,640 kJ/m^3 or 500 Btu/ft^3). This is only a small fraction of the quantities used as recently as 1982.

The gas produced by the basic oxygen process has not been utilized by the U.S. steel industry due to the cost of the equipment required to gather and clean the gas versus the cost of alternative fuels. In Europe and Japan, where substitute fuels are more expensive, BOF gas has been collected and utilized by many of the steel works for a number of years. Approximately 0.70 GJ/tonne (0.60 million Btu/ton) of offgas can be collected from each heat in a BOF with a typical size of 181 tonne (200 ton). The recovered gas has a calorific value of 8837 kJ/m^3 (225 Btu/ft^3).

6.4.1 Natural Gas

Natural gas and petroleum are related closely to each other in their chemical composition and in geographical distribution. Both are made up predominantly of hydrocarbons. Petroleum rarely is free of natural gas, and the same fields usually produce both fuels. When natural gas exists indigenous to an oil stratum and its production is incidental to that of oil, it is called casinghead gas. Gas found in a field is usually under pressure which diminishes with extended use or, sometimes, from the presence of too many other wells. The life of a well varies from a few months to twenty years. Rocks bearing gas are sandstones, limestones, conglomerates, and shales, never igneous rocks. Natural gas is derived from the remains of marine animal and plant life—in theory, the same as described previously for petroleum.

Natural gas, as found, is usually of singular purity and is composed principally of the lower gaseous hydrocarbons of the paraffin series, methane and ethane, some of the heavier liquefiable hydrocarbons (which are recovered as casinghead gasoline or sold in bottled form as butane, propane, pentane, etc.) and a small amount of nitrogen or carbon dioxide. Some natural gases contain small quantities of helium. Occasionally, wells are found in which the gas contains hydrogen sulfide and organic sulfur vapors. Sour gas is defined as a natural gas which contains in excess of 0.0343 grams of hydrogen sulfide or 0.686 grams of total sulfur per cubic metre, equivalent to $1^1/_2$ grains of hydrogen sulfide or 30 grains of total sulfur per 100 cubic feet. It is fortunate, however, that by far the greater part of natural gas available in this country is practically sulfur-free.

The principal constituent of natural gas is methane, CH_4. Because natural gas contains from 60 to 100% CH_4 by volume, the characteristics of methane gas, which were shown in Section 6.1, largely dominate the parent gas. Comparing methane with the other principal combustible gases, it will be noted that it has a low rate of flame propagation, a high ignition temperature, and a narrow explosive range. Methane, as well as all other hydrocarbons (of which it is the lowest member), burns with a luminous flame. Typical compositions of natural gas are presented in Table 6.20.

The iron and steel industry consumed a total of 7,892 million cubic metres (278,711 million cubic feet) of natural gas in 1995 in blast furnaces and other uses in the blast-furnace area, steel-melting furnaces, heating and annealing furnaces, heating ovens for wire rods, and other uses.

6.4.2 Manufactured Gases

The four most important of the commercially used manufactured gases are producer gas, water gas, oil gas, and liquefied petroleum gases. Because none of these gases except liquefied petroleum gases are used presently in steel manufacturing or processing in the U.S., only a brief description of their manufacture and characteristics will be given here.

Table 6.20 Typical Composition of Natural Gas in Various States in the United States (Based on GRI Survey for 1992) [a]

Constituents (% by Volume)	Louisiana[b]	Illinois[c]	Ohio[d]	Pennsylvania[d]	California[e]
Methane	93.7	92.6	89.7	96.1	91.2
Ethane	2.3	3.6	4.5	2.2	4.1
Propane	0.6	0.6	1.3	0.3	1.1
Butanes	0.3	0.2	0.4	0.2	0.4
Pentanes	0.1	0.1	0.1	0.1	0.1
Hexane +	0.1	0.1	0.1	0.1	0.1
Oxygen	0	0	0	0	0
Inerts (CO_2 & N_2)	2.9	2.9	3.9	1.1	3.0
Gross Heating Value					
Btu/Scf [g]	1023.1	1031.3	1044.9	1029.8	1048.4
MJ/m^3 [h]	40.19	40.51	41.04	40.45	41.18
Specific Gravity	0.597	0.601	0.619	0.581	0.615

[a] Bulletin GR92-0123
[b] State Wide Summary Data
[c] Gate Station B
[d] Company #1 Station A
[e] City #1 Gate Station E
[f] At 30″ Hg, 60°F, Dry
[g] At 760 mm Hg, 0°C, Dry

6.4.2.1 Manufacture of Producer Gas

Producer gas is manufactured by blowing an insufficient supply of air for complete combustion, with or without the admixture of steam, through a thick, hot, solid-fuel bed. A large proportion of the original heating value of the solid fuel is recovered in the potential heat of carbon monoxide, hydrogen, tarry vapors, and some hydrocarbons, and in the sensible heat of the composite gas which also contains carbon dioxide and nitrogen. When the gas is cleaned, the sensible heat of the gases and the potential heat of the tar vapors is lost.
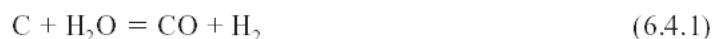
Table 6.21 gives the composition of clean producer gas made from various fuels in a well-operated updraft producer.

The gross heating value of raw producer gas, including tar, made from a high-volatile coal, 8% ash, is about 6678 to 7463 kilojoules per cubic metre (170 to 190 Btu per cubic foot).

Producer gas has a very low rate of flame propagation due to the relatively large amount of inert gases, N_2 and CO_2, it contains. The hot gas, containing tar, burns with a luminous flame; the cold gas is only slightly luminous, while it is non-luminous if made from anthracite coal or coke. Producer gas is a relatively heavy gas and has a wide explosive range. The theoretical flame temperature is low, approximately 1750°C (3180°F), and the gas generally was preheated when utilized in steel plant processes.

6.4.2.2 Manufacture of Water Gas

Water gas or blue gas is generated by blowing steam through an incandescent bed of carbon. The gas-forming reactions are primarily:

$$C + H_2O = CO + H_2 \qquad\qquad (6.4.1)$$

$$C + 2H_2O = CO_2 + 2H_2 \qquad\qquad (6.4.2)$$

Table 6.21 Composition of Clean Producer Gas [a]

Constituent	Anthracite Coal	Coke 100 to 125 mm (4 to 5″) Lump	Breeze	Bituminous Coal A	B
CO_2	6.3%	9.2%	8.7%	3.4%	9.2%
Illuminants	0.0	0.1	0.0	0.8	0.4
O_2	0.0	0.0	0.0	0.0	0.0
CO	25.0	21.9	23.3	25.3	20.9
H_2	14.2	11.1	12.8	9.2	15.6
CH_4	0.5	0.2	0.4	3.1	1.9
N_2	54.0	57.5	54.8	58.2	52.0
Total	**100.0%**	**100.0%**	**100.0%**	**100.0%**	**100.0%**
Gross Heating Value,					
kJ/m^3 [b]	5185	4753	5146	6088	6128
Btu/ft^3 [c]	132	121	131	155	156

[a] U.S. Bureau of Mines, Bulletin 301.
[b] At 760 mm Hg, 0°C, dry.
[c] At 30 in. Hg, 60°F, dry.

Fuel oil may be cracked in a separate heating chamber to form gases that are added to water gas to enrich it when carburetted water gas is made.

While coke generally is used as the fuel in the production of water gas because of its high carbon content and cleanliness, anthracite and bituminous coal and mixtures of coal and coke also have been used successfully, but with some sacrifice in overall operating efficiency.

Water gas burns with a clear blue flame; hence, the name blue gas. It is used in a number of chemical processes to supply a basic gas for synthetic processes, but it is not suitable for distribution as a domestic fuel unless it has been enriched with cracked fuel oil, when it is called carburetted water gas.

Water gas made from coke burns with a nonluminous flame. Carburetted water gas burns with a highly luminous flame. Both gases have a high rate of flame propagation. The speed of combustion for water gas exceeds that of any other extensively used fuel gas; that for carburetted water gas is practically the same as for coke-oven gas. Water gas has a slightly lower specific gravity than natural gas, but is somewhat heavier than coke-oven gas. Carburetted water gas is heavier than natural gas but lighter than producer gas. The theoretical flame temperature of both blue and carburetted water gas is very high, approximately 2020°C and 2050°C (3670° and 3725°F), respectively, exceeding that of all other industrial fuel gases commonly used. Both gases have a relatively wide explosive range.

6.4.2.3 Oil Gas

Oil gas is a combination of cracked petroleum and water gas made by passing oil and steam through hot refractory checker work. Oil gas is commercially important in localities where coal or coke is expensive and oil is cheap.

6.4.2.4 Liquefied Petroleum Gas

Liquefied petroleum gases (LPG), sometimes referred to as bottled gases, have become commercially important because of the concentration of fuel energy in liquid form which may be converted easily into a gas. They are distributed for household use in steel cylinders, called bottles, and in tank cars or trucks for industrial purposes. They are sometimes sold under various trade names but are composed mainly of butane, propane, and pentane. A steel cylinder of propane as sold for domestic purposes contains approximately 50,300 kilojoules per kilogram (21,640 Btu per pound) of liquid gas. Larger versions of these containers have been used by the steel industry as back up supply for natural gas systems.

6.4.2.5 Alternative Fuel Sources

Drastic escalation of oil prices by the Organization of Petroleum Exporting Countries (OPEC) in the 1970s stimulated interest in alternative sources of fuels to supplement existing supplies. A number of projects began operation during the early 1980s. Tennessee Eastman built a coal gasification plant to provide synthetic gas for conversion to chemicals. The Cool Water Project in California integrated coal gasification with the generation of electricity by a combination of gas and steam turbines. Union Oil Company began operation of a shale oil facility at Parachute, Colorado, and a consortium built the Great Plains Coal gasification plant to produce synthetic natural gas. Companies also started to recover gas from sanitary landfills.

Once oil and gas prices stabilized at more normal levels, many of these projects became uneconomic. Over time, these types of alternative fuel sources may once again become economically attractive.

6.4.3 Byproduct Gaseous Fuels

The two major byproduct gaseous fuels recovered by the steel works are blast-furnace and coke-oven gases. A number of other unavoidable gaseous fuels are created by regular manufacturing processes. Some of these are of minor economic consequence, but the majority are useful and generally utilized at the plant where they are produced. An exception is oil-refinery gas which is sometimes piped and marketed to industries adjacent to refineries. The calorific value and flame characteristics of byproduct gases have wide ranges. Blast-furnace gas has probably the lowest heat content of any, and oil refinery gas the highest, respectively about 3535 and 72,668 kilojoules per cubic metre (90 and 1850 Btu per cubic foot), although both vary from these values.

6.4.3.1 Blast-Furnace Gas

Blast-furnace gas is a byproduct of the iron blast furnace. The paramount objective in blast-furnace operation is to produce iron of a specified quality, economically; the fact that usable gas issues from the top of the furnace is merely a fortunate attendant circumstance. When air enters the tuyeres, its oxygen reacts with the coke. The resulting gas passes up through the shaft of the furnace which has been charged with coke, ore, and limestone, and after a number of chemical reactions and a travel of some 25 metres (80 feet), issues as a heated, dust-laden, lean, combustible gas. The annual volume production of this gas is greater than that of any other gaseous fuel. Two and one-half to three and one-half tons of blast-furnace gas are generated per ton of pig iron produced. While the purpose of the gases generated by the partial combustion of carbon is to reduce iron ore, the value of a blast furnace as a gas producer is evident from the relation just noted.

The percentage of CO and CO_2 in blast-furnace gas is directly related to the amount of carbon in the coke and the amount of CO_2 in the limestone charged per ton of iron produced. The rate of carbon consumption depends principally upon the kind of iron to be made, the physical and chemical characteristics of the charged material, the distribution of the material in the furnace stack, the furnace lines, and the temperature of the hot blast. The total $CO+CO_2$ content of the top gas is approximately 40% by volume, and when producing ordinary grades of iron the ratio of CO to CO_2

will vary from 1.25:1 to 2.5:1. The hydrogen content of the gas varies from 3 to 5% depending on the type and amount of tuyere-injected fuels. The remaining percentage is made up of nitrogen, except for approximately 0.2% CH_4.

Blast-furnace gas leaves the furnace at a temperature of approximately 120° to 370°C (approximately 250° to 700°F), and at a pressure of 345 to 1380 mm Hg gauge pressure (15 inches w.g. to 14.5 psig), carrying with it 22 to 114 grams of water vapor per cubic metre (10 to 50 grains per cubic foot) and 18 to 34 grams of dust per cubic metre (8 to 15 grains per cubic foot). The particles of dust vary from 6.4 to 0.000254 mm in diameter. In early days of blast-furnace operation, the gas was used as it came from the furnace without cleaning, causing a great deal of trouble with flues, combustion chambers, and stoves due to clogging. The gas now is cleaned almost universally, the degree depending upon the use.

The outstanding characteristics of blast-furnace gas as a fuel are: (1) very low calorific value—approximately 2946 to 3535 kilojoules per cubic metre (75 to 90 Btu per cubic foot) depending on blast-furnace coke rate, (2) low theoretical flame temperature—approximately 1455°C (2650°F), (3) low rate of flame propagation—relatively lower than any other common gaseous fuel, (4) high specific gravity—highest of all common gaseous fuels, and (5) burns with a non-luminous flame.

6.4.3.2 Coke-Oven Gas

The steel industry, which uses the majority of the total coke-oven gas generated in the U.S., generally classifies coke-oven gas as a byproduct of coke manufacture. This undoubtedly is due to the former waste of coke-oven gas and other coal products for so many years in the beehive coke process. Actually, the production of coke-oven gas and other coal chemicals is a part of an important manufacturing process, in which large sums have been expended for their recovery, as they have a value almost equal to that of the coke. Coke-oven gas is produced during the carbonization or destructive distillation of bituminous coal in the absence of air. Approximately 310 cubic metres of 19,640 kJ/m^3 gas are produced per metric ton of coal coked (about 11,000 cubic feet of 500-Btu gas per net ton of coal coked) in conventional high-temperature coking processes.

The composition of coke-oven gas varies in accordance with the grade and density of coal and operating practices. Typical percentage ranges for constituents of dry coke-oven gas by volume are presented in Table 6.22.

Table 6.22 Typical Properties of Coke-Oven Gas

CO_2 (includes H_2S)	1.3–2.4%
O_2	0.2–0.9%
N_2	2.0–9.6%
CO	4.5–6.9%
H_2	46.5–57.9%
CH_4	26.7–32.1%
Illuminates	3.1–4.0%
Specific Gravity	0.36–0.44
Heating Value (Gross)	
kJ/m^3	21,093–22,782
Btu/ft^3	537–580
Heating Value (Net)	
kJ/m^3	18,854–20,543
Btu/ft^3	480–523

Coke-oven gas contains hydrogen sulfide, H_2S. Approximately 40% of the sulfur in coal, not removed in the washing process, is evolved with the distillation products. Much of this remains in the gas. Carbonization of coals containing 1.20% sulfur evolves a gas containing approximately 9.7 grams of sulfur per cubic metre (424 grains per 100 cubic feet), and those containing 1.60% sulfur approximately 14 grams of sulfur per cubic metre (600 grains per 100 cubic feet). Commercial coals in the eastern part of the U.S. usually run from 0.5 to 1.5% sulfur. Gases high in sulfur content are very undesirable for metallurgical purposes.

Coke-oven gas normally is saturated with water vapor. In distribution systems, means must be provided for draining off the condensation due to any temperature change.

Coke-oven gas burns with a non-luminous to semi-luminous flame, depending upon the degree of mixing air and gas. Its rate of flame propagation is high, considerably higher than natural, producer, or blast-furnace gas. It has a low specific gravity, in fact the lowest of any of the gaseous fuels commonly utilized by the steel industry. It has a high theoretical flame, approximately 1980°C (3600°F), which is a little higher than that of natural gas. The explosive range is roughly twice that of natural gas.

6.4.3.3 Basic Oxygen Furnace Gas

One fuel that has not been economically recovered by the domestic steel industry is basic oxygen furnace gas. The utilization of this fuel requires special collection and cleaning equipment which would allow for its use in the steel plant. The special equipment includes such items as an adjustable skirt on the vessel hood, a flare, a gas holder, by-pass valving and a wet electrical precipitator. BOF gas of sufficient quality to be used is collected only during part of the blowing cycle. For example, the start of gas recovery begins when the CO content is above 30% and the O_2 content falls below 2%. The stoppage of gas recovery occurs when the O_2 content is above 2% or the CO content falls below 30%. These parameters may vary from plant to plant. The composition of the gas varies throughout the blow but a typical analysis (by volume) is as follows: 57% CO, 26% CO_2, 2% H_2O, 15% N_2, and $O_2 < 1\%$ (most of the cycle).

In steel plants in other countries which utilize BOF gas, the most predominate use is in the boiler plant, either directly or blended with blast-furnace gas. More recently, BOF gas has also been utilized along with blast-furnace gas in gas turbine combined cycle units, which are much more efficient in producing power than a conventional boiler and steam turbine generator set.

6.4.4 Uses for Various Gaseous Fuels in the Steel Industry

Gaseous fuels are ideal for many steel plant applications. Below are the more important applications where gaseous fuels either must be used because of the nature of the work or facility, or where they are preferred over liquid or solid fuel:

- Coke-Oven Heating
- Blast-Furnace Stoves
- Gas Turbines for Power Generation
- Boilers
- Soaking Pits
- Reheating Furnaces
- Forge and Blacksmith Furnaces
- Normalizing and Annealing Furnaces
- Controlled-Cooling Pits
- Foundry Core Ovens
- Blast Furnace and Steel Ladle Drying
- Drying of Blast-Furnace Runners
- Hot-Top Drying
- Ladle Preheating
- Oxy-Fuel Burners

The choice of the most desirable fuel for each of the many facilities in a steel plant is not always possible, but by judicious planning the most efficient fuel or combination can be selected from those available. The general characteristics of each gas govern, wherever possible, its selection for a specific purpose in a steel plant. An outline of the important applications of the major gaseous fuels follows.

6.4.4.1 Use of Blast-Furnace Gas

For many years the use of blast-furnace gas for purposes other than for the firing of stoves and boilers was not economical. A number of factors have contributed, however, to the enlarged use of blast-furnace gas, the more important of which are: (1) rising cost of purchased fuel; (2) technical progress in gas cleaning, in the use of regeneration and recuperation, and in the mixing of gaseous fuels; (3) the economic advantage of using pulverized coal in boiler houses to substitute for blast-furnace gas, thereby permitting its substitution elsewhere for the more expensive liquid and gaseous fuels; and (4) seasonal shortages in the availability of purchased liquid and gaseous fuels.

In certain applications, in addition to preheating the air, the gas itself may be preheated to provide higher temperature potential. For the facilities listed, blast-furnace gas may be utilized successfully without preheat: blast furnace stoves, soaking pits, normalizing and annealing furnaces, foundry core ovens, gas engines for blowing or power generation, gas turbines for power generation, and boilers.

The thermal advantage of using blast-furnace gas in gas engines for blowing and for electric-power generation must overcome the heavy investment and maintenance expense of this equipment. The modern boiler house utilizing high steam pressure and temperature with efficient turbo-blowers and generators has sufficiently reduced the thermal advantage of gas engines, such that their use is difficult to justify. Some steel plants in Asia and Europe have been successful in the use of direct-connected gas turbines for driving generators.

Preheated blast-furnace gas burned with preheated air has been used successfully in coke-oven heating, soaking pits, and reheating furnaces.

When blast-furnace gas is preheated, it should have a minimum cleanliness of 0.023 grams per cubic metre (0.01 grains per cubic foot); and in all cases where this gas is used, extra precautions must be taken to prevent the escape of fuel or unburned gas into attendant surroundings because it contains a large percentage of toxic CO gas. Blast-furnace gas is used for many applications in the steel plant and, in addition, is used frequently for heating coke ovens and sometimes is mixed with other gases as a fuel. In blast furnace operations, where the blast-furnace gas has a heating value approaching a low value of 2946 kilojoules per cubic metre (75 Btu per cubic foot), it is necessary to switch the gas with other fuels to obtain very high hot-blast temperature from the stove.

6.4.4.2 Use of Coke-Oven Gas

Coke-oven gas has had a more extended use than blast-furnace gas because of: (1) relatively low distribution costs due to its low specific gravity and high calorific value; (2) its ability to develop extremely high temperatures by combustion; and (3) the high rate at which it can release heat, thereby eliminating excessively large combustion chambers. The low specific gravity of coke-oven gas is a disadvantage, and for this reason, it is supplemented wherever possible with a driven liquid fuel. In addition, the sulfur (in the form of H_2S) present in raw (not desulfurized) coke-oven gas is a distinct disadvantage, particularly in heating certain grades of alloy steel for rolling. Its presence also requires the use of materials resistant to sulfur attack in pipelines, valves, and burners.

There are a number of fuel applications in a steel plant where neither blast-furnace gas nor coke-oven gas, when burned alone, develop the desired flame characteristics or temperature level for optimum results. By mixing two fuels of such great variance in characteristics, a more ideal fuel can be obtained for specific applications.

The speed of combustion is very high for coke-oven gas and very low for blast-furnace gas. The desired speed can be attained through the proper proportioning of the two fuels. The speed also can be modified to a limited extent when necessary by suitable combustion technique. Mixed blast-furnace and coke-oven gas is particularly suitable for application to soaking pits and reheating furnaces.

6.4.4.3 Use of Natural Gas

Due to plant balances requiring the purchase of outside gaseous fuels, mixtures of coke-oven gas and natural gas are often utilized. While the temperature-developing characteristics of these two gases are nearly identical, they have differences in other characteristics, notably in the rate of flame propagation and in luminosity. By proper proportioning, the advantage of a short, intensive cutting flame or a long, luminous, soft flame may be had to suit the applications. Use of natural gas for flame cutting and scarfing has been increasing steadily.

6.4.4.4 Use of Producer Gas

Raw, hot, producer gas was used extensively in the past in steel plant operations for open-hearth furnaces, soaking pits, and reheating furnaces. It was customary to preheat this gas regeneratively when used in batch-type reheating furnaces. In continuous-type reheating furnaces, the fuel seldom was preheated. With good gas making, producer gas develops a soft, heavy, long, luminous flame desirable for reheating steel. The use of this gas has been superseded in all plants by natural gas and byproduct gaseous and liquid fuels.

6.4.5 Combustion of Various Gaseous Fuels

The major combustion reactions of the components of gaseous fuels with air and a table of essential gas combustion constants were given in Section 6.1.2.5. From chemical equations, the quantity of air required to provide perfect combustion and the resultant products may be calculated for any given gaseous fuel. Table 6.23 shows the air requirements, products of combustion, and pertinent characteristics of several gaseous fuels. The degree of mixing of air with a gaseous fuel, and the degree of excess or deficiency of air to the theoretical requirements are pertinent combustion problems. The degree of mixing is controlled by burner design. Burners have been developed to produce short, intense flames or long, slow-burning flames. The short, intense flame is usually nonluminous or semi-luminous, while the long flame is luminous. This relation is not always the case, however, because a gas must contain hydrocarbons to develop luminosity. Burners capable of producing short, intense flames will liberate a large amount of heat in a small space. Some gases, due primarily to the constituents of which they are composed, are capable of a high rate of heat release; others, of a very low rate of heat release. The two extremes are evident in two common steel-plant fuels, coke-oven gas and blast-furnace gas, which give high and low rates of heat release, respectively. There is also a limit to the length of flame which can be produced. It is determined by the ability of the flame to provide enough heat to propagate itself. If the short, intense-flame type burner is used with coke-oven or natural gas, combustion will be so intense that no flame will be visible, and heat can be liberated at rates over 40 million watts per cubic metre per hour (up to several million Btu per cubic foot per hour) of combustion space; while the long, slow-burning-flame burner firing the same gases is capable of developing a visible flame 6 to 9 metres (20 to 30 feet) long with a heat liberation of 155,000 to 210,000 watts per cubic metre (15,500 to 21,000 Btu per cubic foot per hour). Both types of flames are desirable for specific steel plant applications. It is obvious that burner selection based on degree of mixing is important. Carrying an excess or deficiency of air for combustion is practiced usually to control scale formation, but this is done sometimes to control flame characteristics. An excess of air tends to shorten, while a deficiency lengthens, a flame. An excess of air above theoretical requirements causes higher heat losses as any extra air absorbs its share of the heat of combustion. Fuels containing hydrogen must have the exit stack temperature high enough to avoid condensation of water within the furnace system and subsequent corrosion of furnace parts. In some cases, it is necessary to burn the fuel with

Table 6.23 Properties of Typical Gaseous Fuels

Fuel Gas	Constituents of Fuel Gas % by Volume (Dry Basis)							Illumi-nants		Specific Gravity	Unit Vols. of Air Required for Combustion of Unit Vol. of Gas (m^3 or ft^3)	Heating Value per Unit Volume of Gas [a]			
	CO_2	O_2	N_2	CO	H_2	CH_4	C_2H_6	C_2H_4	C_3H_6			kJ/m^3		Btu/ft^3	
												Gross	Net	Gross	Net
Natural Gas (Pittsburgh)	—	—	0.8	—	—	83.4	15.8	—	—	0.61	10.58	44,347	40,105	1129	1021
Reformed Natural Gas	1.4	0.2	2.9	9.7	46.6	37.1	—	1.3	0.8	0.41	5.22	23,529	21,054	599	536
Coke-Oven Gas	2.2	0.8	8.1	6.3	46.5	32.1	—	3.5	0.5	0.44	4.99	22,547	20,190	574	514
Water Gas (Coke)	5.4	0.7	8.3	37.0	47.3	1.3	—	—	—	0.57	2.10	11,273	10,291	287	262
Carburetted Water Gas	3.0	0.5	2.9	34.0	40.5	10.2	—	6.1	2.8	0.63	4.60	21,604	19,954	550	508
Oil Gas (Pacific Coast)	4.7	0.3	3.6	12.7	48.6	26.3	—	2.7	1.1	0.47	4.73	21,643	19,483	551	496
Producer Gas (Bituminous Coal)	4.5	0.6	50.9	27.0	14.0	3.0	—	—	—	0.86	1.23	6403	6010	163	153
Blast Furnace Gas	11.5	—	60.0	27.5	1.0	—	—	—	—	1.02	0.68	3614	3614	92	92
Butane (Commercial) 93% C_4H_{10}—7% C_3H_8	—	—	—	—	—	—	—	—	—	1.95	30.47	126,678	116,937	3225	2977
Propane (Commercial) 100% C_3H_8	—	—	—	—	—	—	—	—	—	1.52	23.82	101,028	93,133	2572	2371

Table 6.23 *(continued)*

Fuel Gas	Products of Combustion in Unit Vol. per Unit Vol. of Fuel (m³ or ft³)				Ultimate % CO_2	Net Heat Content per Unit Volume of Products of Combustion[b]		Theoretical Flame Temperature, No Excess Air	
	H_2O	CO_2	N_2	Total		kJ/m³	Btu/ft³	°C	°F
Natural Gas (Pittsburgh)	2.22	1.15	8.37	11.73	12.1	3417	87.0	1961	3562
Reformed Natural Gas	1.30	0.53	4.16	5.99	11.3	3519	89.6	1991	3615
Coke-Oven Gas	1.25	0.51	4.02	5.78	11.2	3417	87.0	1988	3610
Water Gas (Coke)	0.53	0.44	1.74	2.71	20.1	3794	96.6	2021	3670
Carburetted Water Gas	0.87	0.76	3.66	5.29	17.2	3779	96.2	2038	3700
Oil Gas (Pacific Coast)	1.15	0.56	3.77	5.48	12.9	3555	90.5	1999	3630
Producer Gas (Bituminous Coal)	0.23	0.35	1.48	2.06	18.9	2930	74.6	1746	3175
Blast Furnace Gas	0.02	0.39	1.14	1.54	25.5	2337	59.5	1454	2650
Butane (Commercial)	4.93	3.93	24.07	32.93	14.0	3555	90.5	2004	3640
Propane (Commercial)	4.0	3.0	18.82	25.82	13.75	3582	91.2	1967	3573

[a] From: "Combustion," American Gas Association (Third Edition); "Gaseous Fuels," American Gas Association (1948); and "Gas Engineers Handbook" (see bibliography at end of chapter).

[b] kJ/m³ at 0°C, 760 mm Hg (dry); Btu/ft³ at 60°F, 30 in. Hg (dry).

excess air to maintain the flue gases above their dewpoint. When there is a deficiency of air, potential heat is lost. In problems of design and fuel conservation, the air requirements and volume and constituents of the products of combustion must be known to effect a practical solution.

6.5 Fuel Economy

Because fuel represents the largest single item of raw material expense for the manufacture of iron and steel, the subject of fuel economy is of consequence to both the producer and consumer of steel products. The world steel industry accounts for nearly 20% of the worldwide total industrial energy consumption. The efficient utilization of this large quantity of fuel is also pertinent to the conservation of our fuel resources. The history of the steel industry shows great progress has been made in reducing the amount of fuel required to produce a ton of steel. During the Revolutionary War, ironmaking required large quantities of charcoal, as the source of carbon, to reduce the ore. If a substitute had not been found for charcoal, our forests would have disappeared many years ago and our industrial progress arrested. In the past one hundred years, which really represents the modern era of steelmaking, a number of important developments have taken place to reduce the fuel requirements in producing steel. Some of these developments could be listed by historical sequence, while others are of such a nature that they cannot be designated by any period of time.

The major contributions to fuel economy in ironmaking and steelmaking plants have been:

1. Development of the Bessemer converter.
2. Development of the Siemens-Martin regenerator.
3. Development of the hot blast.
4. Utilization of blast-furnace gas.
5. Installation of byproduct coke plants and utilization of byproduct fuels.
6. Integration of steel plants.
7. Electric drives for rolling mills.
8. Improved efficiency of steam-generating equipment and steam prime movers.
9. Large producing units.
10. Balancing of producing units.
11. Use of raw materials with improved chemical and physical quality.
12. Recovery of waste heat by recuperators, boilers and other forms of heat exchangers.
13. Development and utilization of instruments and control equipment.
14. Insulation of high-temperature facilities.
15. Utilization of the optimum fuel for specific facilities.
16. Improvements in manufacturing technique and production control.
17. More highly skilled operators.
18. Development of oxygen-blown steelmaking processes.
19. Development of continuous casting of steel and, more recently, thin slab casting.
20. Recovery of sensible heat by hot charging and direct rolling.
21. Gas turbine combined-cycle facilities.

The results of the above contributions now have made it possible to produce a ton of raw steel utilizing far less energy than was ever thought possible. The consumption of primary fuels in the iron and steel industry for 1995 is shown in Table 6.24.

Table 6.24 Primary Fuels Consumed by the Steel Industry in 1995 [a]

Fuel	Gigajoules[b]	Million BTUs[b]
Coal and Coke	688,302,130	652,510,419
Natural Gas	294,056,779	278,765,826
Electricity[c]	91,068,079	86,332,539
Liquid Fuels	25,496,395	24,170,582
Oxygen[d]	77,337,694	73,316,134
Steam	3,088,522	2,927,919
Net Energy Consumed	**1,179,349,599**	**1,118,023,419**
Gross Steel Shipments	48,248,612 (metric tons)	53,194,095 (short tons)
Fuel Consumption/Ton	24.44	21.02

[a] From: "Annual Statistical Reports" (1995), American Iron and Steel Institute
[b] Higher Heating Valve
[c] 3600 Kilojoules/kW (3413 Btu/kW)
[d] 37.2 Kilojoules/m^3 (175 Btu/ft^3)

In addition to these outstanding contributions to fuel economy in steel mills, the importance of the effect that the rate of operations has on fuel economy should be stressed. Historically, the iron and steel industry follows the general business level maintained in the country, but its rate of operations often fluctuates more than that of many other industries. During peak production, optimum fuel economy is the natural result of operating the facilities which require fuel under the conditions for which they were designed to operate most economically. During periods of low production, fuel consumption undergoes a severe increase per unit of output; careful scheduling of production and facilities are required during this period to maintain minimum fuel losses.

The effectiveness with which byproduct fuels are used in steel plants is of major significance in reducing the quantity of primary or purchased fuel required to produce a ton of steel. The efficiency of heat utilization by steelmaking furnaces is discussed in the chapters dealing with the design and operation of these units in Chapters 8 and 10.

The heat lost from the combustion of fuel in steel plant metallurgical and service facilities represents an appreciable part of the total supply. The amount lost differs among the various processes. In general, those processes having the higher temperature levels have the greatest thermal losses and, therefore, offer the best opportunity for heat recovery. For a specific facility, the amount and causes for these losses can be determined quantitatively by conducting a heat balance, and the results of this heat balance can then be used for planning a program aimed at heat conservation. Usually, the largest losses are contained in the waste flue gases and in radiation from the furnace walls. Additional losses are associated with combustion control (providing insufficient air for combustion at the burners and/or inadequate mixing of fuel and air), heating practice and air infiltration. Most important common denominators underlying all successful programs of heat conservation are proper maintenance of the facility and its instrumentation and proper scheduling of operations so that the facility is, as closely as practical, fully utilized for its intended purpose.

6.5.1 Recovery of Waste Heat

The recovery of heat from waste flue gases of high-temperature processes has been practiced for nearly 100 years. These high-temperature flue gases contain both sensible heat and the latent heat of vaporization of water and sometimes potential heat (unburned flue gases). The recovery of the heat of vaporization of water is not practical; however, the recovery of the sensible heat is accomplished

by one or a combination of several methods, including the use of regenerators, recuperators, waste-heat boilers, or utilization of a furnace design in which the waste heat is used to preheat the product.

Regenerators are used alternately to absorb heat from one fluid and then transfer it to another fluid; recuperators are used to transfer heat continuously from one fluid to another. The fluids referred to in these two definitions are: (1) hot gaseous products of combustion which give up heat during passage through the regenerator or recuperator and (2) fuel gases or air for combustion which undergo heating while passing through the regenerator or recuperator. The importance of recuperators or regenerators for preheating the air to be used for combustion is shown in Fig. 6.4. In this illustration, the amount of fuel saving (in percent) is plotted vertically, and the temperature of the flue gas at exit is plotted horizontally. The temperature of the preheated air is shown on the curves, and from these an estimate can be obtained of the amount of fuel saving to be gained from using preheated air.

Regenerators are applied usually to furnaces which can be fired alternately from the ends, the flow of gases through the furnace and regenerators being reversed according to predetermined time and/or temperature cycles. Coke ovens, and many batch-type reheating furnaces and soaking pits, are equipped with regenerators. Blast-furnace stoves also use the regenerative principle but operate over a much longer cycle and in a somewhat different manner than that practiced in other installations. In a blast-furnace stove, checker brick of the regenerator are heated by burning of fuel exclusively for the purpose of heating the regenerator brick, while in other furnace installations the checker brick are heated by waste gases. In both cases, the heat stored in the regenerators is used to preheat air for the combustion of fuel in the furnace they serve.

Recuperators have been applied to many modern batch and continuous-type reheating furnaces, and to steam boilers. When applied to steam boilers, they commonly are called air preheaters.
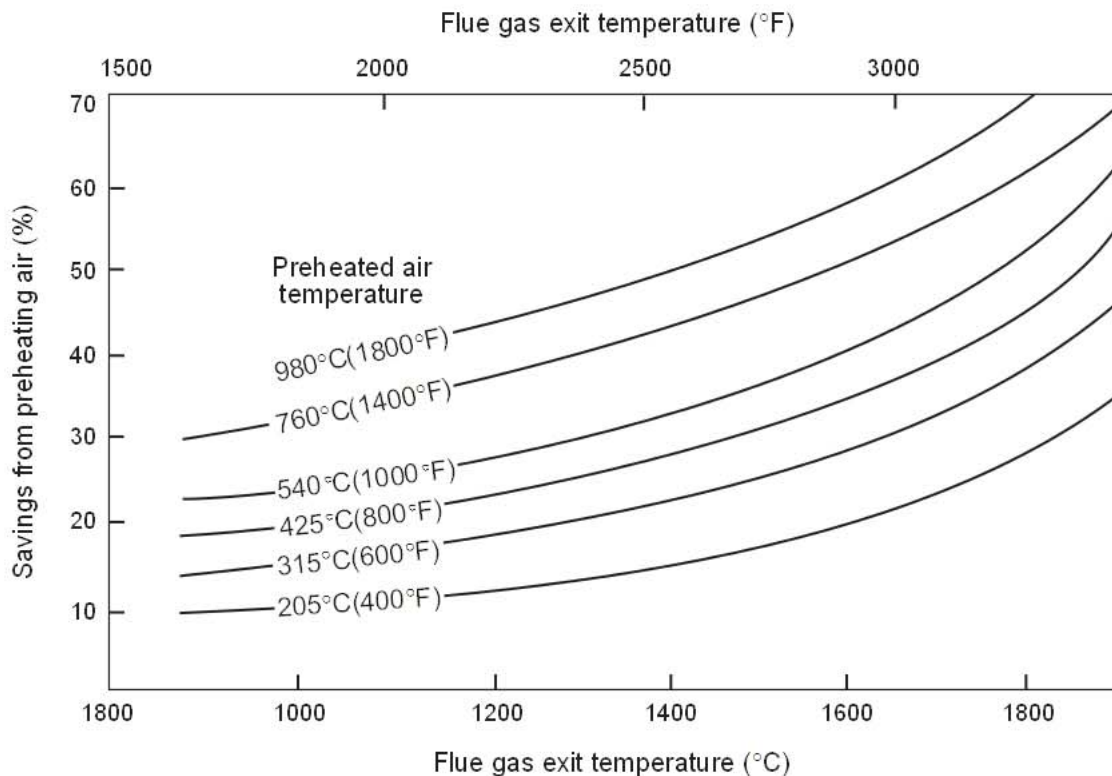

Fig. 6.4 Fuel savings resulting from use of preheated air.

Recuperators are of three general types, classified according to the direction of flow of the waste gases and air, as follows: counter-flow, parallel or co-current flow, and cross-flow.

Counter-flow is used to attain maximum air-preheat temperatures, and cross-current flow is used to secure optimum heat-transfer rates (kilojoules per square metre of recuperator surface per degree Celsius temperature difference per hour, or Btu per square foot of recuperator surface per degree Fahrenheit temperature difference per hour). Parallel flow is used where it is necessary, such as in metallic recuperators, to maintain the temperature difference of the division wall between the two fluids as uniform as possible throughout its length and to keep the temperature of the hot end below a maximum so that the metallic elements will not be overheated. Generally, a combination of counter-flow and cross-flow is applied to many steel-mill furnace applications where a refractory material is used to divide the two fluids. A combination of the two types is accomplished by baffling the flow of one of the fluids. In such designs, the general direction of flow of fluids exchanging heat is counter-current and the flow in each baffle is cross-current. When the temperature of waste gas from which heat is to be extracted is relatively low, under 980°C (approximately 1800°F), metallic tubes (e.g., stainless steel) are generally used because they possess an advantage against leakage. Higher-temperature recuperators are generally constructed of clay or silicon-carbide materials; often, however, these recuperators suffer the disadvantage of air leakage.

Waste-heat boilers are used to obtain heat recovery when a practical limit of recovery has been obtained by regenerators or recuperators and there is still sufficient heat left in the waste gases to justify expenditures for the waste-heat boilers. Boilers sometimes are used in place of regenerators or recuperators, depending upon conditions such as where preheated air is undesirable or where the generation of steam solves the problem of fuel conservation more satisfactorily. Waste-heat boilers are most applicable to high-temperature, continuous processes and have been used principally in the steel plant in conjunction with basic oxygen vessels, gas turbines and, to a lesser degree, with reheating furnaces and soaking pits. Fire-tube and water-tube boiler types have been installed, the former being the preferred type and generally of horizontal single-pass design. Waste-heat boilers usually are provided with superheaters and sometimes with economizers.

6.5.2 Minimizing Radiation Losses

Radiation losses from the walls and roofs of the furnaces can be minimized by the selection and use of an insulating system. Thermal insulating materials have been used in steel plants for a great many years. There are many different kinds of insulating materials, each being most suitable for a specific temperature level and for the degree of insulation desired and improvements in insulating materials are continuing. A detailed discussion of insulating systems for steel-mill furnaces is given in Section 3.6.3.

6.5.3 Combustion Control

As mentioned previously, one of the large losses in a heating process is the heat contained in the waste flue gases. The amount of sensible heat in the waste flue gases is the product of the heat content per unit volume (m^3 or ft^3) or unit weight (kg or lbm) of gas multiplied by the total volume or total weight of the gas respectively, in the appropriate units. The total loss of heat in waste flue gases can be minimized by providing the proper amount of air for combustion. If too much air is provided, the volume of the waste gases is increased. In addition, an excess of air over that required for combustion lowers the flame temperature and increases the time necessary to heat the product. In a similar manner, an excess of fuel (or a deficiency of air) also decreases the flame temperature and prolongs the heating time and, in addition, results in unburned fuel being carried into the waste flue gases. This results in unnecessary usage of fuel and can be dangerous because this unburned fuel can burn in the flue and cause damage to the stack and/or waste heat recovery systems. In other words, fuel economy is optimized by the use of proper combustion conditions.

In modern steel plant furnaces, and in boilers, the amount of air supplied for combustion is maintained only a little above theoretical requirements by special pressure regulators and valves which

accurately proportion the amounts of fuel and air fed to the burners. For most burners, an amount of air approximately 10% above theoretical is considered to be optimum. The use of instruments to continuously monitor the products of combustion and automatically control the air-fuel ratio to achieve this desired level of excess air has led to improved fuel economy and heating efficiency.

The amount of waste flue gases can be minimized, and the heating rate of the unit can be increased, by the oxygen enrichment of combustion air. Air is composed of only approximately 20.9% oxygen (by volume), with the remainder consisting of inert nitrogen plus a small amount of several other inert gases. When combustion takes place, the oxygen combines with the carbon and hydrogen of the fuel and liberates heat. The inert gases of the air absorb heat from the combustion and carry it out of the furnace, and it is lost so far as the furnace process is concerned. These gases reduce flame temperature by absorbing heat, thus reducing the rate of transfer of heat to the work.

Obviously, if the inert content of the air could be diminished, more efficient combustion could be obtained. Recent technical developments that have lowered the cost for producing oxygen of commercial purity have made large-scale use of this gas economical for some industrial processes. Consequently, many plants have experimented with the addition of oxygen to ordinary air used for combustion, with generally good results. In effect, increasing the oxygen content lowers the inert content of the air; consequently, when a given amount of fuel is burned with oxygen-enriched air, the volume of the waste gas is less than if ordinary air were used. If the temperature of the waste gas is not increased, the sensible-heat loss in the flue gas will be decreased, due to the smaller heat capacity of the smaller volume. In furnaces operated at high thermal head, a decrease in the amount of the inert gases usually results in a decrease in the waste-gas temperature. With the same fuel input, enriched air for combustion raises the flame temperature of a given fuel, thereby improving heat-transfer rate and increasing production; alternatively, the fuel input may be decreased when enriched air is used to maintain the same production rate as obtained with fuel using ordinary air. Increased production rates almost always reduce the heat losses per ton of product in any furnace employing a high thermal head.

6.5.4 Air Infiltration

If the pressure of the gases in the heating chamber of the furnace is below atmospheric, cold outside air will be drawn into the furnace through any openings that exist. If the interior pressure is above that of the outside air, the hot gases will be forced out of the furnace through these same openings, and if too much higher will, in addition, tend to penetrate the refractories and overheat the furnace bindings with, in some cases, damaging effect. Generally, it is desirable to operate a furnace with a slight positive pressure in the heating chamber (i.e., furnace pressure slightly higher than atmospheric). It should be noted that the pressure from top to bottom of the heating chamber is not uniform, due to the stack effect of the hot gases. Control, therefore, is aimed at maintaining the desired pressure at the hearth level. Air drawn into a furnace operating under negative pressure upsets the fuel-air ratio which is controlled automatically or by valve settings. In some units such as reheating or heat-treating furnaces, this air aggravates the problem of oxidation (or scaling) of the work because of the ingressed oxygen.

If the pressure in the furnace at the hearth level is equal to atmospheric or slightly positive, better heating conditions are obtained. This is especially so in furnaces where most of the heating of the work takes place through heat transfer by radiation from the flame to the bath or work. The positive pressure must be controlled to prevent excessive sting-out of flame from furnace openings (a small pressure imparts a high velocity to hot gases), as well as to avoid the buildup of excessive back pressure that would interfere with proper flow of fuel (if gaseous) and combustion air. Positive pressures maintained at hearth level in practical work are quite low, ranging only up to approximately one millimetre (a few hundredths of an inch) of water. Furnace pressure is controlled by adjusting the opening in the stack damper.

Positioning of the damper can be done manually, using the flame sting-out as an indication of the existence of positive pressure, but it is difficult to adjust the opening for the frequent changes in

furnace conditions. The development, about the year 1928, of industrial-type instruments with sufficient sensitivity to measure differential gas pressures with an accuracy of ± 0.06 mm (0.0025 inch) of water made possible the use of automatic control of furnace pressure.

Automatic furnace-pressure control has been provided for a majority of steel plant furnaces and has been a principal factor in the improvements in fuel economy and efficiency of melting and reheating furnaces during the years following its adoption.

6.5.5 Heating Practice

The primary objective of any furnace operation is to heat the product (steel, as in the case of most furnaces, or air as in the case of blast-furnace stoves) to the desired temperature at the desired heating rate. The actual practice used to achieve the desired temperature and the desired rate will vary with each specific installation, and in each installation will vary with the level of operation. Consequently, it is beyond the scope of this discussion to provide such specific details. However, several general principles apply to all facilities.

The use of excessive amounts of fuel (high heating rate) is wasteful of the fuel itself and results in high furnace exit-gas temperatures and damage to refractories. In some processes, high fuel rates not only do not hasten transfer of heat to the material being processed, but also may cause it actual damage. On the other hand, the use of insufficient fuel reduces the rate of heat transfer and prolongs process time, thereby increasing thermal losses. The optimum rate for protection either of the material being heated or the furnace refractories, and often for control of heating or production rate, is maintained in most furnaces by automatic temperature-measuring instruments which control the fuel rate through a system of electrical relays or other units which control the operation of motors, hydraulic systems or other means for regulating fuel valves. Many heating installations have adopted computerized control for the heating operations.

A basic requirement for all heating operations is good temperature measurement. One problem involved in temperature measurement is the difficulty and almost impossibility of measuring the temperature inside a solid piece of steel, and in most cases the difficulty is encountered in measuring the surface temperature in one spot. Because of this inability to measure the temperature of solid steel directly, measurement is made of some other temperature that is closely related to the steel temperature. Depending upon the specific furnace installation, this involves measuring the temperature of the roof or wall of the furnace or a measurement of the temperature of the gases in the furnace. These measurements are achieved in the steel industry by instruments operating on four main principles: (1) by measuring the intensity of radiation emitted by the hot furnace or object being heated, (2) by measuring the minute electrical current generated in a circuit composed of two wires of dissimilar metals, joined end to end, when one of the joints is heated (this is the principle of the thermocouple), (3) by measuring the change in the electrical resistance of conductors when heated to the temperature in question, and (4) by measuring the change in the ratio of two separate wavelengths of radiation emitted from the hot object or furnace.

6.6 Water Requirements for Steelmaking

6.6.1 General Uses of Water in Steelmaking

Water is such a common substance and generally has been so abundant that its importance to the iron and steelmaking processes is seldom emphasized in the discussion of operations and metallurgical problems. Without water, steel could not be made. Because early steel mills were built adjacent to ample sources of fresh water, the availability and quality of water was taken for granted. Today, greater attention is given to the management of available water resources in the steel mill environment, particularly in terms of water quality, quantity, and how it is used.

Water is used for direct contact cooling and cleaning of the steel in process, for cooling the process offgases, for product rinsing, and for process solution makeup; however, the vast majority of the

water used in steel making is for non-contact cooling of associated processing equipment. Water is also used for steam and power generation, potable uses, and dust and moisture control.

Several factors make water a versatile material. It is normally plentiful, readily available, and inexpensive. It is easily handled. It can carry large amounts of heat per unit volume (high specific heat). It neither expands nor compresses significantly within ambient temperature ranges. It does not decompose. It can dissolve, entrain, suspend, and subsequently transport other material.

The overall use of water in the steel industry has been reduced since the 1970s as a result of modernization, more continuous processes, and greater reuse (recycle) of the available water supplies. This reduction has been the result of the more efficient use of existing water supplies and compliance with environmental regulations governing the quantity and quality of water discharged from the plants.

6.6.1.1 Raw Water Sources

Water can be generally classified as: seawater, with a total dissolved solids (TDS) or salt content of more than 3.5% (35,000 ppm); brackish water, with dissolved solids between 1500 and 35,000 ppm; and fresh water, with a dissolved solids content less than 1500 ppm. While some facilities are located adjacent to oceans, bays or other sources of high salinity waters, fresh water is the overwhelming preference and source of water consumed and utilized in steel mills.

Fresh water can be further classified into surface water and ground water. All fresh water originates as rainfall in the continuous cycle of atmospheric evaporation and condensation. Once fallen, the water either collects on the surface in streams, lakes, and rivers, or seeps into the earth's crust. Ground water is 'old' water originated from wells and springs. Depending on the size of the aquifer being used, ground water will most likely be the most consistent in terms of temperature and chemical content. Water chemistry can also vary relative to the depth and extraction point of the well. As compared to surface waters, good clarity, higher TDS, and low total suspended solids (TSS) levels would be characteristics of ground water because it has flowed through miles of porous rock strata prior to extraction.

Ground water quality is a function of the geological characteristics of the area. The chemical content will vary, depending on the rock strata through which the water has percolated. Water flow through the strata is usually slow, measured in feet per year. Seasonal changes will typically be minimal. Over time, the chemical content may change, particularly if large quantities are extracted, reflecting ground water migration in the aquifer.

Surface water is typically obtained from shallow wells, rivers, and large lakes or reservoirs. Compared to ground water, surface water in general will have higher suspended solids and lower dissolved solids, depending on rainfall in the area being drained. Quality may vary seasonally, depending on local rainfall patterns, as dilution affects constituent concentrations. In addition, water quality can be affected by upstream use and sources, including farm runoff, mine drainage, treatment plants, and practices such as road salt application. In larger water bodies, such as the Great Lakes, observable change may be minimal because of the volume of water contained and its turnover rate. Table 6.25 lists typical makeup water chemistries from various sources, by geography.

6.6.1.2 Cooling Water and Other Applications

Water usage in the steelmaking process can be generally classified as either non-contact or contact water. Non-contact application is the use of water for general cooling purposes where only equipment is being cooled and the water does not contact the steel in process, offgases or fluids. Contact water includes all applications of water directly on the steel in process, process gas cleaning applications, process fluid applications (oils, cleaners, etc.) and rinse applications. Contact waters are subject to treatment, as discussed in Section 6.6.4.

Other applications include steam generation, process solutions makeup, dust control, and potable systems. Each of these uses is discussed below.

Table 6.25 Typical Water Chemistry

Constituent	Units	Lake Michigan	Well South East	Well Mid-West	Ohio River
Calcium	ppm as $CaCO_3$	80	17	282	70
Magnesium	ppm as $CaCO_3$	41	6	86	30
Sodium	ppm as Na	9	5	39	9
Alkalinity – Bicarb	ppm as $CaCO_3$	113	20	352	30
– Carb	ppm as $CaCO_3$	0	0	0	0
Sulfate	ppm as SO_4	17	2	52	76
Chloride	ppm as Cl	7	6	18	13
Nitrate	ppm as NO_3	not detected	1	1	1
Fluoride	ppm as F	trace	not detected	1	trace
pH	S.U.	8.2	6.4	7.6	7.3
Silica	ppm as SiO_2	2.3	5	31	5.6
Iron	ppm as Fe	0.1	.2	6.5	.3
Turbidity	NTU	12	<5	<5	88
TDS	ppm	171	46	488	143

6.6.1.2.1 Steam Generation   Prior to steam generation in a boiler, most raw waters must be pretreated to meet the water quality requirements set by the boiler manufacturer. Such treatment typically involves filtration, hardness removal (softening) and/or silica reduction, deaeration, and pH/alkalinity adjustment. If improperly conditioned, water-related problems, including mineral precipitation and corrosion, can result in permanent damage to the steam generating unit along with energy inefficient operation.

Higher-pressure power boilers are used in most integrated mills and coke plants to provide the energy source for blowers to the ironmaking facilities, and to generate electrical power. Waste heat recovery boilers (steaming BOF hoods, slab reheat furnaces, etc.) are sometimes utilized to provide additional steam to plant systems, while doubling as the heat removal equipment for the specific process. Smaller capacity and lower pressure satellite or package boilers will typically generate steam for specific user requirements (vacuum degassing, acid heating, etc.). In all cases, recovery of uncontaminated condensed steam can improve operational economics and reduce makeup water requirements.

6.6.1.2.2 Process Solutions   Pickling, cleaning, and coating operations typically performed in the finishing mills utilize water as the diluent for inhibitors, lubricants or plating solutions prior to their application to the steel in-process. Once applied, excess material is recaptured, or transferred to a suitable waste treatment facility prior to discharge, or sent offsite (spent acids) for disposal or reuse. Water that meets the necessary quality requirements for rinse applications is used to remove the residue of process chemicals from the surface of the steel. These rinse waters are normally treated in a wastewater treatment facility.

6.6.1.2.3 Raw Materials Preparation   The principal raw materials are coal (most of which is converted to coke), iron-bearing materials (natural lump ore, iron pellets, recycled agglomerates, and more recently iron carbide and DRI), and fluxes (lime, limestone, and dolomite). In coal preparation, considerable quantities of water are used for dust control in the mines and in coal preparation (washing) facilities for foreign matter removal. Similarly, large amounts of water are used in the beneficiation of iron ores to remove foreign matter and concentrate the iron content. Water may also be added in the forming operation (balling mill) to facilitate agglomeration.

In primary facilities, water may be used for dust suppression to meet plant air emissions requirements with or without the use of dust suppressants for roads, conveyor transfer points, and storage

piles. In pulverized coal injection (PCI) for blast furnaces, moisture content is monitored and additions may be made.

6.6.1.2.4 Potable Systems These systems provide the drinking and convenience water for human consumption. Primary concerns are for heavy metal content, water clarity, selected organic compounds, and the absence of biological activity. Except in remote plant sites, both potable supplies and sanitary wastewater treatment are normally provided by municipal systems.

6.6.2 Water-Related Problems

Some of the properties of water that make it useful for so many purposes can also contribute to the creation of problems in its use. Water's ability to dissolve, entrain, and suspend solids, liquids, or gases can affect the purity of the water being used and can subsequently affect piping, equipment, and the process. Contamination of the water can subsequently limit its use in many instances until suitable treatment can remove or modify the concentration of offending constituents.

Water-related problems can be generally classified in four different categories: corrosion, scaling, fouling, or biological activity.

6.6.2.1 Corrosion

Corrosion is an electrochemical process by which a base metal reverts to its oxide form. Corrosion can be of a general nature, localized (pitting), or galvanic. For corrosion to occur, a corrosion cell, consisting of an anode, a cathode, and an electrolyte, must be present. Water is an excellent electrolyte. The most common evidence of corrosion is the visible loss of base metal in piping and wetted equipment, and the presence of the resultant oxide (rust). Impurities in the water can affect the rate of metal loss.

Specific mechanisms can be responsible for the metal loss or failure. Galvanic corrosion occurs when two dissimilar metals are in contact in an aqueous environment, resulting in loss of the anodic metal; this can occur on a macro or micro level. Beneath deposition, concentration cell corrosion can be established via various mechanisms, resulting in potentially aggressive localized attack (pitting). Stress corrosion cracking can occur when metal is subjected to tensile stress in a corrosive environment. Fatigue corrosion occurs in an acidic environment when the metal is subjected to cyclic application of stress. Impingement or erosion/corrosion attack occurs when entrained solids or gases repeatedly wear the affected metal due to physical/chemical mechanisms.

6.6.2.2 Scaling

Scaling is a chemical process by which certain minerals become insoluble, precipitate from the solution, and deposit onto equipment surfaces. Scaling is most commonly associated with salts of calcium and magnesium. Common to both of these elements is their inverse solubility in water relative to temperature; as the localized water temperature rises, the solubility of these species drops. The solubility of these minerals is greatly dependent on their relative concentrations, water temperature, pH, alkalinity, types of anions present, and other water parameters. Should localized boiling to dryness occur, elements including normally soluble ions such as sodium may also precipitate out. The most common evidence of scale formation is the growth of mineral deposition in piping and heat transfer surfaces.

6.6.2.3 Fouling

Fouling is the deposition of suspended material in the water, originating from internal or external sources. The most common evidence of fouling is the accumulation of foulants in low-flow areas and in flow channel restrictions. Foulants can include items such as insects, mollusks, silt, rust, oils and greases, scale formed in other areas, and other miscellaneous debris. The presence of soft films (i.e., oils/greases/biological masses) can facilitate the growth of deposition by capturing normally suspended material and forming a fouling matrix of material.

6.6.2.4 Biological Activity

The aqueous nature of a cooling water system can provide an extremely favorable environment for microorganisms to grow and rapidly reproduce. These organisms include algae, fungi, and different classifications of bacteria: aerobic, anaerobic, and iron depositing. The most common evidence is the accumulation of slimy, possibly odorous, biomass in or on wetted equipment. Specific anaerobic bacteria found beneath deposits can accelerate localized corrosion via the metabolic acids generated by these species. Other species, namely fungi, can deteriorate wooden structures (cooling towers).
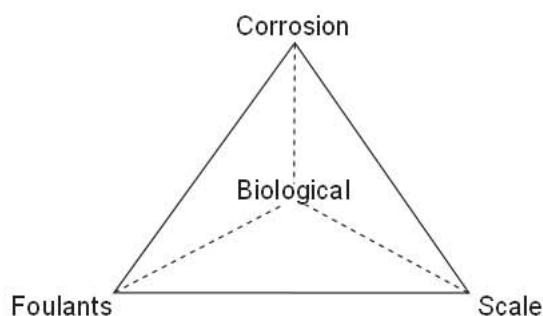

Fig. 6.5 Interrelationship of water-related problems.

Fig. 6.5 illustrates the interrelationship of the water-related problems. For example, when a mild steel pipe corrodes, a significant amount of soluble and insoluble iron is released, which can lead to fouling. Should the pipe or water passage be sufficiently restricted, the lower flow may result in localized overheating, resulting in scale formation. The presence of biological mass would only compound the problem because it has high volume but relatively light mass. Anaerobic bacteria beneath the deposition could result in a localized pitting attack.

The various undesirable properties of water can be combatted by the consideration of the following: materials of construction; steelmaking equipment design with sufficient water flows and velocities; water treatment equipment designed to meet the intended use; operating modes; maintenance procedures; control of additives to the water, both intentional and incidental; and proper chemical treatment.

Because there are usually several possible alternatives or combinations of measures which can be applied, and because two or more problems can co-exist, selection of the proper methods for water use and treatment is a highly specialized activity.

Table 6.26 briefly summarizes the most common water treatment techniques for various constituents.

6.6.3 Water Use by Steelmaking Processes

Because of the great variety of steelmaking facilities, their layout, discharge limitations, and available water supplies, water usage varies widely in both integrated and mini-mill facilities. In the following paragraphs, some specific water uses are discussed.

6.6.3.1 Cooling Water

By far, the largest application and usage of water in iron and steelmaking is for cooling purposes. In addition to categorization by contact and non-contact criteria, cooling water systems use can be generalized in the following categories.

6.6.3.1.1 Once-through Systems   Water is used once prior to discharge, as in the cooling of condensers, furnace components, and other miscellaneous applications. This mode of cooling is typically in non-contact cooling applications where the water is intentionally restricted from coming into contact with the steel in process or resultant process streams originating from the facility, such as exhaust gas, steelmaking fluids, etc. This approach is more prevalent in mills located adjacent to large water bodies, rivers, lakes, and at times, oceans.

6.6.3.1.2 Evaporative Recirculating Systems   Both contact and non-contact applications utilize evaporative systems. When water absorbs heat from a process, this heat can be easily transferred to the environment (air) by exposing the water to the atmosphere. This evaporation reduces the bulk water

Table 6.26 Common Water Treatment Methods

Substance in Water	Removal Process	Chemicals Used
Hardness	Precipitation	Lime, soda ash, caustic, phosphate
	Ion exchange	Salt, acid
Alkalinity	Precipitation	Lime, gypsum
	Ion exchange	Acid, salt
	Neutralization	Acid
CO_2	Precipitation	Lime, gypsum
	Ion exchange	Acid, salt
	Neutralization	Lime
	Degasification	None
Dissolved Solids	Reverse osmosis	Anti-scalants, biocides
	Demineralization	Acid, caustic, salt
	Specific ion removal	Ion specific resin
Particulate	Screening, Straining	None
	Settling basins	None
Suspended Solids	Coagulation	Alum, aluminate, ferric chloride
	Flocculation	Coagulant, flocculants
	Sedimentation	None
	Filtration	None
Fe/Mn	Oxidation	Chlorine, air
	Precipitation	Lime, caustic
	Filtration	None
	Ion exchange	Salt, acid
SiO_2	Precipitation	Iron salts, magnesium oxide
	Ion exchange	Caustic
Organic Matter	Clarification	Alum, aluminate
	Bio-oxidation	None
	Oxidation	Chlorine, chlorine dioxide, ozone
	Adsorption	Activated carbon
O_2	Degasification	None
	Reduction	Sulfite, O_2 scavengers
Macro Aquatic Organisms (Zebra Mussels, Asiatic Clams, Fish)	Heating	None
	Straining	None
	Sterilization	Chlorine, bromine
	Organism specific toxin	Proprietary biocides/ biocide neutralization
Micro-organisms	Clarification	Coagulants, flocculants
	Filtration	None
	Heating	None
	Sterilization	Chlorine, ozone, sterilants, ethylene oxide

temperature, enabling the water to be reused. This cooling method is commonly used in evaporative cooling towers, and to a lesser extent, in lagoons and spray ponds.

In non-contact systems, the limit to which water can be recycled in this manner is dependent on the water quality requirements of the process being cooled, the raw water quality, and ambient air temperature. As the water is evaporated, the minerals and other constituents for the most part remain in the water and become concentrated. This concentration mechanism increases the TDS in

the system and, if not compensated, may lead to water-related problems, as discussed in Section 6.6.2. Normally, the TDS concentration in the system is controlled by bleeding off some of the water from the system (blowdown).

The same is true for contact cooling water systems, and consideration must be given to the constituents originating from the process. These systems often require some treatment for the removal of solids, oil, etc., prior to cooling and recycle.

In both contact and non-contact cooling systems, the amount of recycle that is obtainable is highly dependent on the water quality requirements and constraints of the systems being cooled. Because of this, some discharge blowdown is required from these systems to maintain the desired water quality. The balance for an evaporative water system is dictated by the following interrelationship between makeup, evaporation, and blowdown. (Note that blowdown in this equation includes uncontrolled losses such as tower drift, windage losses, exhaust entrainment, spillage, and leakage.)

$$\text{Makeup (MU)} = \text{Evaporation (EV)} + \text{Blowdown (BD)} \tag{6.6.1}$$

Cycles of concentration and concentration ratio are terms used to indicate the degree of concentration of the recirculating water as compared to that of the makeup water. The degree of concentration is dictated by the relationship of makeup to blowdown, given that evaporation (heat load) is constant over time. The evaporating water is pure water vapor, leaving behind soluble water impurities that can be measured. Analytically, measurement of these dissolved minerals in the makeup and blowdown can also indicate this concentration phenomenon as shown below:

$$\text{Concentration Ratio (CR)} = \frac{\text{MU (gpm)}}{\text{BD (gpm)}} = \frac{\text{Concentration (BD)}}{\text{Concentration (MU)}} \tag{6.6.2}$$

An accepted rule of thumb to estimate evaporation in a recirculating system is for every 6°C (10°F) temperature drop across the evaporative process, 1% of the recirculating water is lost to evaporation. This 1% rule of thumb may vary. In areas of high humidity (Gulf Coast), evaporative loss may be as low as 0.75%, while in arid areas, as high as 1.2%. A second method to determine makeup (MU) is as follows:

$$MU = EV\left(\frac{CR}{CR-1}\right) \tag{6.6.3}$$

In direct contact systems, when water is applied to hot steel in process, analytical measurement of dissolved salts may be skewed. Some of the mineral content may precipitate out on the hot surface of steel in process as the water evaporates. Conversely, soluble elements from the process may also dissolve in the water, increasing their level, as in the gas cleaning applications of water.

6.6.3.1.3 Non-evaporative (Closed) Recirculation Systems   Incorporating the use of a heat exchanger mechanism, the recirculated water system heat is transferred to a second water system or to the air through conductive cooling. This transfer is accomplished through water/water heat exchangers of plate and frame or shell and tube design, or through air coolers of wet surface or dry design. The same cooling water is used in a continuous cycle with little or no water loss. Usually associated with higher water quality applications, these systems are typically not exposed directly to the environment and do not have a concentration mechanism. In everyday life, the automobile radiator cooling system is a common example of a closed loop cooling system.

6.6.3.1.4 Application of Cooling Water Systems   Most once-through systems are limited to non-contact or indirect cooling applications. Previously, contact or direct cooling applications were of the once-through design, but these generally have been converted to recirculating systems, incorporating primarily evaporative cooling towers to meet discharge requirements. Most closed non-evaporative systems are used to cool process equipment requiring higher quality water in terms of hardness, suspended solids, and dissolved solids. Often these requirements necessitate pretreatment of the water to meet the desired characteristics.

In terms of water resource management, many mills utilize cascading water systems, whereby water is intentionally transferred from one system to another. A common example would be to use the blowdown from a non-contact system as makeup to a contact system. Rarely is the reverse employed without additional treatment because the contact waters may contain potentially troublesome constituents originated from the steelmaking process. Because of constituent levels in contact water, the use of non-contact water is preferred in indirect heat exchange equipment, where practical and feasible. In some applications, boiler feed water is required.

6.6.3.2 Water Use and Wastewater Generation by Ironmaking and Steelmaking Operation

The following is a brief outline of water use and wastewater generation for each major operation in steel making. Table 6.27, summarizes the water use and wastewater generation of these operations.

Table 6.27 Water Usage and Wastewater Generation at Steel Making Operations

Operations	Water Use	Wastewater Generation
Coke plant	Gas and product cooling Process water Steam heating Coke quenching	Excess ammonia liquor Final coolers Light oil recovery Desulfurization processes Condensates
Sinter plant	Process water Dust control Sinter cooling Flue gas cooling/cleaning	Flue gas cleaning blowdown
Blast furnace	Process cooling Flue gas cooling/cleaning Slag granulation	Flue gas cleaning blowdown
Steelmaking (EAF, BOF and open hearth furnaces)	Process cooling Flue gas cooling/cleaning Cooling system blowdown	Flue gas cleaning blowdown
Vacuum degassing	Gas cleaning system Process cooling	Gas cleaning blowdown
Continuous casting	Mold cooling Machine cooling Product/Process cooling Scale removal	Cooling system blowdown Contact cooling waters
Rolling mills (hot and cold rolling)	Reheat furnace cooling Product/process cooling Scale removal Equipment lubrication Flume finishing	Contact cooling waters Run out table Scale pit
Finishing mills	Pickling Cleaning Process solutions Process water Rinse water	Spent cleaning solutions Spent pickle acids Spent rinse water Spent process solutions

6.6.3.2.1 Coke and Coal Chemical Plants   The largest volume of water used in these plants is for non-contact cooling in a variety of cooling and condensing operations. Moisture from the coal being coked and from process steam condensation makes the byproduct operation a net generator of process water. Process wastewater sources include: excess ammonia liquor from the primary cooler tar decanter, and barometric condenser wastewater from the crystallizer, the final coolers, light oil recovery operations, desulfurization processes, and air pollution control operations. Most of the wastewater generated at the coke plant results from moisture in the coal and steam condensate. Additional sources can include condensates from drip legs and gas lines.

The largest consumption of water in coke plants is for the quenching of coke. The amount of water required for coke quenching can vary and has been reported to be from 400 to 3000 litres/tonne (120 to 900 gallons per ton). A sufficient quantity of water is needed to cool the coke, yet leave enough heat in the coke to evaporate any entrained water. Some facilities utilize untreated process wastewater for coke quenching, while others use treated process waters or service waters. In some areas, the level of TDS in the quench water must be controlled due to potential air pollution concerns. This requirement has impacted the use of untreated process wastewater in coke quenching.

6.6.3.2.2 Sinter Plants   The principal uses of water in a sintering plant are for controlling the moisture content of the pre-sinter mix, for dust control, and for sinter product cooling. Some indirect cooling of equipment is involved. For emissions control in sinter plants, either electrostatic precipitator or wet venturi-type scrubber technology is typically employed for dust control. In precipitator applications, some water may be added to control exhaust temperature and to condition the particulate prior to capture.

In scrubber systems, water is sprayed into the gas stream to capture the emissions from the sinter operation to meet stack emissions requirements. The associated water system will typically include clarifying thickeners, a cooling tower, and pH Adjustment.

6.6.3.2.3 Blast Furnace   The blast furnace is one of the largest water users in an integrated steel mill operation. The primary water use is for non-contact cooling of various parts of the furnace and auxiliaries, including the tuyeres, hearth staves, bosh, cooling plates and staves, cinder notch, and stove valves. The historical approach has been to use once-through cooling water, but recent construction and modernizations have incorporated evaporative cooling systems along with closed-loop water systems for hot blast valves, tuyeres, and staves. Additional water is used for furnace moisture injection (steam), dust control, and slag granulation.

Contact water use is primarily associated with blast-furnace gas cleaning operations necessary to recover the fuel value of the offgas for use in stove and boiler operations. In venturi-type scrubbers and spray-cooled gas coolers, water contacts, cleans, and cools the gas for reuse. This water system usually consists of thickeners, dewatering devices, and evaporative cooling towers. Chemical treatment may consist of settling aids, pH adjustment, and inhibitors, depending on the nature of the particulate and gas exiting the furnace. As the amount of recycle is increased in these systems, the control of total dissolved solids (TDS) and the increased concentration of specifically monitored elements or compounds become concerns.

Treatment for the reduction of TDS would be dependent upon the parameters of concern and could involve more sophisticated treatment systems. Typically, the blast-furnace process waters contain ammonia, phenols, cyanide, lead, and zinc. Additional treatment for these parameters may be required prior to discharge of any blowdown from the recycle system. In many facilities, a significant portion of the recirculated water can be consumed rather than discharged by utilizing it for slag quenching.

6.6.3.2.4 Alternative Iron Technologies   With the increased tonnage produced via the electric arc furnace, the direct reduced iron, iron carbide, and Corex processes play a meaningful role in the steel industry. Likewise, they also have water requirements. Because these technologies produce a source of iron units in varying forms, their process requirements can be similar to those of a blast furnace. However, their gas handling system is much more complex due to the nature of the technologies. In general, each of these processes has non-contact cooling requirements for compres-

sors, coolers, and various furnace shell components. Closed non-evaporative systems are prevalent for this application.

The gas exiting the shaft furnace in these processes is utilized extensively in the process and requires cleaning prior to reuse. Wet scrubbers are installed in the dirty system to perform this function. The water system usually consists of thickeners, dewatering devices, and evaporative cooling towers. Chemical treatment may consist of settling aids, pH adjustment, and inhibitors because of the nature of the particulate and gas composition in the dirty gas exiting the furnace.

A clean gas contact system, using water mainly as a process gas coolant, is also used to maintain process gas temperature requirements. This system is cooled via an open evaporative cooling tower.

Water treatment to meet the process requirements for each of the systems can be extensive. The contact systems in particular may require extensive water treatment and quality adjustment in process to maintain plant operations.

6.6.3.2.5 Electric Arc Furnaces   The EAF can also be an extensive user of water, particularly for non-contact cooling functions. In the melt shop, emissions in the exhaust gas stream are typically handled using baghouse technology, requiring no contact water. Non-contact water applications include water-cooled ductwork, roof, sidewalls, doors, injection lances, panels, electrode clamps, cables, and arms. These systems usually incorporate evaporative cooling towers, while a number of applications incorporate closed cooling loops. Some applications utilize closed-loop high-purity systems for electrical apparatus cooling requiring low conductivity (dissolved solids) water. As with other primary operations, the control of TDS in evaporative cooling systems for electric arc furnaces is a significant concern.

6.6.3.2.6 Basic Oxygen Furnace   The BOF and its derivatives are extensive users of water. Non-contact cooling is used for the vessel hood, ductwork, trunnion, and oxygen lance. Both closed-loop and evaporative systems are prevalent for handling the cooling requirements for these components, based on manufacturer recommendations. The trend for hood cooling in recent years has been toward the closed-loop cooling approach to extend hood life. Some BOF hoods are steam generating, with water requirements similar to those of high pressure boiler applications.

Gas handling for the various basic oxygen processes can be categorized as either full combustion (open) or suppressed combustion (closed) hood systems. In full combustion systems, excess air is allowed to enter the exhaust stream in the hood. This enables the oxygen blow to accomplish a complete reaction, converting CO to CO_2. In suppressed combustion systems, the hood is skirted to prevent excess air from entering the exhaust. Typically, the amount of particulate emissions generated by either approach equals 1–3% of the steel tonnage produced. The suppressed combustion approach has gained favor because the particulate generated is generally larger (except in the OBM or Q-BOP process), the temperatures generated in the hood are generally lower, and the volume of gas is lower, thereby reducing the size of the equipment required to convey and clean the gas.

In either full or suppressed combustion gas cleaning systems, water is used for initial cooling of the gas in the ductwork and/or in a quencher to reduce gas temperature and volume. Full combustion gas cleaning systems can incorporate either electrostatic precipitator (semi-wet) or venturi scrubber (wet) technology. After initial conditioning in a precipitator-based system, little or no water is used because the captured dust is handled on a dry basis. Precipitators are generally not used on suppressed combustion systems because the potential for explosion exists due to the presence of CO gas; the few facilities with suppressed combustion and precipitators have incorporated design considerations accommodating the potential explosion hazards.

The scrubber-based system typically incorporates separate quencher and venturi-type scrubbers for gas cooling and cleaning purposes. The auxiliary water systems typically consist of a clarifying thickener and dewatering devices for the solids captured. Upon exiting the thickener, the cleaned water is returned to the venturi, typically without cooling. After the venturi scrubber, the venturi effluent is typically reused as supply to the quencher. In some facilities, a separate gas cooler with a dedicated cooling tower is in line, after the scrubber but prior to the exhaust fan and stack.

Because of the lime carryover in the exhaust gas, the high gas temperature, and the fine particulate nature of the dust evolved, water-related problems, including mineral precipitation and fouling, can interfere with scrubber operations. Problems include plugging of the venturi nozzles and fouling in the venturi/quencher throats. Various water quality treatment approaches are incorporated, including pH/alkalinity control, solids management, and various inhibitor programs.

6.6.3.2.7 Ladle Metallurgy Furnace Water usage for the LMF is similar to the EAF, although its function and design are different. Non-contact water is used to cool the roof, clamps, arms, cables, and associated equipment. Cooling is typically via an open recirculating system and is combined with the EAF system if plant layout allows.

6.6.3.2.8 Vacuum Degasser Water usage is primarily associated with the vacuum generating/gas cleaning system. The vacuum is generated by injecting steam through multi-point eductors leading to a barometric condenser. As the steel exhaust emissions are drawn in contact with the steam, the particulate is wetted and collects in the condenser water. The water system may consist of an evaporative cooling tower, solids settling, and solids removal equipment.

Depending on the facility design, non-contact water may be used to meet equipment cooling requirements. Typically, these cooling requirements will be met by evaporative towers associated with the EAF/LMF facilities.

6.6.3.2.9 Continuous Casting Water use and quality are critical to the success of continuous casting. Water use in the caster is categorized by function in the casting process: primary (mold); secondary (spray); and auxiliary (equipment). When continuous casting was initially adopted by the steel industry, little attention was given to water quality and one evaporatively cooled system was installed to provide the cooling requirements.

As with the casting process itself, water management practices evolved as demands for equipment reliability and quality grew. A significant improvement was made when the mold circuit was isolated as a non-contact (closed) system, virtually eliminating process contamination and mineral scaling as the cause for mold related failures. Further improvements were made when contact cooling and non-contact requirements were separated into separate water systems.

The primary cooling process is the non-contact cooling of the molten steel shell in the mold to its semi-finished form by passing high quality water through a highly conductive copper mold. Closed-loop non-evaporative cooling is primarily employed when high surface and strand quality are required. Because of the high heat flux encountered in the mold, pretreatment is normally specified for removal of scale-forming constituents. Open recirculating evaporative systems are sometimes used where makeup water quality and caster quality requirements allow.

Secondary or spray cooling occurs as the strand exits the mold, with contact water sprays covering the surface of the strand. Spray cooling allows for the extraction of heat as it migrates from the molten core to the surface until solidification is complete. This contact water system will typically incorporate settling basins (scale pits), oil skimmers, straining devices, and deep bed filtration equipment when low suspended solids levels are to be maintained. Water treatment should include consideration of contamination from grease, hydraulic fluids, and mold lubricants that will be collected and concentrated in this system. As with other contact systems, this system will typically utilize evaporative tower systems for cooling.

Auxiliary cooling is non-contact or internal cooling of the casting equipment. Applications typically include heat exchangers, internal roll cooling, frames, bearings, compressors, exposed instrumentation, and other miscellaneous components. Evaporative cooling systems are prevalent for these applications. Electromagnetic stirring devices and high temperature exposed components such as center bearings may require the installation of closed-loop cooling systems, which may require high-quality water.

Cascading water systems are not unusual in caster systems as water quality requirements are typically less stringent for contact systems than for non-contact systems. Cascading often occurs unintentionally because of equipment leaks during normal operations.

6.6.3.2.10 Hot Rolling Mills   After casting, the semi-finished steel is transferred to a reheat furnace to bring the metal to a uniform temperature. Whether the furnace is of skid, walking beam, or tunnel design, non-contact cooling water is typically utilized to provide the cooling for doors, internally cooled rolls, skid pipes, beams, bearings, and miscellaneous equipment. Though once-through water can be used, an evaporative cooling tower is generally employed to allow water recycle.

In a thin slab caster complex, the strip enters the finishing stands directly, after passing through a continuous in-line reheating furnace. Direct rolling of thin cast slabs without reheating is more energy efficient and thus requires less indirect non-contact cooling water.

In the hot mill, the mill stand work rolls are cooled by a contact water system to maintain roll contour, to prevent surface cracking of the steel rolls due to sudden temperature changes, to minimize fire checking, and to generally extend roll life. Water is used in the form of high pressure jets to remove scale from the steel (descale) before rolling to maintain surface quality. It is also used between certain roll stands to maintain surface cleanliness of the steel in process. In addition, water is used as flume flushing to transport the scale to the scale pits for removal. When the product is coiled, cooling sprays or laminar cooling are employed to cool the strip to enable the coiling operation.

The rolling mill water system will typically incorporate settling basins (scale pits), oil skimmers, straining devices, solids removal with clarifiers and/or deep bed filtration equipment (when low suspended solids levels are to be maintained), and a cooling tower. Wastewater treatment should include consideration of contamination from fine mill scale, grease, hydraulic fluids, and rolling oils which will be collected in this system. The laminar system used on the runout tables may be separated from the rolling mill, with separate settling, cooling, straining, and water filtration facilities.

6.6.3.2.11 Finishing Mills   In finishing operations including pickling, cold reduction, annealing, temper, cleaner, and coating lines (tin, galvanized, terne, etc.), water is used primarily as non-contact cooling water, solution makeup, and rinse water. Non-contact cooling typically incorporates evaporative cooling towers, while some equipment may include closed-loop systems to meet specific high purity water quality requirements. Typical process wastewaters from these operations include rinses and spent concentrates from alkaline cleaners, pickling solutions, plating solutions, and electrochemical treating solutions. Many technologies are being utilized to recycle and/or reuse the concentrated solutions; however, the rinse waters require treatment to meet discharge requirements. In treatment of these wastewaters, consideration should be given to the type of plating solutions, cleaners, and pickling solutions utilized; oil and grease; dissolved metals; organic compounds; and lubricants that may be present in the wastewater.

6.6.4 Treatment of Effluent Water

In the iron and steelmaking industry, as in any major industry, the large volumes of process water that come into direct contact with the raw materials, products, and offgases must be treated for removal of regulated parameters prior to discharge or reuse of water. As discussed previously, the main operations in an integrated steel plant that require wastewater treatment include cokemaking; ironmaking; steelmaking; hot and cold rolling; and finishing operations such as pickling, electrolytic tinning, and other coating processes.

For the iron and steel industry, the parameters of most significance, which are generally regulated by the terms of discharge permits, are suspended solids, oil and grease, phenol, cyanide, ammonia, and heavy metals such as lead, zinc, chromium, and nickel. In addition, several organic compounds that are on the priority pollutant list compiled by the U.S. Environmental Protection Agency are regulated for cokemaking and cold rolling operations. The following discussion describes the conventional wastewater treatment technologies employed for effective treatment of steel industry wastewaters. Table 6.28 presents a summary of where these technologies would be applicable in steel mill operations.

Table 6.28 Steel Processing Wastewater Control Parameters

Mill Operation	Dissolved Organics	Dissolved Inorganics[a]	Oils	Suspended Solids	Metals	pH
Coke Plant	X	X	X	X		X
Sinter Plant			X	X	X	X
Blast Furnace	X	X	X	X	X	X
Electric Arc Furnace				X	X	X
Basic Oxygen Steelmaking				X	X	X
Vacuum Degassing				X	X	X
Continuous Casting			X	X	X	X
Hot Forming			X	X	X	X
Finishing Mills:						
Cold Forming	X		X	X	X	X
Acid Pickling			X	X	X	X
Alkaline Cleaning			X	X		X
Hot Coating			X	X	X	X

[a] Ammonia, cyanide, sulfide, thiocyanate, etc.

6.6.4.1 Control of Suspended Solids

Removal of suspended solids is necessary for the wastewaters from practically all of the production steps in the iron and steel industry, from cokemaking to product finishing. Solid particulates become suspended in process water streams during cleaning and cooling of flue gases, descaling, roll and product cooling, and flume flushing in rolling mills, and during product rinsing in finishing operations. The three general methods for removing suspended solids are sedimentation, centrifugal separation, and filtration. Sedimentation or clarification, which is settling by gravity, can be accomplished in a clarifier or inclined plate separator specially designed for a given application. Clarifiers are generally circular but also may be constructed in a rectangular shape. An advantage of inclined plate separators over clarifiers is that inclined plate separators occupy much less ground space; however, care should be exercised in their use when the wastewater contains a high oil and grease concentration. The disadvantage is the small storage volume for sludge at the bottom of inclined plate separators. Both clarifiers and inclined plate separators are designed for continuous removal of the collected sludge from the bottom of the unit. The underflow sludge may be gravity thickened before being further dewatered in one of several types of sludge dewatering units such as a filter press, a belt press, or a centrifuge, to reduce the volume for ease in handling and economy of disposal.

Coagulant aids, such as alum, ferric chloride, ferric sulfate, ferrous sulfate, ferrous chloride, and commercial organic polyelectrolytes, are often added to the wastewater prior to clarification to promote flocculation of the solid particles, which increases their effective size and thus increases their settling rate.

Centrifugal separation is a technique to remove suspended materials from the water column via centrifugal forces, sometimes termed cyclone separation. The process is highly dependent upon particle size and specific gravity. Larger particles and higher specific gravity enhances performance.

Multi-media or single media filtration, by either pressure or gravity, is another method for removal of fine suspended particulates which is commonly applied to steel industry wastewaters. The water is passed through a filter media contained in a vessel. The system usually is comprised of a number of individual filtration units in parallel. Often side-stream filtration can be utilized to treat a portion of the wastewater that is then blended with the unfiltered portion. It is desirable to design

a filter system with the highest feasible flow rate through the filter media to minimize the required size and cost.

In a typical multi-media system, the water first passes through a relatively coarse layer of media such as anthracite coal, and then through a layer of fine sand. Most of the particulates are removed by the coarse layer, while the fine layer does the final polishing. Multi-media filters are often used when oil and grease concentrations are elevated in the wastewaters. High oil and grease concentrations can result in fouling and/or plugging of the media in both single and multi-media filters. Periodically, the collected particulate must be removed from the filter media by backwashing. In this operation, the influent flow of wastewater is shut off and a stream of treated water, and occasionally air, is passed through the filter in the opposite direction to flush out the collected solids. By having a number of filter units installed in parallel, one unit can be put through the backwash cycle without interrupting the continuous treatment of the wastewater stream. The backwash stream is usually settled in a backwash holding tank, and the solids are processed through a thickener and sludge dewatering equipment. Both single media and multi-media filters can produce a high degree of clarity in effluent streams. However, clarifiers should be considered for pretreatment of wastewater heavily laden with solids to remove the majority of the particulates prior to filtration. Filters can be used alone without prior clarification for waste streams with less solids.

The quantity of suspended solids and other particulates discharged to a receiving stream can usually be greatly reduced by recirculating the water back to the process. However, the degree of recirculation that is feasible is limited by the amount of suspended solids present in the wastewater and the buildup in the concentration of dissolved salts in the system, which can eventually lead to deposition and plugging in equipment and piping. Therefore, a certain portion of the circulating water volume must be released as blowdown to control the concentration of dissolved salts to a tolerable level.

6.6.4.2 Control of Oil

Oil and grease are commonly found in wastewaters from continuous casting, hot and cold rolling, pickling, electroplating, and coating operations. The oils originate from machinery and product lubricants and coolants; hydraulic systems; and preservative coatings applied during certain phases of the production operations. Oil and grease can be removed from process wastewaters by several methods including skimming, filtration, gravity separation, air flotation, and ultrafiltration. If the oils are insoluble in water, they can be controlled by gravity separation and skimming. Gravity oil separators are usually rectangular chambers in which the velocity of the water stream is slowed down sufficiently to allow time for the oil to float to the surface, from where it is removed by one of several types of skimming devices. Such devices include the rotary drum, rope and belt type skimmers, and scraper blades, which are also used to scrape the heavier solids that have settled to the bottom. Insoluble oils also can be removed along with suspended solids in the multi-media filters previously described. If the oils are emulsified or water soluble, such as those found in waste cold rolling solutions or rinse waters, they can be treated by acid or commercial emulsion breakers to break the emulsion, followed by gravity sedimentation and skimming, or by air flotation and/or membrane separation techniques.

Skimming may be used on any wastewater containing constituents that float to the surface and is commonly used to remove free oil, grease, and soaps. Skimming is often used with air flotation or clarification to improve removal of both settling and floating materials. The removal efficiency of a skimmer is a function of the density of the material to be floated and the retention time of the wastewater in the tank. API or other gravity-type separators tend to be more suitable for use where the amount of surface oil flowing through the system is fairly high and consistent.

Air flotation is a process that is used to separate floatable materials having a specific gravity close to that of water, which therefore cannot be effectively separated by gravity alone. In a flotation system, gas bubbles, usually air, are released in the wastewater and attach to the oil and fine solid particles, causing them to float more rapidly to the surface where they are skimmed off as a froth.

Foam, dispersed air, dissolved air, gravity, and vacuum flotation are the most commonly used techniques. Chemical additives are often used to enhance the performance of the flotation process.

Ultrafiltration (UF) includes the use of pressure and semi-permeable polymeric or ceramic membranes to separate emulsified or colloidal materials suspended in a liquid phase. The membrane of an ultrafiltration unit forms a molecular screen which retains molecular particles based upon their differences in size, shape, and chemical structure. The membrane permits passage of solvents and lower molecular weight molecules.

In the ultrafiltration process, the wastewater is pumped through a tubular membrane unit. Water and some low molecular weight materials pass through the membrane under the applied pressure of 10 to 100 psig. Emulsified oil droplets and suspended particles are retained, concentrated, and removed continuously.

6.6.4.3 Control of Heavy Metals

Limitations on the discharge of heavy metals have been established by the U.S. Environmental Protection Agency (EPA) for steel industry process waters from blast furnaces; steelmaking furnaces; and pickling, cold rolling, electroplating, and hot coating operations. The conventional method used for removal of these trace metals is chemical precipitation followed by clarification or filtration. As shown in Fig. 6.6, the solubility of heavy metals in water is a function of pH. Generally, metals become less soluble as the pH increases; therefore, to remove dissolved metals, a wastewater stream is treated with an alkaline material in a mixing tank with a pH controller.
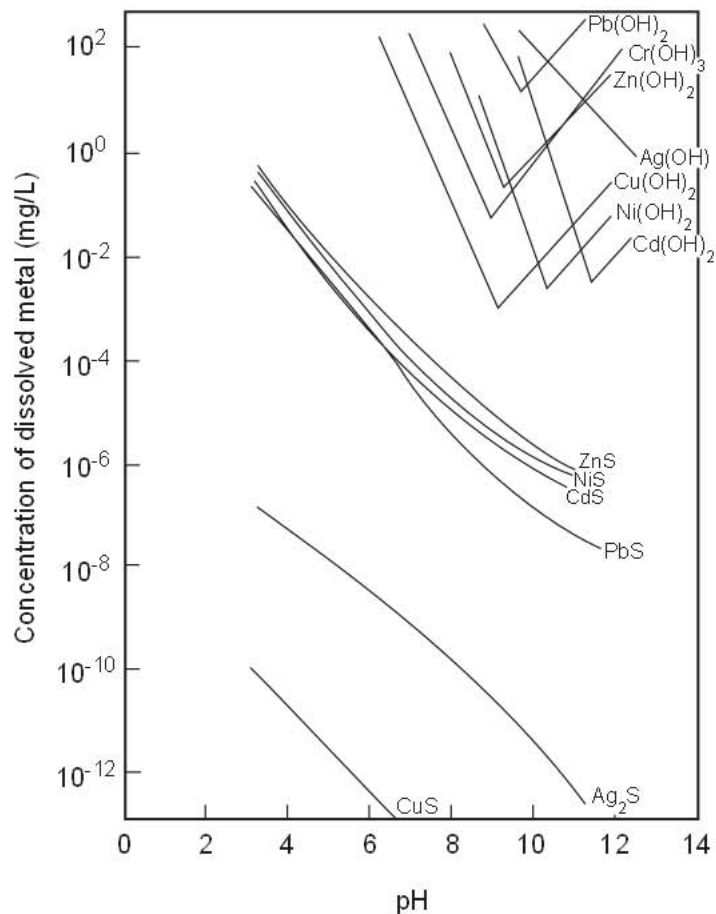

Fig. 6.6 Solubility of metal hydroxides and sulfides as a function of pH. *From Ref. 77.*

Common chemical precipitation processes include hydroxide and sulfide precipitation. In hydroxide precipitation, lime, which is the least expensive reagent, is most often used, although caustic soda, magnesium hydroxide, or other alkali may also be employed for this purpose. After the pH is raised to a level where the dissolved metals will precipitate as hydroxides, the water passes to either a clarifier and/or a filter for removal of the precipitated solids. The addition of a coagulant aid is usually required. The use of a coagulating agent such as ferric chloride at an alkaline pH results in the formation of an oxy-hydroxide surface, which enhances additional removal of metals by adsorption. Other coagulants such as alum, ferrous sulfate, and polymeric flocculants also can be used to enhance particle formation.

If chromium is present in the hexavalent form, it must first be chemically reduced to the trivalent form before it will precipitate. The rate of this reduction reaction is a function of the pH condition of the system. For example, the pH of the system must be adjusted to between 2.0 and 3.0 if sulfur dioxide, sodium bisulfite, or spent pickle liquor is used as the reducing agent. Hexavalent chromium can also be reduced to trivalent chromium with sodium hydrosulfite at a relatively higher pH (between 8.5 and 9.5). The reduced trivalent chromium ion is then converted to insoluble chromium hydroxide and is removed by sedimentation.

As indicated above, dissolved metal ions and certain anions may be chemically precipitated and removed by physical means such as sedimentation or filtration. In addition to the use of alkaline compounds, the following other reagents can be used:

1. Metal sulfides—Except for chromium sulfide, the solubility of metal sulfides is lower than that of metal hydroxides (see Fig. 6.6). Therefore, the removal of dissolved metals can be enhanced using the sulfide precipitation process. Both soluble sulfides, such as hydrogen sulfide or sodium sulfide, and insoluble sulfides, such as ferrous sulfide, may be used to precipitate many heavy metal ions as insoluble metal sulfides. Currently, the use of organic sulfide has become popular in the wastewater treatment industry. Typically, the sulfide precipitation process includes clarification and filtration.

2. Carbonates—Carbonate precipitates may be used to remove metals either by direct precipitation using a carbonate reagent such as calcium carbonate or by converting hydroxides into carbonates using carbon dioxide.

Chemical precipitation as a mechanism for removing metals from wastewater is a complex process consisting of at least two steps: precipitation of the unwanted metals and removal of the precipitate. A small amount of metal will remain dissolved in the wastewater after complete precipitation. The amount of residual dissolved metal depends on the treatment chemicals used, the solubility of the metal, and co-precipitation effects. The effectiveness of this method of removing any specific metal depends on the fraction of the specific metal in the raw waste (and hence in the precipitate) and the effectiveness of suspended solids removal.

6.6.4.4 Biological Treatment

Biological oxidation is the most commonly applied technology for final treatment of coke plant wastewaters. These waters contain significant levels of phenol, cyanide, thiocyanate, and ammonia, plus lesser concentrations of other organic compounds, primarily as a result of condensation from coke-oven gases that contain these substances. A conventional system for treatment of coke plant waste would include ammonia distillation followed by biological oxidation. The ammonia still system may have a free leg, where dissolved gaseous ammonia is removed by steam distillation, and a fixed leg, where ionized ammonia is converted to free ammonia by alkali addition, and then is removed in the free leg. While this distillation process will remove a large percentage of the ammonia and some of the free cyanide from the water, enough of these constituents will remain in the ammonia still effluent, in addition to phenol, thiocyanate, and other organics to require further treatment, such as biological oxidation, prior to disposal.

Because biological oxidation is highly sensitive to fluctuations in constituent loadings and pH, the effluent from the ammonia still is first passed through an equalization basin to level out the concentrations, temperature, and flow volume. Conventional systems consist of either a single-stage or two-stage system. In a single-stage system, the process is designed to reduce the organic compounds as well as ammonia. In a typical two-stage system, the first stage is designed to reduce the organic compounds and the second stage is utilized for nitrification (ammonia removal). Sometimes, with careful control, both carbonaceous and nitrogen treatment can occur in the same aeration basin. It should be noted that the biological treatment of thiocyanates results in an increase of ammonia in the wastewater. This must be accounted for in the design of the treatment system. Both aeration systems typically utilize an activated sludge process, followed by a clarifier. The activated sludge process is a suspended growth process similar to that applied in sewage treatment plants. In the aeration system, a mass of microorganisms or biomass in the form of suspended solids, called an activated sludge, is supplied with oxygen, which enables it to reduce the biologically degradable constituents in the wastewater. Populations of microorganisms can be developed that can effectively degrade phenol and other organics, thiocyanate, free cyanide, and ammonia. The required oxygen is supplied either by mechanical surface aerators or by diffusion of air bubbles through the basin, with or without the use of submerged turbine mixers. The treated water overflows the basin to a clarifier, where the activated sludge is settled out to be recycled to the aeration basin. The overflow water from the clarifier is discharged. Other biological treatment processes also can be used, including fixed film, packed towers, fluidized beds, and suspended growth processes with integral clarification.

6.6.4.5 Terminal Treatment

A common practice in wastewater treatment within the steel industry is to combine wastes from several different types of operations for treatment in a so-called terminal treatment plant. This practice has been particularly successful in the handling of wastes from the various finishing operations. These wastes typically might contain suspended solids, free and emulsified oils from cold rolling, acids from pickling rinse waters, and heavy metals from pickling and coating processes. In a typical system, acid streams are mixed with the emulsified oil streams to break the emulsions. The combined wastes are then passed through a gravity-oil separator, neutralized with lime to remove acids and precipitate heavy metals, and treated for removal of solids and any remaining oils in a clarifier or filter. This general type of terminal treatment system can be applied for environmental control of a number of different steel industry processes more economically than the alternative of providing a separate treatment system for each process.

6.6.4.6 Breakpoint Chlorination

Chlorination is one of the technologies recognized by U.S. EPA for the treatment of ammonia, phenols, and free cyanide. Chlorine has long been utilized as a biocide in municipal drinking water facilities and is known for its strong oxidation potential. When chlorine is added to water, hydrolysis of the chlorine molecule occurs, creating hypochlorous acid and hypochlorite ions which together comprise the free available chlorine. Alkaline chlorination (at pH > 9.5 in the presence of excess chlorine) is required for the destruction of free cyanide.

The term breakpoint chlorination comes from the observation of the point of the maximum reduction of chlorine residual while subjecting a sample to increasing chlorine dosages. The theoretical chlorine dosage for the treatment of ammonia is 7.6 parts of chlorine to one part of ammonia. In practice, dosages of 8:1 to 10:1 may be required. The optimum pH is usually in the range of 6.0 to 7.0. Care must be taken to provide sufficient chlorine to complete the reaction to avoid the formation of chloroamines. Additionally, the competing demand from phenols, nitrite, ferrous iron, sulfites, hydrogen sulfide, free cyanide, and other organics must be accounted for in the total chlorine demand. Alkalinity may also need to be added to the wastewater to maintain the desired pH. Approximately 14.3 mg/litre of alkalinity (as $CaCO_3$) is consumed for each 1.0 mg/litre of ammo-

nia nitrogen oxidized. In some cases, dechlorination of the final discharge will be required. This can be accomplished by adding sulfur dioxide, sodium bisulfite, or activated carbon.

The advantages of the process are that it has rather consistent process performance, has low space requirements, and can reduce the ammonia concentrations in one step. The disadvantages of this treatment method are the potential formation of trihalomethanes (THM), an increase in total dissolved solids (TDS), and the relatively high operating costs. This is why the technology is usually only applied to treat small concentrations of contaminants, or as a polishing treatment.

6.6.5 Effluent Limitations

The Federal Clean Water Act has established effluent limitations for any discharge to a river or lake (public waterway) or to the local publicly owned treatment works (POTW). A direct discharge to a river or lake is regulated by a permit under the National Pollutant Discharge Elimination System (NPDES). The terms of each individual permit can vary from state to state and watershed to watershed. However, at a minimum, the discharge from an existing facility must meet the Effluent Limitation Guidelines (ELG) for the discharge to a public waterway or to a POTW. These guidelines were developed by the U.S. Environmental Protection Agency (EPA) and are established as regulations in 40 CFR 420.

U.S. EPA reviewed the parameters of concern for each category of iron and steel manufacturing operation and established effluent limitations accordingly. This information is presented in the *Development Document for Effluent Limitations Guidelines and Standards for the Iron and Steel Industry* published by the U.S. EPA. These guidelines establish specific categorical limitations for discharges to public waterways and to POTWs. The limitations were developed based on the production operations in industrial facilities as well as the number of tons per day of product produced. The limitations are intended to be uniform treatment standards, such that the location of the facility is not meaningful. The U.S. EPA established limitations for existing sources as well as new sources.

The Agency evaluated the best practicable control technology currently available (BPT) and the best available technology economically achievable (BAT) for each steelmaking process. In some cases, the U.S. EPA indicated that BPT is equivalent to BAT and established BPT as BAT. For our purposes, these cases are referred to as BAT in the following text. All existing sources discharging to a public waterway have to meet the best available technology economically achievable (BAT). All existing sources discharging to a POTW have to meet Pretreatment Standards for Existing Sources (PSES) limitations. Similarly, all new sources have to meet New Source Performance Standards (NSPS) or Pretreatment Standards for New Sources (PSNS).

In addition to the federally-mandated effluent limitations, the states have the authority to impose more restrictive conditions in order to comply with local water quality standards. The more restrictive of the federal or state water quality limitations will be imposed in the NPDES permit. Local municipalities can also impose more restrictive effluent limitations for discharge into their sewer system, based on their need to meet state water quality standards or the ability of the POTW to handle the parameters of concern.

It should be noted that the achievable limitations proposed by U.S. EPA, and summarized below, were used to establish effluent limitation guidelines as published in Federal Regulations 40 CFR 420. These regulations establish limitations on a production basis and are presented as lb/1000 lb of a product or kg/1000 kg. These limitations are typically presented as a maximum for any one day (daily maximum) and an average of daily values for 30 consecutive days (monthly average). Historically, the U.S. EPA has utilized production data from the previous five-year period and has calculated the limitations based on the highest actual monthly production converted to a daily value. This is done by dividing the monthly production by the number of operating shifts in that month and then multiplying by three to determine a daily production rate. The production value is then multiplied by the factors in 40 CFR 420 to calculate the effluent limits. The achievable

limitations presented below and the associated treatment methodologies are all taken from the U.S. EPA development document. This information is presented as a guideline; it is not intended to represent an absolute condition. There are many ways of achieving the required effluent limitations, including alternate treatment methods and/or alternate flow reduction methods. Additionally, the model flows presented in this text are not intended to be requirements to achieve BPT or BAT; rather, these flows are simply guidelines that U.S. EPA believes could be achieved. Table 6.29 presents a general summary of the treatment technologies utilized for the parameters of concern in steel making wastewaters.

Table 6.29   Treatment Technologies for Parameters of Concern in Steelmaking Wastewaters

PARAMETER	Gravity Separation	Filtration	Mechanical Separation	Chemical Precipitation	Neutralization	Carbon Adsorption	Chemical Oxidation	Biological
Dissolved Organics						X	X	X
Dissolved Inorganics[a]							X	X
Metals	X	X	X	X	X			
Suspended Solids	X	X	X					
Oil and Grease	X	X	X					
pH					X			

[a] Cyanide, ammonia, sulfide, thiocyanate, etc.

The expected effluent quality of the treated wastewaters from each of the steelmaking operations is shown in daily maximum and monthly average values in Table 6.30. Note that these values are based on BAT treatment systems. New facilities would have more restrictive effluent limitations as defined under the NSPS. Following Table 6.30 is a discussion of the recommended treatment system for each of the major steel making operations.

6.6.5.1 Cokemaking

The BAT treatment system for cokemaking consists of: 1. the recycle of crystallized wastewaters, if any, to minimize the flow to be treated; 2. the treatment of the remaining wastewater flow in a two-stage or extended biological system. Fig. 6.7 presents the treatment system while Table 6.31 provides the model flows.

6.6.5.2 Sintering

The BAT treatment system for the sintering process involves recycling process wastewaters and filtering a blowdown flow of 120 gal/ton to reduce the levels of toxic materials and suspended solids. The pH of the effluent is adjusted using acid. The BAT system assumes a recycle rate of 92%. The system is illustrated in the Fig. 6.8.

6.6.5.3 Ironmaking

The BAT treatment system for ironmaking consists of recycling process wastewaters and treating the blowdown, as shown in Fig. 6.9. The applied flow rate for BAT is 13,344 litres/tonne (3200 gal/ton). After recycling, the blowdown (70 gal/ton) may be treated with two-stage alkaline chlorination, if required. Lime is added to the blowdown to raise the pH to 10.5 or greater. The toxic

Table 6.30 Summary of Expected Effluent Quality

Subcategory		Coke-making	Sintering	Iron-making	Steel-making	Vacuum Degassing	Continuous Casting	Hot Forming	Salt Bath Descaling	Acid Pickling	Cold Forming	Alkaline Cleaning	Hot Coating
pH (SU)		6–9	6–9	6–9	6–9	6–9	6–9	6–9	6–9	6–9	6–9	6–9	6–9
TSS	Max.	270	150	150	150	150	70	40	70	70	60	70	70
(mg/l)	Avg.	140	50	50	50	50	25	15	30	30	30	30	30
Oil & Grease	Max.	10	30	—	—	—	30	10	—	30(c)	25	30	30
(mg/l)	Avg.	—	10	—	—	—	10	—	—	10	10	10	10
Ammonia–N	Max.	85	30(a)	30	—	—	—	—	—	—	—	—	—
(mg/l)	Avg.	25	10	10	—	—	—	—	—	—	—	—	—
Benzene	Max.	0.05	—	—	—	—	—	—	—	—	—	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	—	—	—	—	—
Benzo–pyrene	Max.	0.05	—	—	—	—	—	—	—	—	—	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	—	—	—	—	—
Cyanide	Max.	10	6(a)	6	—	—	—	—	0.75(b)	—	—	—	—
(mg/l)	Avg.	5.5	3	3	—	—	—	—	0.25	—	—	—	—
Chromium	Max.	—	—	—	—	—	—	0.3	1	1.0(d)	1.0(e)	—	0.06(f)
(mg/l)	Avg.	—	—	—	—	—	—	0.1	0.4	0.4	0.4	—	0.02
Lead	Max.	—	0.9	0.9	0.9	0.9	0.9	0.3	—	0.45	0.45	—	0.45
(mg/l)	Avg.	—	0.3	0.3	0.3	0.3	0.3	0.1	—	0.15	0.15	—	0.15
Naphthalene	Max.	0.05	—	—	—	—	—	—	—	—	0.1	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	—	—	—	—	—
Nickel	Max.	—	—	—	—	—	—	—	0.9	0.9(d)	0.9(e)	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	0.3	0.3	0.3	—	—
Phenols	Max.	0.1	0.2(a)	0.2	—	—	—	—	—	—	—	—	—
(mg/l)	Avg.	0.05	0.1	0.1	—	—	—	—	—	—	—	—	—
Residual Chlorine	Max.	—	0.5(a)	0.5	—	—	—	—	—	—	—	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	—	—	—	—	—
Tetrachloroethylene	Max.	—	—	—	—	—	—	—	—	—	0.15	—	—
(mg/l)	Avg.	—	—	—	—	—	—	—	—	—	—	—	—
Zinc	Max.	—	1.35	1.35	1.35	1.35	1.35	0.45	—	0.3	0.3	—	0.3
(mg/l)	Avg.	—	0.45	0.45	0.45	0.45	0.45	0.15	—	0.1	0.1	—	0.1

(a) Applicable only when sintering wastewater is treated with ironmaking wastewater.
(b) Applicable at reducing operations only.
(c) Applicable only when pickling wastewater is treated with cold rolling wastewater.
(d) Applicable at combination acid pickling only.
(e) Applicable only when cold rolling wastewaters are treated with descaling or combination acid.
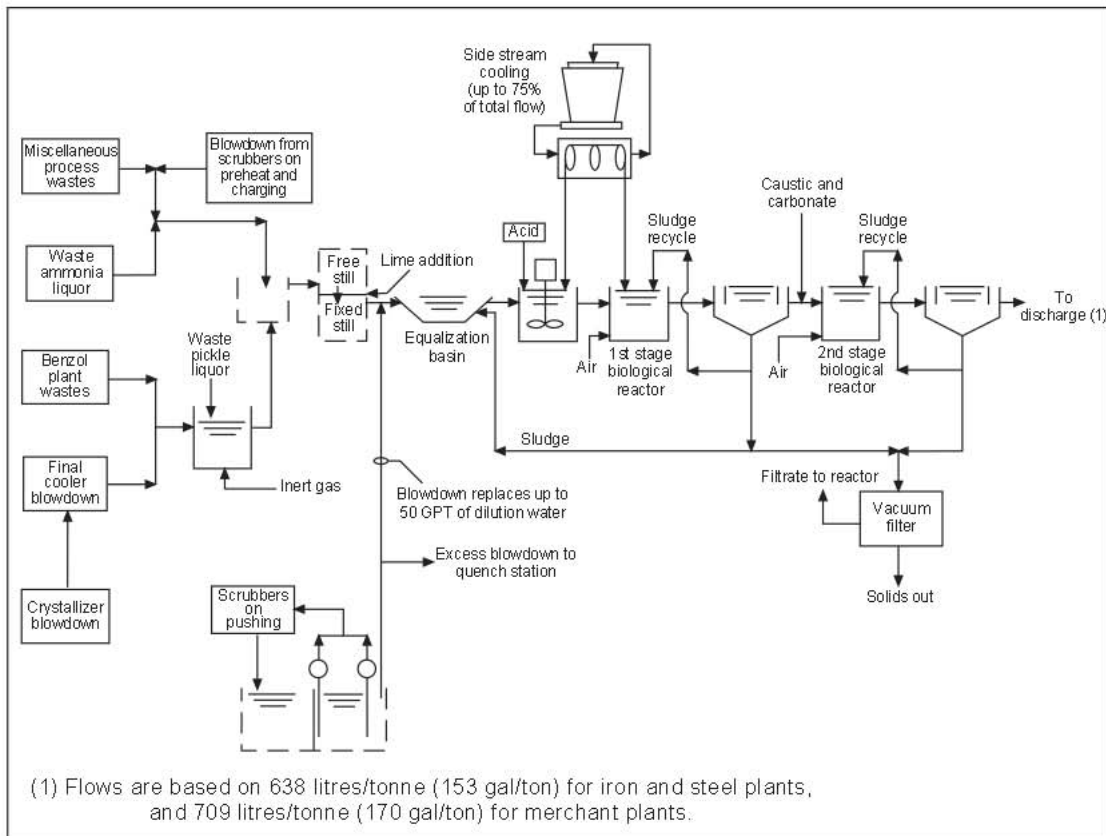(f) Hexavalent chromium.

(1) Flows are based on 638 litres/tonne (153 gal/ton) for iron and steel plants, and 709 litres/tonne (170 gal/ton) for merchant plants.

Fig. 6.7 Byproduct cokemaking subcategory, biological treatment system; BAT model.

### Table 6.31 BAT Flow Summary for Byproduct Cokemaking Subcategory

(All flows in gal/ton of coke.)

Wastewater Source	Flow Basis BAT Effluent	
	Integrated Producers	Merchant Producers
Waste Ammonia Liquor	32	36
Final Cooler Blowdown	10	12
Barometric Condenser Blowdown	3	5
Benzol Plant Wastewater	25	28
Steam & Lime Slurry	13	15
Miscellaneous Sources (leaks, seals, test taps, drains)	20	24
Subtotal—Process Wastewaters	103	120
Dilution to optimize bio-oxidation	50[a]	50[a]
BASIC TOTAL FLOW	**153**	**170**
Additional Flow Allowances Provided in the Regulation:		
For Qualified Desulfurizers (Wet), up to:	25	25
For Indirect Ammonia Recovery, up to:	60	60
No Additional Allowances For:		
Air Pollution Control Scrubbers:		
Coal Drying or Preheating – up to 15 gal/ton blowdown*	0	0
Charging/ Larry Car – up to 5 gal/ton blowdown*	0	0
Pushing Side Scrubber – up to 100 gal/ton blowdown*	0	0
MAXIMUM TOTAL FLOW	**238**	**255**

[a] Up to 50 gal/ton of dilution water is replaced by blowdown from air pollution control scrubbers. Any excess blowdown (from pushing only) is disposed via quenching operations, or treated and reused in the scrubber system.
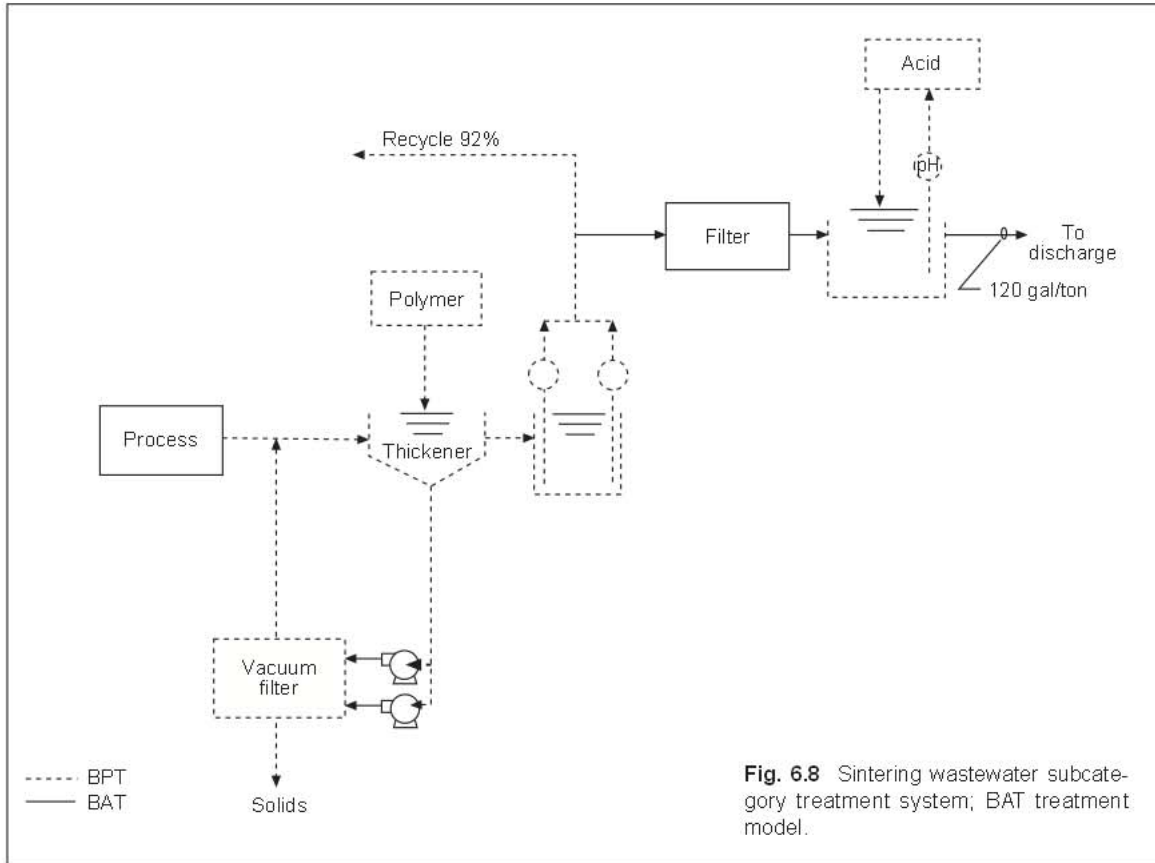
Fig. 6.8 Sintering wastewater subcategory treatment system; BAT treatment model.

BPT
BAT
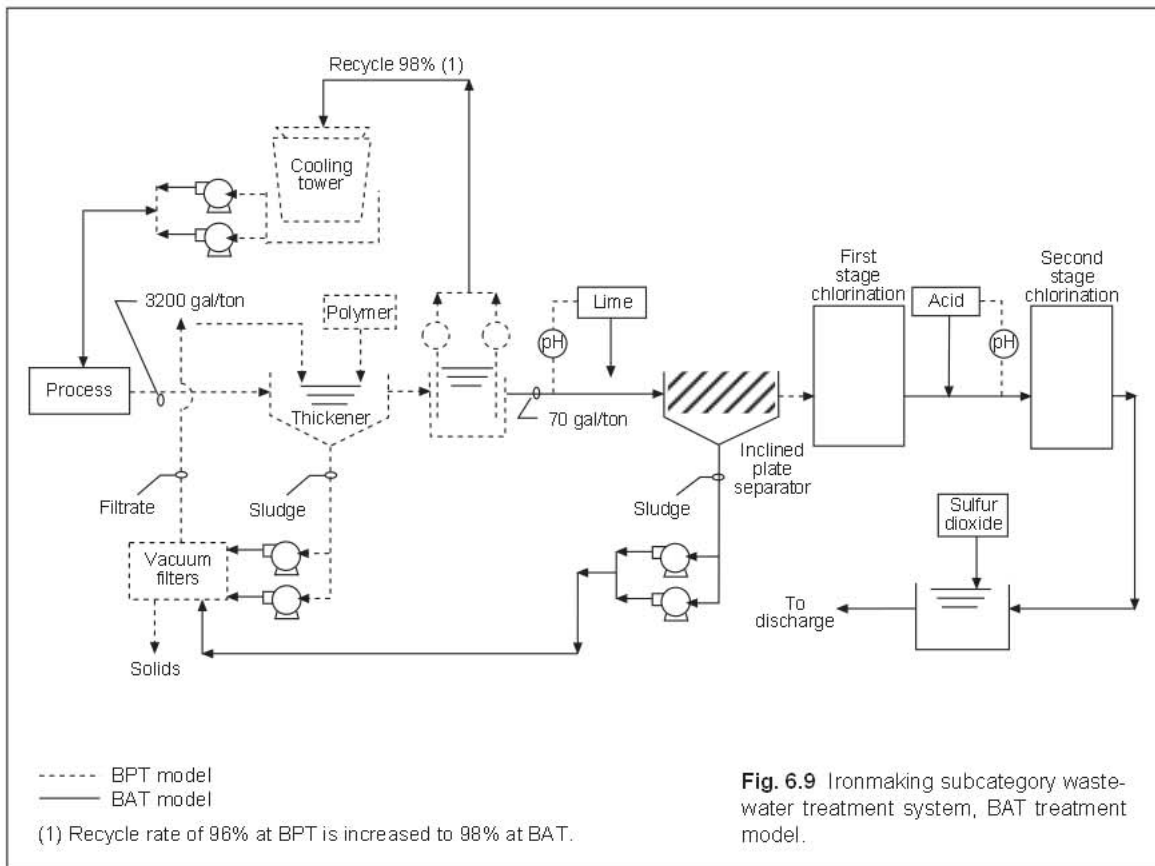
Fig. 6.9 Ironmaking subcategory wastewater treatment system, BAT treatment model.

BPT model
BAT model

(1) Recycle rate of 96% at BPT is increased to 98% at BAT.

metal precipitates and other suspended solids formed by lime addition are separated prior to alkaline chlorination. Chlorine is added in a two-stage system. In the first reactor, chlorine converts the cyanides to cyanates and oxidizes ammonia–N and phenolic compounds. As the wastewaters leave the first reactor, acid is added to reduce the pH to 8.5. Additional chlorine is added in the second reactor to complete the oxidation of the cyanides as well as residual ammonia–N and phenolic compounds. The effluent is then dechlorinated with appropriate reducing agents prior to discharge.

6.6.5.4 Steelmaking

The applied and effluent flows included in the BAT treatment system for each segment are shown in Table 6.32.

Table 6.32 Flow Rates for Steelmaking Subcategory

Operation	Applied Flow (gal/ton)	BAT Effluent Flow (gal/ton)
BOF—Wet-Suppressed Combustion	1000	50
BOF—Wet-Open Combustion	1100	110
Open Hearth—Wet	1700	110
Electric Arc—Wet	2100	110

The BAT treatment system for the wet subdivision consists of pH adjustment and solids separation, as shown in Fig. 6.10. Lime is added to increase the pH for the purpose of providing both dissolved and particulate toxic metals removal. The suspended solids generated in this process are then removed. Final pH adjustment of the treated effluent is also required.

6.6.5.5 Vacuum Degassing

The BAT treatment system for the vacuum degassing process includes lime precipitation, sedimentation, and pH control to remove dissolved and particulate toxic metals, as presented in Fig. 6.11. The applied and discharge flows are 1400 gal/ton and 25 gal/ton, respectively.

6.6.5.6 Continuous Casting

The model flow for continuous casting is 25 gal/ton. The BAT system includes recycling and treatment of the blowdown with lime precipitation and sedimentation to remove both particulate and dissolved toxic metals, as shown in Fig. 6.12.
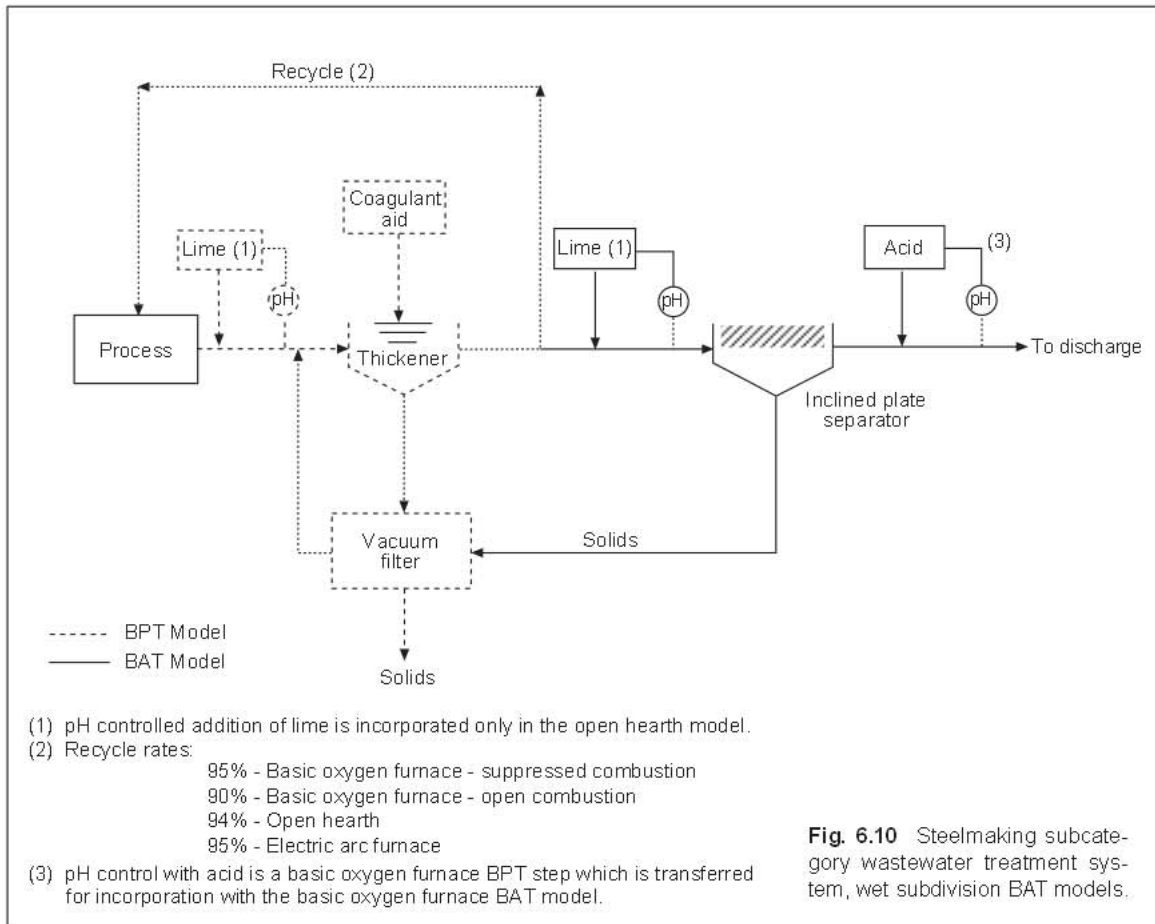
6.6.5.7 Hot Forming

In the BAT treatment system for hot forming waste streams, the water discharged from the mill is collected in a scale pit where large particles settle out and surface skimmers remove floating oils. The BAT treatment system includes recycle of the process wastewaters followed by a roughing clarifier and then a filter for additional suspended solids and oil removal, as presented in Fig. 6.13. Depending on the hot forming subdivision, anywhere from 58 to 77% of the primary scale pit effluent is recirculated to the mill. A vacuum filter is used to dewater the underflow from the clarifier. Although EPA has suggested model flows for the hot forming processes, as presented in Table 6.33, these recycle rates are not mandatory.
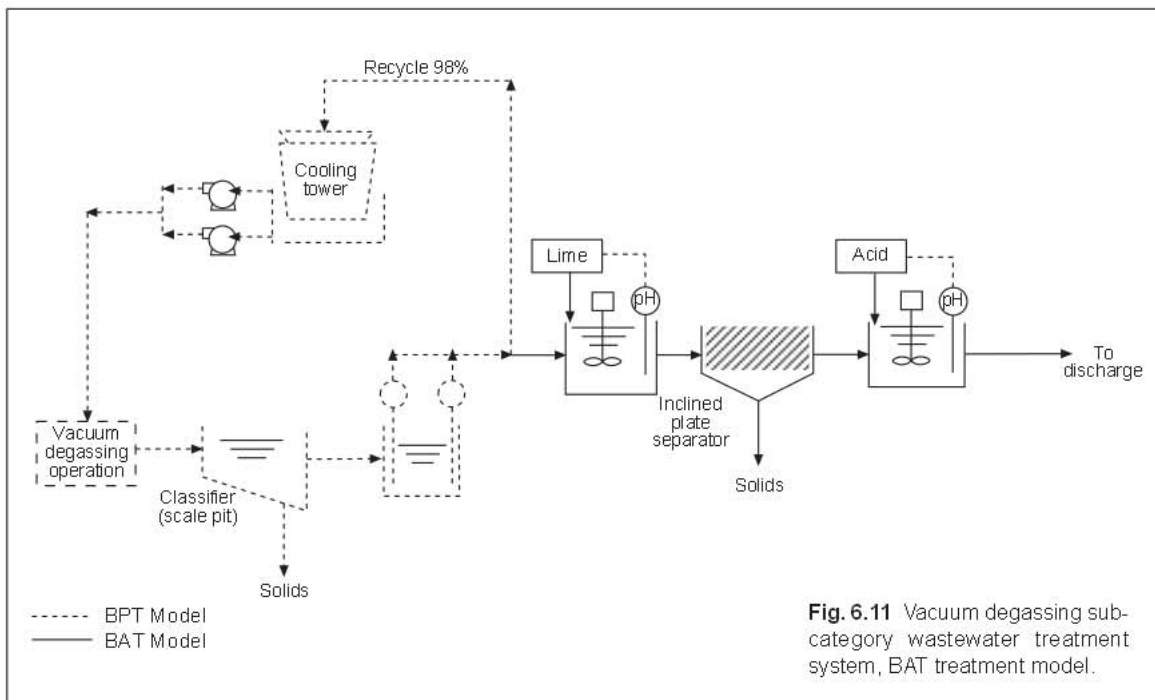
6.6.5.6 Salt Bath Descaling

The BAT system for oxidizing operations includes acidification followed by chemical reduction of hexavalent chromium with sulfur dioxide, sodium metabisulfite, or sodium hydrosulfite. Chemical

Recycle (2)

Coagulant aid

Lime (1)

Lime (1)

Acid

(3)

Process

Thickener

Inclined plate separator

To discharge

Vacuum filter

Solids

Solids

----- BPT Model

——— BAT Model

(1) pH controlled addition of lime is incorporated only in the open hearth model.
(2) Recycle rates:
        95% - Basic oxygen furnace - suppressed combustion
        90% - Basic oxygen furnace - open combustion
        94% - Open hearth
        95% - Electric arc furnace
(3) pH control with acid is a basic oxygen furnace BPT step which is transferred for incorporation with the basic oxygen furnace BAT model.

Fig. 6.10 Steelmaking subcategory wastewater treatment system, wet subdivision BAT models.

Recycle 98%

Cooling tower

Lime

Acid

To discharge

Inclined plate separator

Solids

Vacuum degassing operation

Classifier (scale pit)

Solids

----- BPT Model

——— BAT Model

Fig. 6.11 Vacuum degassing subcategory wastewater treatment system, BAT treatment model.
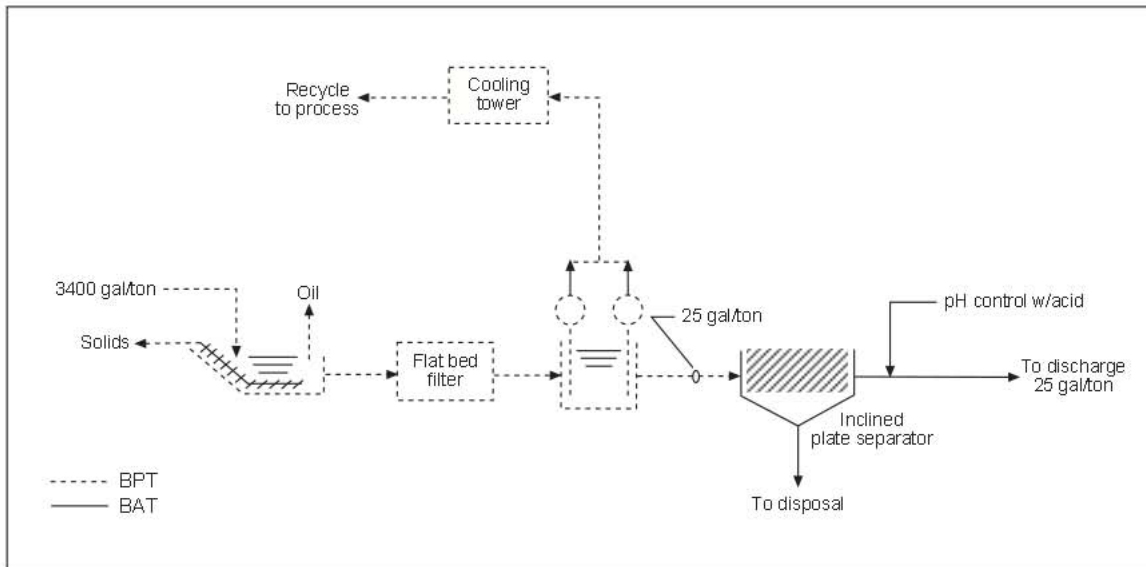
Fig. 6.12 Continuous casting subcategory wastewater treatment system, BAT treatment model.
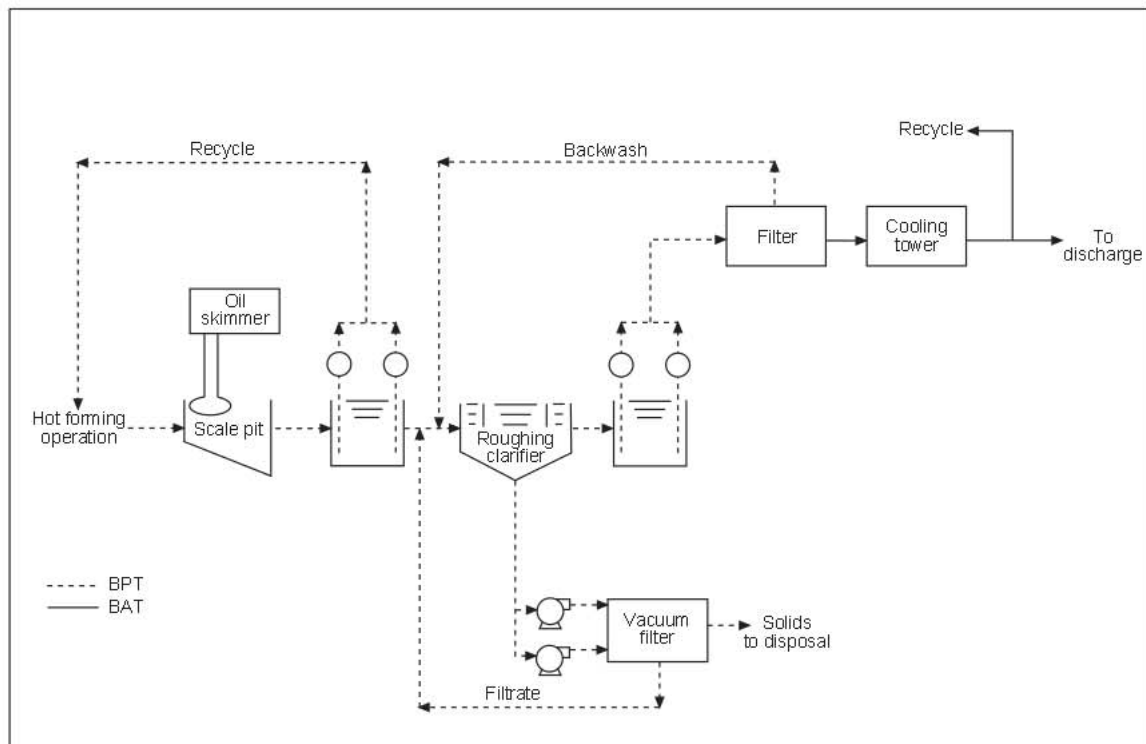
Fig. 6.13 Hot forming subcategory wastewater treatment system, BAT models.

reduction is followed by oil separation or skimming, neutralization/precipitation with lime, chemical coagulation with polymer, and settling in a clarifier. Sludges are dewatered in vacuum filters. In reducing operations, chemical oxidation with chlorine for cyanide destruction is followed by neutralization/precipitation with acid, chemical coagulation with polymer, and settling in a clarifier. Sludges are dewatered. The model flows are shown in Table 6.34.

Table 6.33 Flow Rates for Hot Forming Subcategory

Subdivision	Applied Flow (gal/ton)	Primary Scale Pit Recycle (%)	BPT Discharge Flow (gal/ton)	BAT Recycle Increase[a] (%)	BAT Discharge Flow (gal/ton)
Primary:					
w/o Scarfer	2300	61	897	35	90
w/ Scarfer	3400	61	1326	35	140
Section:					
Carbon	5100	58	2142	38	200
Specialty	3200	58	1344	38	130
Flat:					
Hot Strip	6400	60	2560	36	260
Carbon Plate	3400	60	1360	36	140
Specialty Plate	1500	60	600	36	60
Pipe and Tube	5520	77	1270	19	220

[a]Increase over Primary Scale Pit recycle. Total overall BPT/BAT system recycle = 96%.

Table 6.34 Flow Rates for Salt Bath Descaling Subcategory

Oxidizing Operations	Flow (gal/ton)
Batch	
Sheet, Plate	700
Rod, Wire, Bar	420
Pipe, Tube	1700
Continuous	330
Reducing Operations	**Flow (gal/ton)**
Batch	325
Continuous	1820

6.6.5.7 Acid Pickling

The BAT flows for acid pickling are shown in Table 6.35. The BAT system includes equalization of spent pickle liquor, fume scrubber recycle, equalization of spent pickle liquor, rinse water, fume scrubber blowdown, and absorber vent scrubber wastewaters, where applicable. Following equalization, treatment consists of lime neutralization/precipitation, polymer addition, aeration, clarification, and vacuum filtration, as shown in Fig. 6.14. The BAT flow rates are presented in Table 6.35.

6.6.5.8 Cold Forming

The BAT flows are 90 gal/ton, 400 gal/ton, and 300 gal/ton for single-stand, multiple-stand and combination-mill operations, respectively. The BAT treatment system for the cold rolling subdivision includes oil separation and equalization, chemical addition (alum and acid) to break any oil emulsions, neutralization, flocculation with polymer, and dissolved air flotation, as shown in Fig. 6.15.
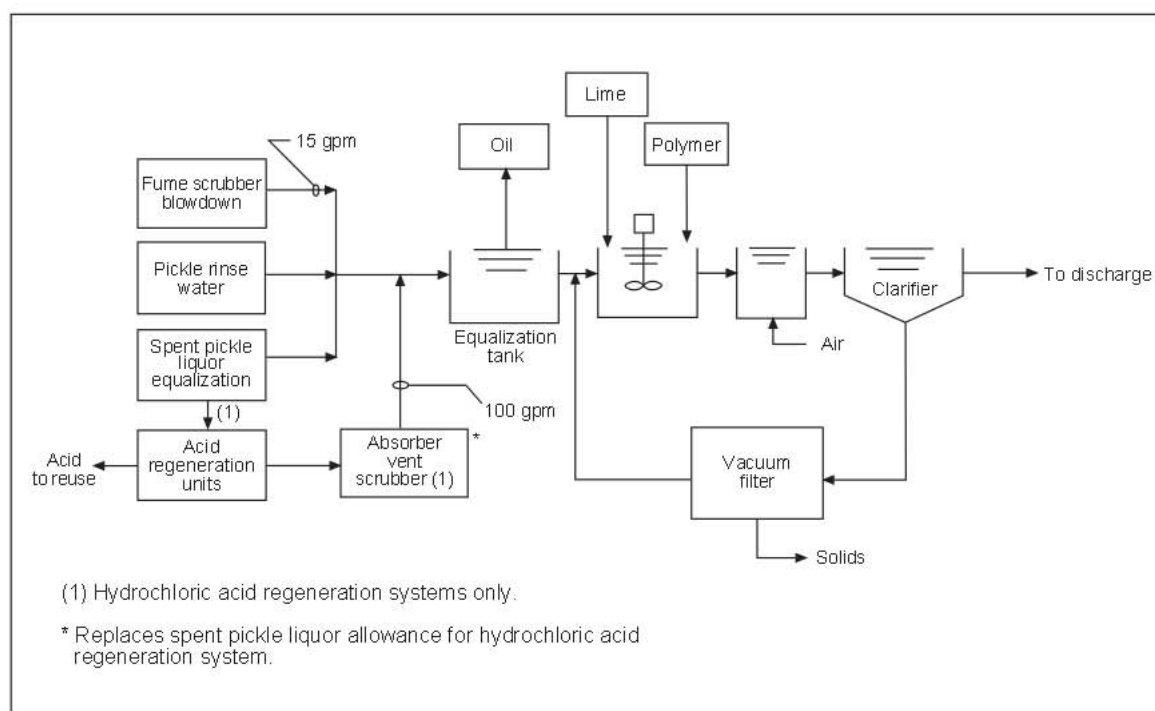
Fig. 6.14 Acid pickling wastewater treatment system; BPT/BAT model.

Table 6.35 Development of Applied Flows Acid Pickling Subcategory

Sulfuric Acid	Discharge Flow (gal/ton)
Strip/Sheet/Plate	180
Rod/Wire/Coil	280
Bar/Billet/Bloom	90
Pipe/Tube/Other	500
Fume Scrubber[a]	15 gpm
Hydrochloric Acid	
Strip/Sheet/Plate	280
Rod/Wire/Coil	490
Pipe/Tube	1020
Absorber Vent Scrubber[b]	100 gpm
Fume Scrubber[a]	15 gpm
Combination Acid	
Batch – Strip/Sheet/Plate	460
Cont. – Strip/Sheet/Plate	1500
Rod/Wire/Coil	510
Bar/Billet/Bloom	230
Pipe/Tube	770
Fume Scrubber[a]	15 gpm

[a] The fume scrubber limitations which is given in Kg/day is in addition to the kg/tonne limitations shown for other acid pickling segments.

[b] The absorber vent scrubber limitation, which is given in Kg/day, is in addition to the kg/Kkg limitation for other pickling segments and the Kg/day fume scrubber limitation for the hydrochloric acid subdivision.
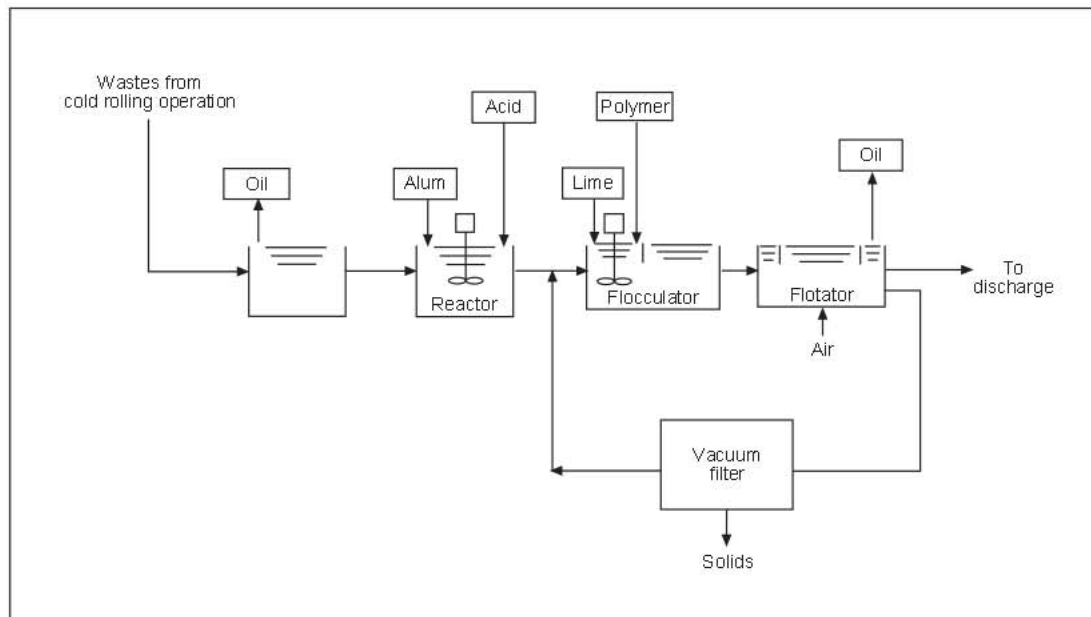
Fig. 6.15 Cold forming subcategory wastewater treatment system; cold rolling BPT/BAT model.

The BAT treatment systems for the cold worked pipe and tube subdivision is divided into two further categories: plants using water and plants using soluble oil solutions. For the plants using water, the BAT treatment system includes settling of the raw wastewater in a primary scale pit equipped with oil skimming equipment. All of the treated wastewater is then recycled to the process. The BAT treatment system for the plants using soluble oil includes settling of the raw wastewater in a primary scale pit equipped with oil skimming equipment that removes tramp oils. Nearly all of the solution is then recycled to the process. The spent solution is periodically removed by a contract hauler so that there is no discharge to navigable waters.

6.6.5.9 Alkaline Cleaning

The model flows in the alkaline cleaning subcategory are 250 gal/ton and 350 gal/ton for batch and continuous operations, respectively. The BAT treatment system includes the following wastewater treatment steps: equalization, oil skimming, neutralization with acid, and addition of a polymer followed by sedimentation in a flocculation-clarifier, as shown in Fig. 6.16.

6.6.5.10 Hot Coating

The BAT flows in the hot coating subcategory are 600 gal/ton and 2400 gal/ton for strip, sheet, and miscellaneous (SSM) and wire products and fasteners (WPF) , respectively. The treatment system alternative selected for hot coating operations relies on flow reduction by recycling fume scrubber wastewaters and limiting blowdown streams from the scrubber system to 15 gpm. This reduced scrubber discharge is combined with the rinse water and treated in the BAT treatment system. The BAT system for galvanizing consists of chrome reduction, equalization, pH adjustment, polymer addition, and solids separation, as shown in Fig. 6.17. The BAT system for terne and other metals is similar, but does not include a chromium reduction step.

6.6.6 Boiler Water Treatment

Of the many uses for energy in the U.S. today, in industry, in transportation, in homes and commercial buildings, the largest portion of total use is directed toward producing steam through the
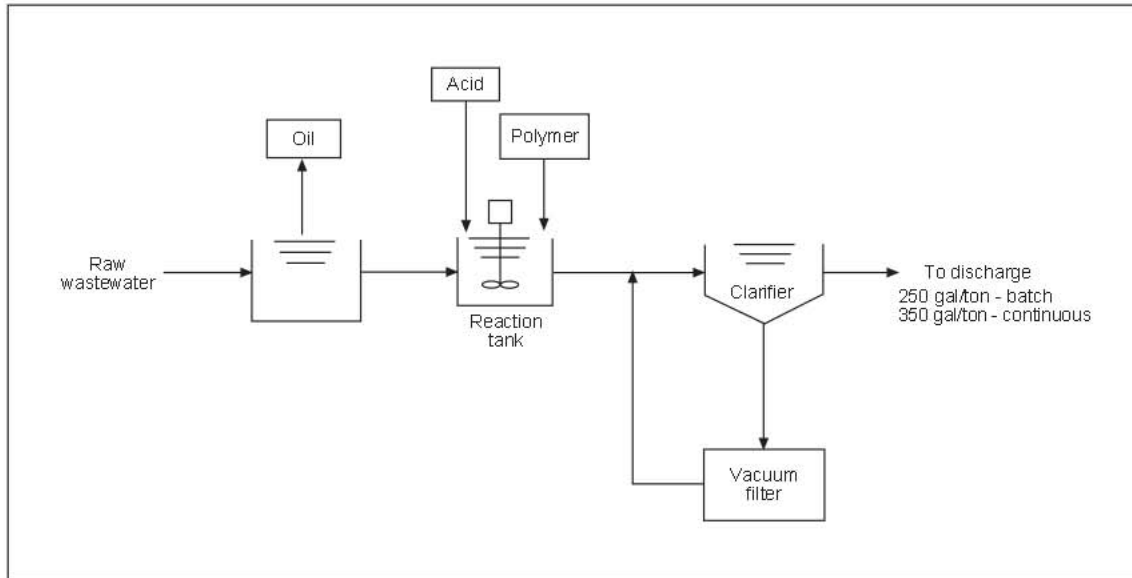
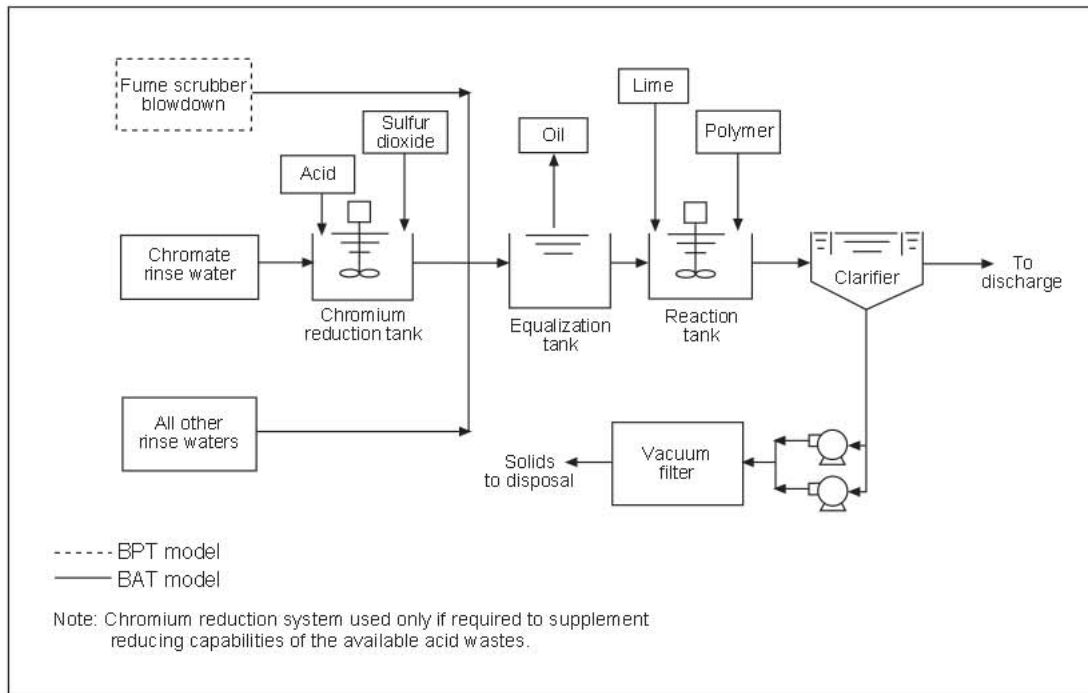**Fig. 6.16** Alkaline cleaning wastewater treatment system; BPT/BAT model.

Fig. 6.17 Hot coating/galvanizing subcategory wastewater treatment system; BAT model.

combustion of fossil fuels. Utilities account for the greatest share of this, but industrial plants also produce enormous quantities of steam for process uses, often generating electric power through turbines of a byproduct fuel (co-generation).

The treatment of water for steam generation is one of the most sophisticated branches of water chemistry. An understanding of the fundamentals of boiler water chemistry is essential to the power engineer who continually strives to increase the efficiency of the boilers and steam-using equipment.

The pressure and design of a boiler determine the quality of water it requires for steam generation. Municipal or plant water of good quality for domestic use is seldom good enough for boiler feed water. These sources of makeup are nearly always treated to reduce contaminants to acceptable levels; in addition, corrective chemicals are added to the treated water to counteract any adverse effects of the remaining trace contaminants. The sequence of treatment depends on the type and concentration of contaminants found in the water supply and the desired quality of the finished water to avoid the three major boiler system problems: deposits, corrosion, and carryover.

6.6.6.1 Deposits

Deposits, particularly scale, can form on any water-washed equipment surface, especially on boiler tubes, as the equilibrium conditions in the water contacting these surfaces are upset by an external force, such as heat. Each contaminant has an established solubility in water and will precipitate when it has been exceeded. If the water is in contact with a hot surface and solubility of the contaminant is lower at higher temperatures, the precipitate will form on the surface, causing scale. The most common components of boiler water deposits are calcium phosphate, silicate, various forms of iron oxide, silica adsorbed on the previously mentioned precipitates, and alumina; see Table 6.36. If phosphate salts are used to treat the boiler water, calcium will preferentially precipitate as the phosphate before precipitating as the carbonate, and calcium phosphate becomes the most prominent feature of the deposit.

Table 6.36 Expected Composition of Boiler Sludge

Constituent	Coagulation-Type Treatment	PO₄ Residual Treatment
Calcium carbonate	High	Usually less than 5%
Calcium phosphate	Usually less than 15%	High
Calcium silicate	Usually less than 3%	Trace or none
Calcium sulfate	None	None
Calcium hydroxide	None	None
Loss on Ignition	Usually less than 5%	Usually 8–12% except higher in very pure feed waters
Magnesium phosphate	None	Usually less than 5% except in some high-pressure boilers
Magnesium hydroxide	Moderate	Moderate
Magnesium silicate	Moderate	Moderate
Silica	Usually less than 10%	Usually less than 10%
Alumina	Less than 10%	None
Oil	None	None
Iron oxide	Usually less than 5%	Usually less than 5% except in high-purity feed waters
Sodium salts	Usually less than 1.5%	Usually less than 1.5%
Copper	Trace	Usually low
Other Metals	Trace	Low

At the high temperatures found in a boiler, deposits are a serious problem, causing poor heat transfer and a potential for boiler tube failure. In low-pressure boilers with low heat transfer rates, deposits may build up to a point where they completely occlude the boiler tube.

In modern intermediate and higher pressure boilers with heat transfer rates in excess of 5000 cal/m^2/hr (200,000 Btu/ft^2/h), the presence of even extremely thin deposits will cause a serious elevation in the temperature of tube metal. The deposit coating retards the flow of heat from the fur-
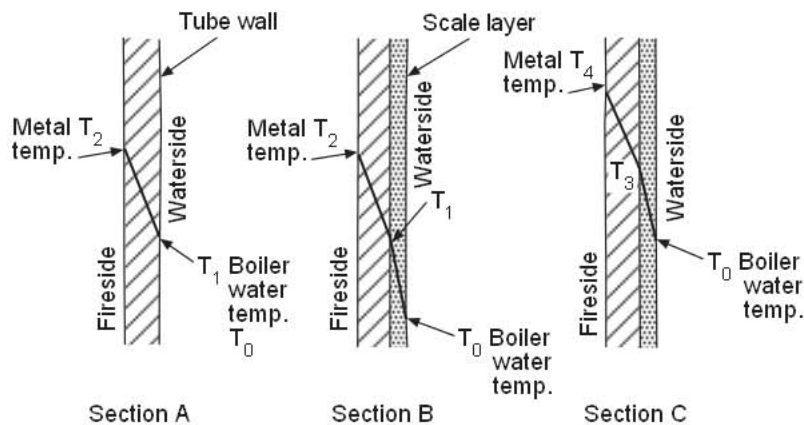
Fig. 6.18 Temperature profile across a clean tube, Section A, and tubes having a water-side deposit, Section B and Section C.

nace gases into the boiler water. This heat resistance results in a rapid rise in metal temperature to the point at which failure can occur. The action that takes place in the blistering of a tube by deposit buildup is illustrated by Fig. 6.18. For simplification, no temperature drops through gas or water films have been shown. Section A shows a cross section of the tube metal with a completely deposit-free heating surface. There is a temperature drop across the tube metal from the outside metal (T_2) to the metal in contact with boiler water (T_1). Section B illustrates this same tube after the development of a heat-insulating deposit layer. In addition to the temperature drop from T_2 to T_1, there would be an additional temperature drop through the deposit layer from T_1 to T_0. This condition would, of course, result in a lower boiler water temperature T0. However, boiler water temperature is fixed by the operating pressure, and operating conditions require that the same boiler water temperature be maintained as before the development of the deposit layer. Section C illustrates the condition that actually develops. Starting at the base boiler water temperature of T0, the increase through the scale layer is represented by the line from T_0 to T_3. The further temperature increase through the tube wall is represented by the line from T_3 to T_4. The outside metal temperature T_4 is now considerably higher than the temperature T_2, which was the outside metal temperature prior to the formation of deposits on the tube surfaces.

If continued deposition takes place, increasing the thickness of the heat-insulating deposits, further increases will take place in the tube metal temperature until the safe maximum temperature of the tube metal is exceeded. Usually this maximum temperature is 480 to 540°C (900 to 1000°F). At higher heat transfer rates, and in high-pressure boilers, the problem is more severe. At temperatures in the 482 to 732°C (900 to 1350°F) range microstructural transformations take place in carbon steel. At temperatures above 427°C (800°F) spheroidization of carbon begins to take place, with a resultant reduction in strength properties. Temperatures within the boiler furnace are considerably above this critical temperature range.

Water circulating through the tubes normally conducts heat away from the metal, preventing the tube from reaching this range. Deposits insulate the tube, reducing the rate at which this heat can be removed, as shown in Fig. 6.19; this leads to overheating and eventual tube failure. If the deposit is not thick enough to cause such a failure, it can still cause a substantial loss in efficiency and disruption of the heat transfer load in other sections of the boiler.

Deposits may be scale, precipitated in situ on a heated surface, or previously precipitated chemicals, often in the form of sludge. These drop out of water in low-velocity areas, compacting to form a dense agglomerate similar to scale, but retaining the features of the original precipitates. In the operation of most industrial boilers, it is seldom possible to avoid formation of some type of precipitate at some time. There are almost always some particulates in the circulating boiler water which can deposit in low-velocity sections, such as the mud drum. The exception would be high-purity systems, such as utility boilers, which remain relatively free of particulates except under conditions where the system may become temporarily upset.
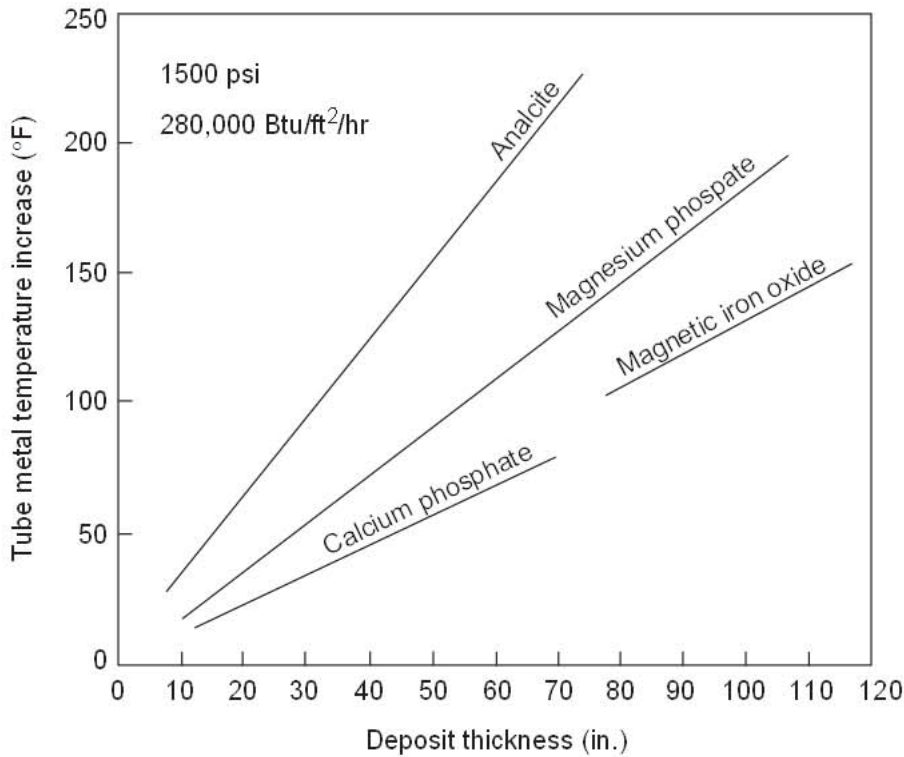
Fig. 6.19 Tube metal temperature increase vs. deposit thickness.

6.6.6.2 Corrosion

The second major water-related boiler problem is corrosion, the most common example being the attack of steel by oxygen. This occurs in water supply systems, preboiler systems, boilers, condensate return lines, and in virtually any portion of the steam cycle where oxygen is present. Oxygen attack is accelerated by high temperature and by low pH. A less prevalent type of corrosion is alkali attack, which may occur in high pressure boilers where caustic can concentrate in a local area of steam bubble formation because of the presence of porous deposits.

Some feed water treatment chemicals, such as chelants, if not properly applied can corrode feed water piping, control valves, and even the boiler internals.

While the elimination of oxygen from boiler feed water is the major step in controlling boiler corrosion, corrosion can still occur. An example is the direct attack by steam of the boiler steel surface at elevated temperatures, according to the following reaction:

$$4H_2O + 3Fe \rightarrow Fe_3O_4 + 4H_2 \qquad (6.6.4)$$

This attack can occur at steam-blanketed boiler surfaces where restricted boiler water flow causes overheating. It may also occur in superheater tubes subjected to overheating. Because this corrosion reaction produces hydrogen, a device for analyzing hydrogen in steam is useful as a corrosion monitor.

6.6.6.3 Carryover

The third major problem related to boiler operations is carryover from the boiler into the steam system. This may be a mechanical effect, such as boiler water spraying around a broken baffle; it may be caused by the volatility of certain boiler water scales, such as silica and sodium compounds; or it may be caused by foaming. Carryover is most often a mechanical problem, and the chemicals

found in the steam are those originally present in the boiler water, plus the volatile components that distill from the boiler even in the absence of spray.

There are three basic means for keeping these major problems under control. External treatment of makeup water, condensate, or both, is performed before their entry into the boiler to reduce or eliminate chemicals (such as hardness or silica), gases or solids. Internal treatment of the boiler feed water, boiler water, steam, or condensate with corrective chemicals may be performed. Control of the concentration of chemicals in the boiler water may be performed by blowdown of the water from the boiler.

6.6.6.4 External Treatment

Most of the unit operations of water treatment can be used alone or in combination with others to adapt any water supply to any boiler system. The suitability of the processes available is judged by the results they produce and the costs involved. Water treatment processes include: sodium zeolite softening, lime softening, lime softening followed by sodium zeolite softening, split stream dealkalization, demineralization, and reverse osmosis.

The boiler treatment program aims at control of seven broad classifications of impurities: suspended solids, hardness, alkalinity, silica, total dissolved solids (TDS), organic matter, and gases.

6.6.6.4.1 Suspended Solids   The removal of suspended solids is accomplished by coagulation/flocculation, filtration, or precipitation. Just about all unit processes require prior removal of solids. For example, water to be processed by ion exchange should contain less that 10 mg/litre suspended solids to avoid fouling of the exchanger and operating problems.

6.6.6.4.2 Hardness   A number of unit operations can remove calcium and magnesium from water, as well as other impurities. Partial cold lime softening and complete hot lime softening are used in most heavy industrial plants. These processes remove hardness, alkalinity, silica, and suspended solids. Sodium exchange can be used alone or in conjunction with lime softening.

6.6.6.4.3 Alkalinity   It is desirable to have some alkalinity in boiler water, so complete removal of alkalinity from boiler makeup is seldom practiced except in demineralization. Some alkalinity is also needed to provide optimum pH in the feed water to prevent corrosion if piping and equipment.

The makeup alkalinity may be present as HCO_3^-, CO_3^{2-}, or OH^-. If the makeup is city water that has been zeolite softened, alkalinity is usually in the bicarbonate (HCO_3^-) form; if lime softened, it is mostly carbonate (CO_3^{2-}), but the water may also contain some hydroxide (OH^-). When bicarbonates and carbonates are exposed to boiler temperatures, they break down to release CO_2:

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2 \qquad (6.6.5)$$

The sodium carbonate then breaks down further to caustic:

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2 \qquad (6.6.6)$$

The carbon dioxide gas redissolves when the steam condenses, producing corrosive carbonic acid:

$$CO_2 + H_2O \rightarrow H^+ + HCO_3^- \qquad (6.6.7)$$

The amount of CO_2 generated is proportional to alkalinity. For a given alkalinity twice as much CO_2 is formed from HCO_3^- as from CO_3^{2-} because the bicarbonate breakdown is the sum of both reactions 6.6.5 and 6.6.7 above. The carbonic acid is usually neutralized by chemical treatment of the steam, either directly or indirectly through the boiler, to produce a condensate pH in the range of 8.5 to 9.0. Reduction of feed water alkalinity is desirable, then, to minimize CO_2 formation and reduce chemical treatment costs.

The hydroxide produced by the breakdown of HCO_3^- and CO_3^{2-} is beneficial for precipitation of magnesium, to provide a good environment for sludge conditioning, and to minimize SiO_2 carryover. However, too high an excess of caustic can be corrosive, particularly if localized concentration can occur. The breakdown of HCO_3^- is complete, but not all the CO_3^{2-} converts to caustic. The

conversion varies from one boiler to another and increases with temperature. As a general rule, at 600 lb/in^2 65 to 85% of boiler water alkalinity is NaOH, the remainder being Na_2CO_3. (This is based on the equilibrium in the cooled sample of boiler water).

The degree of alkalinity reduction is therefore dictated by boiler water control limits and steam quality goals. The best unit process for alkalinity reduction may be chosen for the other benefits it provides as well as its efficiency in alkalinity reduction

6.6.6.4.4 Silica   The permissible concentrations of silica in boiler water at various operating pressures are given in Table 6.37. Silica reduction is not always necessary, especially in the absence of a condensing turbine. Low concentrations of silica can be sometimes produce sticky sludge in low-pressure boilers treated with phosphate. A makeup treatment process may be selected to provide just the proper degree of silica reduction required by the steam system.

Table 6.37 Permissible Concentrations of Silica in Boiler Water at Various Operating Pressures

Drum pressure, (lb/in^2)	Silica concentration, (mg/litres)	
	Recommended	To produce 0.02 mg/litre
0–300	150	150
301–450	90	90
451–600	40	55
601–750	30	35
751–900	20	20
900–1000	8	15

6.6.6.4.5 Total Dissolved Solids   Some treatment processes increase dissolved solids by adding soluble byproducts to water; sodium zeolite softening increases solids by adding an ion (sodium) having a higher equivalent weight (23) than calcium (20) or magnesium (12.2) removed from the raw water. Processes to reduce dissolved solids achieve various degrees of success. Usually, reduction of dissolved solids is accomplished by a reduction of several individual contaminants.

6.6.6.4.6 Organic Matter   Organic matter as a general classification is only a qualitative term. It includes a wide variety of compounds that are seldom analyzed as specific materials. Problems in boiler systems attributed to organic matter have often been traced to organic materials from plant processes in returned condensate, rather than makeup water contaminants. However, in higher pressure utility systems, organic matter is the major impurity in makeup and can result in formation of organic acids.

6.6.6.4.7 Dissolved Gases   Degasifiers are commonly used to remove gas mechanically rather than chemically. Blower types are used for CO_2 removal at ambient temperatures following acid or hydrogen-exchange units. Vacuum degasifiers provide the same extent of CO_2 removal, but also reduce O_2 to less than 0.5 to 1.0 mg/litre, offering corrosion protection, especially if the vacuum degasifier is part of a demineralizing system. Steam-scrubbing degasifiers, call deaerating heaters, usually produce an effluent free of CO_2 with O_2 concentrations in the range of 0.005 to 0.01 mg/litre. Direct reaction of this low residual with catalyzed sulfite, hydrazine, or hydrazine substitutes (all-volatile oxygen-reducing compounds) eliminates O_2 completely to prevent preboiler corrosion.

6.6.6.5 Condensate Returns

In addition to makeup treatment, acceptable feed water quality may require cleanup of condensate to protect the boiler system, particularly if there is process condensate containing oil. Boilers

requiring high-quality demineralized water also demand high-quality condensate. Some plants operate both high- and low-pressure boilers; high-quality feed water for the high pressure boilers may be provided entirely by a demineralizer, with lower quality condensate segregated for return to the low-pressure boilers.

Septum filters are usually selected for oily condensate treatment. A cellulose type filter aid (processed wood pulp) is applied both as a precoat and a body feed. The temperature should be less than 93°C (200°F) to avoid degradation of the filter aid. Anthracite filters precoated with a floc produced from alum and sodium aluminate are also effective. However, the pH of the condensate must be controlled in the range of 7.0 to 8.0 to avoid solubilizing the alumina floc. Condensate contaminated with corrosion products and inleakage of hard water is cleaned up through specially designed, high flow rate sodium exchangers. They have been used to process condensate at temperatures up to 149°C (300°F). One serious limitation of the simple sodium exchanger is its ability to pick up neutralizing amines such as morpholine (present in the condensate as morpholine bicarbonate) and exchange this for sodium. This causes excessive use of amines, but a more serious problem arises if the condensate is returned to a high-pressure boiler where the presence of sodium may be objectionable in deterioration of steam quality. Special regeneration procedures would then be needed.

6.6.6.6 Internal Treatment

Scale formation within a boiler is controlled by one of four chemical programs: coagulation (carbonate), phosphate residual, chelation, or coordinated phosphate.

6.6.6.6.1 Coagulation Program In this process, sodium carbonate, sodium hydroxide, or both are added to the boiler water to supplement the alkalinity supplied by the makeup, which is not softened. The carbonate causes deliberate precipitation of calcium carbonate under favorable, controlled conditions, preventing deposition at some subsequent point as scale. Under alkaline conditions, magnesium and silica are also precipitated as magnesium hydroxide and magnesium silicate. There is usually a fairly high concentration of suspended solids in the boiler water, and the precipitation occurs on these solids. This method of treatment is used only with boilers (usually firetube design) using high-hardness feed water and operating below 250 lb/in^2 (17 bars). This type of treatment must be supplemented by some form of sludge conditioner. Even with a supplemental sludge conditioner, heat transfer is hindered by deposit formation, and blowdown rates are excessive because of high suspended solids. Coagulation programs are becoming obsolete as pretreatment systems become more common and competitive with the high internal treatment cost.

6.6.6.6.2 Phosphate Program Where the boiler pressure is above 250 lb/in^2, high concentrations of sludge are undesirable. In these boilers, feed water hardness should be limited to 60 mg/litre, and phosphate programs are preferred. Phosphate is also a common treatment below 250 lb/in^2 with soft makeup.

A sodium phosphate compound is fed either to the boiler feed water or to the boiler drug, depending on water analysis and the preboiler auxiliaries, to form an insoluble precipitate, principally hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Magnesium and silica are precipitated as magnesium hydroxide, magnesium silicate (often combined as $3MgO \cdot 2SiO_2 \cdot 2H_2O$), or calcium silicate. The alkalinity of the makeup is usually adequate to produce the OH^- for the magnesium precipitation. Phosphate residual programs which produce high suspended solids require the addition of a sludge conditioner/dispersant. Because these programs restrict heat transfer, owing to the deposition of calcium and magnesium salts, precipitation programs of this type are often replaced with solubilizing treatments such as chelants and polymer/dispersants.

6.6.6.6.3 Chelant Programs A chelate is a molecule similar to an ion exchanger; it is low in molecular weight and soluble in water. The sodium salts of ethylene diamine tetraacetic acid (EDTA) and nitrilotriacetic acid (NTA) are the chelating agents most commonly used for internal boiler treatment. These chelate (form complex ions with) calcium and magnesium. Because the resulting com-

plex is soluble, this treatment is advantageous in minimizing blowdown. The higher cost compared to phosphate usually limits the use of chelates to feed waters having low hardness. There is the risk that breakdown of the organic molecule at higher temperatures could create a potential problem of control that could result in corrosion, so chelate programs are usually limited to boilers operating below 1500 lb/in^2 (100 bars). The addition of polymers as scale control agents increases the effectiveness of chelate programs. It also reduces the corrosion potential by reducing the chelant dosage below theoretical requirements, so that there is no chelant residual in the boiler water.

Chelates can react with oxygen under boiler water conditions, which can increase the cost of a chelate program substantially. Overfeed of chelates and concentration mechanisms in the boiler can lead to severe localized corrosion and subsequent unit failure.

6.6.6.6.4 Coordinated Phosphate Program   In high-pressure, high heat transfer rate boilers, the internal treatment program must contribute little or no solids. The potential for caustic attack of boiler metal increases with increasing pressure, so free caustic alkalinity must be minimized. The coordinated phosphate program is chosen for these conditions. This differs from the standard program in that the phosphate is added to provide a controlled pH range in the boiler water as well as to react with calcium if hardness should enter the boiler. Trisodium phosphate hydrolyzes to produce hydroxide ions:

$$Na_3PO_4 + H_2O \rightarrow 3Na^+ + OH^- + HPO_4^{2-} \qquad (6.6.8)$$
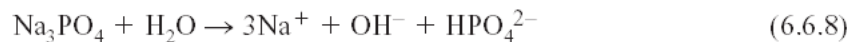
This cannot occur with the ionization of disodium and monosodium phosphate:

$$Na_2HPO_4 \rightarrow 2Na^+ + HPO_4^{2-} \qquad (6.6.9)$$

$$NaH_2PO_4 \rightarrow Na^+ + H^+ + HPO_4^{2-} \qquad (6.6.10)$$
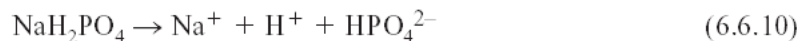
The program is controlled by feeding combinations of disodium phosphate with trisodium or monosodium phosphate to produce pH without the presence of free OH^-. To successfully control a coordinated phosphate program, the feed water must be extremely pure and consistent quality. Coordinated phosphate programs do not reduce precipitation; they simply cause precipitation of less adherent calcium phosphate in the absence of caustic. A dispersant must be added to condition deposits that would otherwise reduce the heat transfer rate. The coordinated phosphate program was first developed for high-pressure utility boilers, and most experience with this program has been gained in this field.

6.6.6.6.5 Complexation and Dispersion   The newest addition to internal treatment technology is the use of synthetic organic polymers for complexation and dispersion. This type of program can be used to 1500 lb/in^2 (100 bars) and is economical in all low-hardness feed water systems typical of those produced by ion exchange. Heat transfer rates are maximized because these polymers produce the cleanest tube surfaces of any of the available internal treatment programs. This treatment solubilizes calcium, magnesium, and aluminum, and maintains silica in solution while avoiding corrosion potential side effects as determined by hydrogen levels in the steam. Iron particulates returned from the condensate system are likewise dispersed for removal via blowdown. A simple measure of ion transport is used to demonstrate on-line performance of this program.

6.6.6.6.6 Program Supplements   In addition to controlling scale and deposits, internal treatment must also control carryover, defined as entrainment of boiler water into the steam. Boiler salts carried as a mist may subsequently deposit in the superheater, causing tube failures or deposit on the blades of a turbine. They may also contaminate a process in which the steam is used. Because a high percentage of carryover is caused by foaming, this program is usually solved by the addition of an antifoam agent to the boiler feed water.

Sludge in boiler water may settle to form deposits, which are as serious a problem as scale. Chemicals are used to condition boiler water particulates so that they do not form large crystalline precipitates; smaller particles will remain dispersed at the velocities encountered in the boiler circuit. At lower pressures both the coagulation and phosphate residual programs incorporate sludge

conditioning agents for this purpose. A variety of natural organic materials are used, including starches, tannins, and lignins.

At intermediate pressures, chemically reacted lignins have been widely used, though synthetic polymers are replacing them. At pressures up to 1800 lb/in^2 (120 bars), heat-stable polymers such as anionic carboxylates and their derivatives are used as effective dispersants. An alkaline environment generally increases their effectiveness. Lignin-type dispersants and other natural organic derivatives are being replaced by these more effective synthetic organic polymers. These dispersants have been designed for specific dispersion problems, with tailored molecules for magnesium silicate, calcium phosphate, and iron particulates being available.

Somewhat related to carryover, in that steam quality is affected, is the discharge of contaminants that volatilize under boiler operating conditions. The major volatiles are CO_2, created by the breakdown of carbonate and bicarbonate mentioned earlier, and SiO_2. Although the CO_2 can be neutralized, it is prudent to reduce feed water alkalinity to minimize its formation. For all practical purposes, external treatment for silica reduction and blowdown are the only means to avoid excessive SiO_2 discharges for protection of turbine blades. Hydroxyl alkalinity helps reduce silica volatility.

Oxygen is the chief culprit in boiler systems corrosion. Deaeration reduces the oxygen to a low concentration in the preboiler system, but does not completely eliminate it. Application of sulfite, hydrazine, or hydrazine-like (all-volatile) compounds after deaeration scavenges the remaining O_2 and maintains a reducing condition in the boiler water. An advantage of hydrazine is that it is discharged into the steam to become available in the condensate as protection against oxygen corrosion in the return system. If oxygen is present, ammonia can attack copper alloys in condensers and stage heaters. The removal of NH_3 by external treatment may be necessary. The corrosive aspects of CO_2 have already been mentioned in relation to condensate systems. The beneficial and detrimental aspects of $NaOH$ in the boiler circuit in relation to corrosion control have also been discussed earlier.

6.6.6.7 Blowdown

Boiler feed water, regardless of the type of treatment used to process the makeup, still contains measurable concentrations of impurities. In some plants, contaminated condensate contributes to feed water impurities. Internal boiler water treatment chemicals also add to the level of solids in the boiler water.

When steam is generated, essentially pure H_2O vapor is discharged from the boiler, leaving the solids introduced in the feed water to remain in the boiler circuits. The net result of impurities being continuously added and pure water vapor being withdrawn is a steady increase in the level of dissolved solids in the boiler water. There is a limit to the concentration of each component of the boiler water. To prevent exceeding these concentration limits, boiler water is withdrawn as blowdown and discharged to water. Blowdown must be adjusted so that the solids leaving the boiler equal those entering and their concentration is maintained at the predetermined limits. Of course it is apparent that the substantial heat energy in the blowdown represents a major factor detracting from the thermal efficiency of the boiler, so minimizing blowdown is a goal in every steam plant. One way of looking at boiler blowdown is to consider it a process of diluting boiler water solids by withdrawing boiler water from the system at a rate that induces a flow of feed water into the boiler in excess of steam demand.

There are two separate blowdown points in every boiler system. One accommodates the blowdown flow that is controlled to regulate the dissolved solids or other factors in the boiler water. The other is an intermittent or mass blowdown, usually from the mud drum or waterwall headers, which is operated intermittently at reduced boiler load to rid the boiler of accumulated settled solids in relatively stagnant areas. The following discussion of blowdown will be confined only to that used for adjusting boiler water dissolved solids concentrations.

Blowdown may be either intermittent or continuous. If intermittent, the boiler is allowed to concentrate to a level acceptable for the particular boiler design and pressure. When this concentration level is reached, the blowdown valve is opened for a short period of time to reduce the concentration of impurities, and the boiler is then allowed to reconcentrate until the control limits are again reached. In continuous blowdown on the other hand, the blowdown valve is kept open at a fixed setting to remove water at a steady rate, maintaining a relatively constant boiler water concentration. Because the average concentration level in a boiler blown down intermittently is substantially less than that maintained by continuous blowdown, intermittent blowdown is less efficient, more costly, than continuous blowdown.

It is common to express blowdown as a percentage of feed water. However, this may give the utilities engineer a false sense of security. If the plant has 80% condensate return and 20% makeup, a 5% blowdown would appear satisfactory, but it indicates that the makeup is being concentrated only four times; of the four units of makeup entering the boiler, one unit is being thrown away. Perhaps that is as much usage as can be made of that particular quality makeup, but the operator should be aware of it.

Because the main purpose of blowdown control is to reach the maximum permissible concentrations for best boiler efficiency without exceeding concentrations that would harm the system, the first step in developing a blowdown control program is to establish allowable limits. The conventional limits recommended to provide boiler cleanliness and adequate steam quality should be followed. These limits cover most situations encountered in industrial boiler operations, but not the coagulation treatment used in low-pressure boilers. With the coagulation treatment, total dissolved solids are usually limited to 3500 mg/litre, and adequate alkalinity is maintained to provide the carbonate for calcium precipitation and the hydroxide for magnesium precipitation. These levels can be established only after the nature of the makeup treatment system has been considered.

The limits on such things as total dissolved solids, silica, and alkalinity are basically related to the amounts of these materials entering the makeup water; these concentrations can be adjusted by blowdown and also by some adjustment in the makeup treatment system if that flexibility is provided. On the other hand, such constituents as phosphate, organics, and sulfite are introduced as internal treatment chemicals, and their concentration can be adjusted both by blowdown and by rate of application.

6.6.6.8 Contaminants in Returned Condensate
With increasing use of demineralized water, even for intermediate pressure boilers (600 to 900 lb/in^2), the major impurities in the feed water are no longer introduced by the makeup water but rather by the returned condensate, principally as corrosion products.

These corrosion products are not solubilized by chelates and are difficult to disperse. If they deposit, boiler salts may concentrate under them because they are relatively porous and permit boiler water to enter with only steam escaping. This may lead to caustic attack. To prevent this, boilers should be cleaned at a set frequency.

The likelihood of alkalinity attack is increased by variable loads and firing conditions, which cause flexing and cracking of the normal dense magnetite film on the boiler metal, exposing fresh metal to attack.

In forced circulation boilers, there is a tendency for deposits to form on the downstream side of flow control orifices. To avoid this, feed water should be free of deposit-forming material, especially corrosion products, so that a chemical program can be applied successfully. Condensate polishing may be required since the condensate is the source of the corrosion products. Steam separators are essential to production of acceptable steam, and their deterioration will depreciate steam quality.

Boilers are often damaged by corrosion during out-of-service periods. Idle boilers are very vulnerable to attack when air contacts moist metal surfaces. To prevent this corrosion, the boiler metal must be protected by either keeping the surfaces completely dry or by excluding all forms of air

from the boiler by completely filling it with properly treated water. Because of variations in boiler design, there is no single, detailed procedure that covers all steps in boiler lay-up, including both chemical and mechanical aspects. The basic principles in protecting boilers against corrosion are simple.

There are two basic ways of laying up boilers: wet and dry. In storing a boiler dry, trays of moisture absorbing chemicals, such as quicklime, are distributed on trays in the boiler drum (or drums) and the boiler is sealed. The alternate method, wet storage, involves forcing air out of the boiler by completely filling to overflow with water which has been specially treated. Nitrogen gas under slight pressure can also be used to displace air and blanket the boiler surfaces. Special consideration must be given to protecting superheaters during lay-up, particularly, the non-drainable type.

The choice between the wet and dry methods of lay-up depends to a great extent on how long the boiler is to be out of service. Dry lay-up is preferable for long outages; the wet method has the advantage of permitting the boiler to be returned to service on reasonably short notice. It is a good idea to drain, flush, and inspect a boiler prior to any lay-up. When times does not permit this, the boiler may be stored wet without first draining it. In this case, the chemical treatment for lay-up, including catalyzed sulfite, caustic, and organic dispersants, is injected into the boiler just before it comes off-line.

6.6.6.9 Condensate Return Systems

Condensate produced when steam is used in any kind of process is seldom cooled measurably below the steam temperature. Because it is hot, close to the steam temperature, the collection system and piping used to handle it must be carefully selected. The piping is generally larger than that used for cold water because pressure drop will cause steam to flash from the flowing condensate, choking the pipe and restricting flow. Condensate may be picked up by a pump for boosting to the best point of return, or it may be delivered to a point of lower pressure simply by the pressure gradient.

Turbine condensate is normally collected in a hotwell, and a level is maintained in the hotwell so that the pump transferring the turbine condenser to the deaerator will have adequate net positive suction head. The level in the hotwell is maintained by returning some of the pump discharge, depending on load fluctuations.

Process condensate is also usually returned by pumps to the deaerating heater. Condensate receivers collect the process condensate and maintain level control so that the pump handling the hot condensate will have adequate suction head. Even so, special designs of centrifugal pumps are usually required for handling hot condensate. Stage heater condensates are normally handled by gravity, returning to a lower pressure stage heater, the deaerator, or even the condenser hotwell.

Once the condensate has been collected, the proper point of return must be decided upon. In the utility station, the entire flow of condensate may be polished through some type of ion exchange system before being returned to the deaerating heater. In industrial plants, if the condensate is contaminated it will be sent to a treatment plant before returning to the deaerator. For the most part, condensates are returned to the deaerating element itself, as they may contain dissolved oxygen and other gases; however, high-pressure returns free of dissolved oxygen may be sent directly to the storage section of the deaerating heater to flash and supply steam for the deaerating operation.

For the most part, the condensate handling system is of ordinary carbon steel construction, although pump impellers, valve trim, and heat exchange tubes are usually of copper alloys. Because the condensate is usually hot, if corrosive agents are present the rate of corrosion will usually be greater than what would be expected in cold water. The principal agents of corrosion are carbon dioxide and oxygen. The CO_2 is normally produced by the breakdown of alkalinity in the boiler and the oxygen may be drawn into the system by inleakage of air or of water containing dissolved oxygen (pump sealing water, for example). Inspection of the condensate piping provides a good clue as to the cause of corrosion. The principal cause of corrosion of copper alloys is ammonia in systems containing O_2.

Without adequate treatment of the steam, the pH of condensate would normally be low because of the presence of carbon dioxide. The application of volatile alkaline amines will control attack by neutralizing carbonic acid, thus raising the pH value of the system. In a tight system, the neutralizing amine is often adequate for the complete corrosion control program. However, many systems are operated intermittently or under throttling (flow-restricting) conditions where oxygen inleakage can occur. At these higher levels of oxygen, neutralization is inadequate as the sole protective measure against corrosion of steel piping. In such cases, volatile filming amines are added to the stream, which upon condensation produce a waxy substance on the metal and provide a barrier between the flowing condensate and the pipe wall so that corrosion cannot occur.

Hydrazine and other all-volatile oxygen scavengers may be used both for pH correction and oxygen scavenging, but it becomes uneconomical when high levels of carbon dioxide and oxygen occur, a common condition in most industrial operations.

In plants where gross contamination occurs, the source and cause should be located and corrected. An example of such an occurrence is the use of steam for producing hot water through a heat exchanger. The industrial operation may require hot water at a specific temperature, 150°F for example, and a thermostatic element is installed in the water line to regulate the steam flow into the heat exchanger according to water flow and exit temperature. At low water flows where the steam demand is low, the steam admission valve may be so fully throttled that there is actually a vacuum in the vapor space. Most of these systems are designed for pressure operation, and under vacuum, air leakage is common. If a neutralizing amine is used in a system of this kind, it may be easy to locate inleakage of this sort because the air in the industrial atmosphere will contain enough CO_2 to drop the pH of the condensate at that particular point. Thus, a way to find the source of air inleakage in a complex industrial plant is to sample condensate at all sources and compare the pH of the sample condensate with the pH of a condensed steam sample or a sample of condensate known to be free of atmospheric contamination.

Where the attack of copper alloy has been found to be caused by ammonia, filming inhibitors will usually prevent further attack by preventing O_2 from reaching the surface. If the ammonia concentration is high, reduction of ammonia in the pretreatment system should be considered.

6.6.6.9.1 Neutralizing Amines   The most commonly used neutralizing inhibitors are amines such as morpholine, cyclohexylamine, and diethylaminoethanol. The ability of each product mentioned to enter the condensate or water phase is indicated by its vapor-to-liquid distribution ratio, Table 6.38. This ratio compares the concentration of amine in the vapor phase to the concentration in the water phase.

Table 6.38 Amine Vapor-to-Liquid Distribution Ratios

Product	Vapor-to-liquid distribution ratio[a]
Morpholine	0.4
Cyclohexylamine	4.0
Diethylaminoethanol	1.7

[a] At atmospheric pressure.

In order to neutralize carbonic acid, the amine must be present in the water phase. The distribution ratio indicates the preference of an amine for the water phase or the vapor phase. An amine such as morpholine, preferring the water phase, will be present in the initially formed condensate at high temperatures. On the other hand cyclohexylamine tends to remain with the steam to enter the condensate as the temperatures decrease.

Because of their differing vapor-to-liquid distribution ratios, two or more such amines may be used together to provide the effective neutralization programs for complex systems.

Neutralizing amines are fed to the feed water after deaeration, boiler steam drum, or steam header. They are controlled by monitoring the returned condensate pH from samples taken at the beginning, middle, and end of a condensate system.

6.6.6.9.2 Filming Inhibitors   Inhibitors used to film condensate systems are amines with chain-like molecules. One end of each molecule is hydrophilic (loves water), and the other end hydrophobic (hates water). The hydrophilic end attaches to the metal, leaving the other end to repel water. As the molecules accumulate, the surface becomes non-wettable. The film, therefore, provides a barrier against metal attack by water containing carbon dioxide, oxygen, or ammonia. Because the molecules also repel each other, they do not tend to build up layers or thick films. Instead, they remain a monomolecular protective film.

A film one molecule thick actually improves heat transfer in condensers, dryers, and other heat exchange equipment. By promoting dropwise condensation, an insulating water film between the water and metal surface is prevented.

Good distribution of filming inhibitors is of prime importance in preventing condensate corrosion. Protection depends on the maintenance of a continuous film. Because steam and condensate can wash away the film, it must be constantly repaired by continuous feed of the inhibitor.

Octadecylamine and certain of its salts were the first chemicals to be used as filming inhibitors in steam-condensate systems. However, because of their wax-like nature (whether supplied in flake or emulsion form), it was difficult to put these chemicals into uniform solutions for feeding. A relatively narrow condensate pH range of 6.5 to 8.0 is required for the octadecylamine to form a film and to remain on the metal surface. To overcome these limitations molecules formulated specifically for boiler plant conditions have been developed as alternatives to octadecylamine.

Most filming inhibitors are normally fed to the steam header, but may be fed to the feed water or boiler drum; the latter feed points result in some loss of product to blowdown. If only the process equipment needs protection, the inhibitor may be conveniently fed into the desuperheating water at the process steam header. Regardless of the feed point, however, the inhibitor should be fed continuously for best results. Dosages are not based on oxygen or carbon dioxide content of the steam. The amount of inhibitor required is set according to the system surface area. Creation of an effective film is a physical process, highly dependent on flow rates, feeding, and testing techniques.

6.6.6.10 Evaluating Results

There are several good ways of determining how much corrosion is occurring in a system and how effective a prevention program is. Because this requires extensive monitoring, it is essential that sampling be done at the significant points of the system and with adequate facilities. There must be a quill installed in the line that projects into the flowing stream; a sample taken along the pipe wall is meaningless. Sample lines must be of stainless-steel tubing.

6.6.6.10.1 pH Monitoring   This involves checking the pH throughout a system, necessary to make sure that: sufficient amine is being fed to neutralize carbon dioxide, the proper amine is used to give total system protection, and process contamination or air inleakage is not occurring.

When taking condensate samples, to avoid carbon dioxide flashing off and giving false results, the sample must be cooled prior to contact with the atmosphere. This means using a sample cooler attached to the condensate line. The sample may be throttled at the outlet but not at the inlet. This is done to prevent a vacuum from occurring in the coil and drawing in air, which will give false results. Failure to set up a cooler properly will give inaccurate and misleading results.

6.6.6.10.2 Conductivity Monitoring   The conductivity of the returning condensate can be an indicator of process contaminants and corrosion.

6.6.6.10.3 Carbon Dioxide Testing   By actually measuring the carbon dioxide content of the condensate, the problem of corrosion from carbon dioxide can be directly monitored.

6.6.6.10.4 Hardness   Similar to conductivity measurement, this can be an indicator of process contaminants, particularly from cooling water leakage.

6.6.6.10.5 Test Nipples   The use of test nipples, installed in steam or condensate lines, permits both visual inspection of system conditions and a measure of corrosion.

6.6.6.10.6 Test Coupons   These have also been used to evaluate condensate corrosion conditions. Preweighed coupons in holders are inserted into condensate lines. After an arbitrary time interval (usually at least 30 days), the coupons are removed, cleaned, and reweighed. The difference in original and final weight, when coupon surface area and exposure time are known, gives an indication of rate of metal loss owing to corrosion. It should be noted, however, that such test coupons usually cannot identify bottom grooving and threaded-joint corrosion as they occur in actual piping.

6.6.6.10.7 Iron and Copper   Testing for corrosion products (iron and copper) in condensate is a preferred and widely used means of observing corrosion trends. Because metal corrosion products in condensate are mainly present as insoluble particulates rather than in dissolved form, methods of sampling that insure representative and proportional collection of particulates are important.

A general level of corrosion products in the 0–50 μg/litre range indicates the system is in control. Because of the problem of sampling error when looking for this small quantity of particulates, a relatively large amount of sample needs to be run. Two accepted methods used are visual estimation and quantitative measurement.

Visual estimation of iron concentration is based on the relative degree of discoloration of a membrane filter through which a known volume of condensate is passed. Estimation is made by comparing the membrane pad, after filtration of the sample, with prepared standard pads having color equivalents for specific iron values.

Very precise quantitative determinations of total iron and copper values are easily made by the Analex method. In this procedure, a sample stream of condensate is allowed to flow through a small plastic cartridge containing a high-purity filter of ion exchange materials for a period of 7 to 30 days. Particulates are captured by filtration, while dissolved solids are retained by ion exchange. By a unique laboratory process, the total weight of each metal is calculated. A series of successive analyses gives a complete and accurate picture of condensate corrosion trends. Normally, when inhibitors are used in a system previously untreated, the corrosion products observed in the condensate will increase temporarily. Most inhibitors have a detergent effect and tend to slough off old oxides. This must be taken into consideration when evaluating test results.

Normally a plant uses more than one of the above monitoring methods (e.g. pH monitoring and corrosion coupons). Although it may seem inconvenient when initially setting up a program to monitor the condensate, the results are more than worth the time invested in avoiding downtime and gaining energy savings in the high-heat value and high-purity of the returned condensate.

6.6.6.11 Steam Sampling

The most difficult sampling is of the steam itself as a representative sample is hard to obtain without making special provisions for it. The ASTM recommended procedure for sampling steam and condensing this for analysis should be followed. The analysis may only require a determination of pH to establish the level produced by the application of a neutralizing amine as a benchmark for interpreting the pH of samples of condensate. On the other hand, steam sampling is extremely valuable as a means of locating sources of trouble in a system.

Hydrogen analysis of steam will help determine boiler corrosion rate with respect to steaming load. Hydrogen evolution results from active corrosion cells or chemical decomposition. Experienced consultants should conduct these tests so that correct interpretations can be made. The corrosion action within the boiler can be easily observed on the hydrogen analyzer chart; destruction of the protective film of magnetite produces hydrogen directly from the attack of the boiler steel.

A common method for determining steam quality is by use of the specific ion electrode for sodium. As the salts dissolved in the boiler water are sodium salts, the presence of sodium in the steam sample is a direct indication of carryover. A trained steam purity consultant should be contracted.

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