CHAPTER
1
DEFINITIONS AND TERMINOLOGY

There is probably no one who can testify with any degree of accuracy (although there is always someone who can testify with a high degree of uncertainty) as to the last time Earth was pristine and unpolluted. Yet, to attempt to return the environment to such a mythical time might have a severe effect on current indigenous life, perhaps a form of pollution in reverse!

However, there is the possibility that through the judicious use of resources and application of the principles of environmental analysis, environmental science, and environmental (disciplines involved in the study of the environment) (Speight, 1996; Manahan, 1999; Woodside, 1999), we can come to a state where pollution is minimal and not a threat to the future. Such a program will involve not only well-appointed suites of analytical tests but also subsequent studies, that range from the effects of changes in the environmental conditions on the flora and fauna of a region to the more esoteric studies of animals in laboratories. These studies can include aspects of chemistry, chemical engineering, microbiology, and hydrology as they can be applied to solve environmental problems (Pickering and Owen, 1994; Speight, 1996; Schwarzenbach et al., 2003; Tinsley, 2004). As an historical aside, environmental engineering (formerly known as sanitary engineering) originally developed as a subdiscipline of civil engineering.

Despite numerous safety protocols that are in place and the care taken to avoid environmental incidents (EPA, 2004), virtually every industry suffers accidents that lead to environmental problems, complexities, and chemical contamination. The petroleum industry is no exception to such accidents. It is therefore helpful to be aware of the nature of the raw material and the products arising therefrom, in order to understand the nature of any contamination and thus the best cleanup methods to choose.

Frequently, the existence and source of such information is unknown thus the data are not examined. Even when the existence and sources of information are known, decisions must be made in order to make an informed, and often quick decision on the next steps, even if later, one decides not to use it for a particular application. Knowing about the relevant data gives investigators and analysts the ability to assess the data based on quality assurance criteria. This is especially true for users near the end of long decision processes, such as site cleanup, ecological risk assessments, and natural resource damage assessments.

Environmental Analysis and Technology for the Refining Industry, by James G. Speight

Considering the composition of petroleum and petroleum products (Speight, 1994, 1999), it is not surprising that petroleum and petroleum-derived chemicals are environmental pollutants (Loeher, 1992; Olschewsky and Megna, 1992). The world's economy is highly dependent on petroleum for energy production, and widespread use has led to enormous releases to the environment of petroleum, petroleum products, exhaust from internal combustion engines, emissions from oil-fired power plants, and industrial emissions where fuel oil is employed.

The toxicity of polynuclear aromatic hydrocarbons is perhaps one of the most serious long-term problems associated with the use of petroleum. They comprise a large class of petroleum compounds containing two or more benzene rings. Polynuclear aromatic hydrocarbons are formed in nature by long-term, low-temperature chemical reactions in sedimentary deposits of organic materials and in high-temperature events such as volcanoes and forest fires. The major source of this pollution is, however, human activity. Polynuclear aromatic hydrocarbons accumulate in soil, sediment, and biota. At high concentrations, they can be acutely toxic by disrupting membrane function. Many cause sunlight-induced toxicity in humans and fish and other aquatic organisms. In addition, long-term chronic toxicity has been demonstrated in a wide variety of organisms. Through metabolic activation, some polynuclear aromatic hydrocarbons *form* reactive intermediates that bind to deoxyribonucleic acid (DNA). For this reason, many of these hydrocarbons are *mutagenic* (tending to cause mutations), *teratogenic* (tending to cause developmental malformations), or *carcinogenic* (tending to cause cancer).

The terminology found in the various areas of petroleum and environmental technology can be extremely confusing to the uninitiated; excellent examples of the confusion that abounds are to be found (Speight, 1990, 1994, 1999). As a beginning of this process of data examination and ingestion, in this chapter we introduce the terminology of environmental technology and petroleum. Chemical waste, as it pertains to petroleum, is also defined and classified into various subgroups.

1.1. THE ENVIRONMENT

To start with an extremely relevant definition, *environmental technology* is the application of scientific and engineering principles to the study of the environment, with the goal of improvement of the environment. Furthermore, issues related to the pollution of the environment are relative.

Any organism is exposed to an *environment*, even if the environment is predominantly many members of the same organism. An example is a bacterium in a culture that is exposed to many members of the same species. Thus, the environment is all external influences, abiotic (physical factors) and biotic (actions of other organisms), to which an organism is exposed. The environment affects basic life functions, growth, and the reproductive success of organisms, and determines their local and geographic distribution patterns. A fundamental idea in *ecology* is that the environment changes in time and space and that living organisms respond to these changes.

Since ecology is that branch of science related to the study of the relationship of organisms to their environment, an *ecosystem* is an ecological community (or living unit) considered together with the nonliving factors of its environment as a unit. By way of brief definition, *abiotic factors* include such influences as light radiation (from the sun), ionizing radiation (cosmic rays from outer space), temperature (local and regional variations), water (seasonal and regional distributions), atmospheric gases, wind, soil (texture and composition), and catastrophic disturbances. The latter phenomena are usually unpredictable and infrequent, such as fire, hurricanes, volcanic activity, landslides, major floods, and any disturbance that drastically alters the environment and thus changes the species composition and activity patterns of the inhabitants.

On the other hand, *biotic factors* include natural interactions (e.g., predation and parasitism) and anthropogenic stress (e.g., the effect of human activity on other organisms). Because of the abiotic and biotic factors, the environment to which an organism is subjected can affect the life functions, growth, and reproductive success of the organism and can determine the local and geographic distribution patterns of the organism.

Living organisms respond to changes in the environment either by adapting or by becoming extinct. The basic principles of the concept that living organisms respond to changes in the environment were put forth by Darwin and Lamarck. The former noted the slower adaptation (evolutionary trends) of living organisms, while the latter noted the more immediate adaptation of living organisms to the environment. Both essentially espoused the concept of the survival of the fittest, alluding to the ability of an organism to live in harmony with its environment. This was assumed to indicate that organisms that competed successfully with environmental forces would survive. However, there is the alternative thought: that organisms that can live in a harmonious symbiotic relationship with their environment have an equally favorable chance of survival. The influence of the environment on organisms can be viewed on a large scale (i.e., the relationship between regional climate and geographic distribution of organisms) or on a smaller scale (i.e., some highly localized conditions determine the precise location and activity of individual organisms).

Organisms may respond differently to the frequency and duration of a given environmental change. For example, if some individual organisms in a population have adaptations that allow them to survive and to reproduce under new environmental conditions, the population will continue but the genetic composition will have changed (Darwinism). On the other hand, some organisms have the ability to adapt to the environment (i.e., to adjust their physiology or morphology in response to the immediate environment) so that the new environmental conditions are less (certainly no more) stressful than the previous conditions. Such changes may not be genetic (Lamarckism).

In terms of *anthropogenic stress* (the effect of human activity on other organisms), there is a need for the identification and evaluation of the potential impacts of proposed projects, plans, programs, policies, or legislative actions on the physical–chemical, biological, cultural, and socioeconomic components of the environment. This activity, also known as *environmental impact assessment* (EIA), refers to the interpretation of the significance of anticipated changes related to a proposed project. The activity encourages consideration of the environment and arriving at actions that are environmentally compatible.

Identifying and evaluating the potential impact of human activities on the environment requires the identification of mitigation measures. *Mitigation* is the sequential consideration of the following measures: (1) avoiding the impact by not taking a certain action or partial action; (2) minimizing the impact by limiting the degree or magnitude of the action and its implementation; (3) rectifying the impact by repairing, rehabilitating, or restoring the affected environment; (4) reducing or eliminating the impact over time by preservation and maintenance operations during the life of the action; and (5) compensating for the impact by replacing or providing substitute resources or environments.

Nowhere is the effect of anthropogenic stress felt more than in the development of natural resources of the Earth. Natural resources are varied in nature and often require definition. For example, in relation to mineral resources, for which there is also descriptive nomenclature (ASTM C294), the terms related to the available quantities of the resource must be defined. In this instance, the term *resource* refers to the total amount of the mineral that has been estimated to be available ultimately. The term *reserves* refers to well-identified resources that can profitably be extracted and utilized by means of existing technology. In many countries, fossil fuel resources are often classified as a subgroup of the total mineral resources.

In some cases, environmental pollution is a clear-cut phenomenon, whereas in others it remains a question of degree. The ejection of various materials into the environment is often cited as pollution, but there is the ejection of beneficial chemicals that can assist the air, water, and land to perform their functions. However, it must be emphasized that even though certain chemicals are indigenous to an environment, their ejection into the environment, in quantities above the naturally occurring limits can be extremely harmful. In fact, the timing and the place of a chemical release are influential in determining whether a chemical is beneficial, benign, or harmful! Thus, what may be regarded as a pollutant in one instance can be a beneficial chemical in another instance. The phosphates in fertilizers are examples of useful (beneficial) chemicals, whereas phosphates generated as by-products in the metallurgical and mining industries may, depending on the specific industry, be considered pollutants (Chenier, 1992). In this case, the means by which such pollution can be prevented must be recognized (Breen and Dellarco, 1992). Thus, increased use of Earth's resources as well as the use of a variety of chemicals that are nonindigenous to the Earth have put a burden on the ability of the environment to tolerate such materials.

Finally, some recognition must be made of the term *carcinogen* since many of the environmental effects noted in this book can lead to cancer. *Carcinogens* are cancer-causing substances, and there is a growing awareness of the presence of carcinogenic materials in the environment. A classification scheme is provided for such materials (Table 1.1). The number of substances with which a person

Table 1.1. Weight-of-Evidence Carcinogenicity Classification Scheme as Determined by the U.S. Environmental Protection Agency

Group	Description
A	Human carcinogen
B1	Probable human carcinogen; limited human data are available
B2	Probable human carcinogen; carcinogen in animals but inadequate evidence in humans
C	Possible human carcinogen
D	Not classifiable as a human carcinogen
E	No carcinogenic activity in humans

Source: Zakrzewski, 1991; Milman and Weisburger, 1994.

comes in contact are in the tens of thousands and there is not a full understanding of the long-term effects of these substances in their possible propensity to cause genetic errors that ultimately lead to carcinogenesis. *Teratogens* are substances that tend to cause developmental malformations.

Pollution is the introduction of indigenous (beyond the natural abundance) and nonindigenous (artificial) gaseous, liquid, and solid contaminants into an ecosystem. The atmosphere and water and land systems have the ability to cleanse themselves of many pollutants within hours or days, especially when the effects of the pollutant are minimized by the natural constituents of the ecosystem. For example, the atmosphere might be considered to be self-cleaning as a result of rain. However, removal of some pollutants from the atmosphere (e.g., sulfates and nitrates) by rainfall results in the formation of *acid rain*, which can cause serious environmental damage to ecosystems within the water and land systems (Johnson and Gordon, 1987; Pickering and Owen, 1994).

Briefly, lakes in some areas of the world are now registering a low pH (acidic) reading because of excess acidity in rain. This was first noticed in Scandinavia and is now prevalent in eastern Canada and the northeastern United States. Normal rainfall has a pH of 5.6, and thus slight acidity (neutral water has a pH equal to 7.0), because the carbon dioxide (CO_2) in the air combines with water to form carbonic acid (H_2CO_3):

$$CO_2 + H_2O \rightarrow H_2CO_3$$

The increased use of hydrocarbon fuels in the last five decades is slowly increasing the concentration of carbon dioxide in the atmosphere, which produces more carbonic acid, leading to an imbalance in the natural carbon dioxide content of the atmosphere, which, in turn, leads to more acidity in the rain. In addition, there is a *greenhouse effect*, and the average temperature of the Earth may be increasing.

In addition, excessive use of fuels with a high sulfur and nitrogen content causes sulfuric and nitric acids in the atmosphere from sulfur dioxide and nitrogen oxide products of combustion, which can be represented simply as

$$SO_2 + H_2O \rightarrow H_2SO_3 \quad \text{(sulfurous acid)}$$

$$2SO_2 + O_2 \rightarrow 2SO_3$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \quad \text{(sulfuric acid)}$$

$$NO + H_2O \rightarrow HNO_2 \quad \text{(nitrous acid)}$$

$$2NO + O_2 \rightarrow NO_2$$

$$NO_2 + H_2O \rightarrow HNO_3 \quad \text{(nitric acid)}$$

A *pollutant* is a substance (for simplicity most are referred to as *chemicals*) present in a particular location when it is not indigenous to the location or is in a greater-than-natural concentration. The substance is often the product of human activity. By virtue of its name, the pollutant has a detrimental effect on the environment, in part or *in toto*. Pollutants can also be subdivided into two classes, primary and secondary:

source → primary pollutant → secondary pollutant

Primary pollutants are those pollutants emitted directly from the source. In terms of atmospheric pollutants by petroleum constituents, examples are hydrogen sulfide, carbon oxides, sulfur dioxide, and nitrogen oxides from refining operations (see above). The question of classifying nitrogen dioxide and sulfur trioxide as primary pollutants often arises, as does the origin of the nitrogen. In the former case, these higher oxides can be formed in the upper levels of the combustors. The nitrogen from which the nitrogen oxides are formed does not originate solely from the fuel but may also originate from the air used for the combustion.

Secondary pollutants are produced by interaction of primary pollutants with another chemical or by dissociation of a primary pollutant, or by other effects within a particular ecosystem. Again, using the atmosphere as an example, formation of the constituents of acid rain is an example of the formation of secondary pollutants (see above).

A *contaminant*, which is not usually classified as a pollutant unless it has some detrimental effect, can cause deviation from the normal composition of an environment.

A *receptor* is an object (animal, vegetable, or mineral) or a locale that is affected by a pollutant.

A *chemical waste* is any solid, liquid, or gaseous waste material that if improperly managed or disposed of, may pose substantial hazards to human health and the environment (Table 1.2). At any stage of the management process, a chemical waste may be designated by law as a *hazardous waste* (Chapter 12). Improper disposal of such waste streams in the past has created a need for very expensive cleanup operations (Tedder and Pohland, 1993). Correct handling of such

Table 1.2. Types of Chemical Waste

Source	Waste Type
Chemical manufacturers	Strong acids and bases Spent solvents Reactive materials
Vehicle maintenance shops	Heavy-metal paints Ignitable materials Used lead–acid batteries Spent solvents
Printing industry	Heavy-metal solutions Waste ink Spent solvents Spent electroplating wastes Ink sludge containing heavy metals
Leather products	Waste toluene and benzene
Paper industry	Paint wastes containing heavy metals
Construction industry	Ignitable paint wastes Spent solvents Strong acids and bases
Cleaning agents and cosmetics manufacturing	Heavy-metal dusts Ignitable materials Flammable solvents Strong acids and bases
Furniture and wood manufacturing and refinishing	Ignitable materials Spent solvents
Metal manufacturing	Paint wastes containing heavy metals Strong acids and bases Cyanide wastes Sludge containing heavy metals

chemicals (NRC, 1981), can, in addition to dispensing with many of the myths related to chemical processing (Kletz, 1990), mitigate some of the problems that occur when incorrect handling is the norm!

1.2. PETROLEUM

Petroleum, and the equivalent term *crude oil*, cover a wide assortment of materials consisting of mixtures of hydrocarbons and other compounds that contain variable amounts of sulfur, nitrogen, and oxygen and which may vary widely in volatility, specific gravity, and viscosity. Metal-containing constituents, notably those compounds that contain vanadium and nickel, usually occur in the more viscous crude oils in amounts up to several thousand parts per million and can have serious consequences during processing of these feedstocks (Speight, 1999, and references cited therein). Because petroleum is a mixture of widely varying constituents and proportions, its physical properties also vary widely, as does its color, from colorless to black.

Indeed, petroleum reservoirs have been found in vastly different parts of the world and their chemical composition varies greatly. Consequently, no single petroleum composition can be defined. Thus, petroleum-derived inputs to the environment vary considerably in composition, and the complexity of petroleum composition is matched by the range of properties of the components and the physical, chemical, and biochemical processes that contribute to the distributive pathways and determine the fate of the inputs.

Put simply, petroleum is a naturally occurring mixture of hydrocarbons, generally in a liquid state, which may include compounds of sulfur, nitrogen, oxygen, metals, and other elements (ASTM, 2004). In more specific terms, petroleum has also been defined (ITAA, 1936) as:

1. Any naturally occurring hydrocarbon, whether in a liquid, gaseous, or solid state;
2. Any naturally occurring mixture of hydrocarbons, whether in a liquid, gaseous, or solid state; or
3. Any naturally occurring mixture of one or more hydrocarbons, whether in a liquid, gaseous, or solid state, and one or more of the following: hydrogen sulfide, helium, and carbon dioxide.

The definition includes any petroleum as defined above that has been returned to a natural reservoir.

In terms of the elemental composition of petroleum, the carbon content is relatively constant; it is the hydrogen and heteroatom contents that are responsible for the major differences. Nitrogen, oxygen, and sulfur are present in only trace amounts in some petroleum, which thus consists primarily of hydrocarbons. On the other hand, a crude oil containing 9.5% heteroatoms may contain essentially no true hydrocarbon constituents insofar as the constituents contain *at least one or more* nitrogen, oxygen, and/or sulfur atoms within the molecular structures.

There are also other *types* of petroleum that differ from conventional petroleum insofar as they are much more difficult to recover from subsurface reservoirs. These materials have a much higher viscosity (and lower API gravity) than those of conventional petroleum, and primary recovery of these petroleum types usually requires thermal stimulation of the reservoir (Speight, 1999, and references cited therein).

When petroleum occurs in a reservoir that allows the crude material to be recovered by pumping operations as a free-flowing dark- to light-colored liquid, it is often referred to as *conventional petroleum*. Heavy oils comprise the other *types* of petroleum; they differ from conventional petroleum in being much more difficult to recover from subsurface reservoirs. The definition of heavy oils is usually based on the API gravity or viscosity value, and the definition is quite arbitrary, although there have been attempts to rationalize the definition based on viscosity, API gravity, and density.

In addition to attempts to define petroleum, heavy oil, bitumen, and residua, there have been several attempts to classify these materials by the use of properties such as API gravity, sulfur content, or viscosity (Speight, 1999). However, any attempt to classify petroleum, heavy oil, and bitumen on the basis of a single property is no longer sufficient to define the nature and properties of petroleum and petroleum-related materials, perhaps even being an exercise in futility.

For many years, petroleum and heavy oil were very generally defined in terms of physical properties. For example, heavy oil was considered to be a crude oil that had gravity between 10 and 20° API. For example, Cold Lake heavy crude oil (Alberta, Canada) has an API gravity equal to 12°, but extra-heavy oil (such as tar sand bitumen), which requires recovery by nonconventional and nonenhanced methods, has an API gravity in the range 5 to 10°. Residua would vary depending on the temperature at which distillation was terminated, but vacuum residua were usually in the range 2 to 8° API.

However, to define conventional *petroleum, heavy oil*, and *bitumen*, the use of a single physical parameter such as API gravity or viscosity is not sufficient and is only a general indicator of the nature of the material. Other properties, such as the method of recovery, composition, and most of all, the properties of the bulk deposit, must also be included in any definition of these materials. Only then will it be possible to classify petroleum and its derivatives (Speight, 1999).

A *residuum* (pl. *residua*, also shortened to *resid*, pl. *resids*) is the residue obtained from petroleum after nondestructive distillation has removed all the volatile materials. The temperature of the distillation is usually maintained below 350°C (660°F), since the rate of thermal decomposition of petroleum constituents is minimal below this temperature but the rate of thermal decomposition of petroleum constituents is substantial above 350°C (660°F) (Speight, 1999, and references cited therein).

Residua are black, viscous materials obtained by distillation of a crude oil under atmospheric pressure (atmospheric residuum) or under reduced pressure (vacuum residuum). They may be liquid at room temperature (generally, atmospheric residua) or almost solid (generally, vacuum residua) depending on the cut point of the distillation or depending on the nature of the crude oil (Speight, 1999; Speight and Ozum, 2002).

1.3. CLASSIFICATION

By definition, *petroleum* (also called *crude oil*) is a mixture of gaseous, liquid, and solid hydrocarbon compounds. Petroleum occurs in sedimentary rock deposits throughout the world and contains small quantities of nitrogen-, oxygen-, and sulfur-containing compounds as well as trace amounts of metallic constituents (Long and Speight, 1998; Reynolds, 1998; Speight, 1999, and references cited therein). Thus, the classification of petroleum as a hydrocarbon mixture should follow from this definition, but some clarification is required.

The original methods of classification arose because of commercial interest in petroleum type and were a means of providing refinery operators with a rough guide to processing conditions. It is therefore not surprising that systems based on a superficial inspection of a physical property, such as specific gravity or API (Baumé) gravity, are easily applied and are actually used to a large extent in expressing the quality of crude oils. Such a system is approximately indicative of the general character of a crude oil as long as materials of one general type are under consideration. For example, among crude oils from a particular area, an oil of 40° API (specific gravity = 0.825) is usually more valuable than one of 20° API (specific gravity = 0.934) because it contains more light fractions (e.g., gasoline) and fewer heavy, undesirable asphaltic constituents.

1.3.1. Chemical Composition

Composition refers to the specific mixture of chemical compounds that constitute petroleum. The composition of these materials is related to the nature and mix of the organic material that generated the hydrocarbons. Composition is also subject to the influence on that composition of natural processes such as migration (movement of oil from source rock to reservoir rock), biodegradation (alteration by the action of microbes), and water washing (effect of contact with water flowing in the subsurface) (Speight, 1993, 1999). Thus, petroleum is the result of the metamorphosis of natural products as a result of chemical and physical changes imparted by the prevailing conditions at a particular locale.

Petroleum varies in appearance from a thin (mobile), nearly colorless liquid to a thick (viscous), almost black oil. The specific gravity at 15.6°C (60°F) varies correspondingly from about 0.75 to 1.00 (57 to 10° API), with the specific gravity of most crude oils falling in the range 0.80 to 0.95 (45 to 17° API). Thus, it is not surprising that petroleum varies in composition from one oil field to another, from one well to another in the same field, and even from one level to another in the same well. This variation can be in both molecular weight and the types of molecules present in petroleum. Petroleum may well be described as a mixture of organic molecules drawn from a wide distribution of molecular types that lie within a wide distribution of molecular weights.

By definition, *a hydrocarbon contains carbon and hydrogen only*. On the other hand, if an organic compound contains nitrogen, and/or sulfur, and/or oxygen, and/or metals, it is a heteroatomic compound and not a hydrocarbon. Organic compounds containing heteroelements (elements such as nitrogen, oxygen, and sulfur), in addition to carbon and hydrogen, are defined in terms of the locations of these heteroelements within the molecule. In fact, it is, to a large extent, the heteroatomic function that determines the chemical and physical reactivity of the heteroatomic compounds; and the chemical and physical reactivity of the heteroatomic compounds is quite different from the chemical and physical reactivity of the hydrocarbons.

Petroleum is a *naturally occurring hydrocarbon insofar* as it contains compounds that are composed of carbon and hydrogen only which do not contain any heteroatoms (nitrogen, oxygen, and sulfur as well as compounds containing metallic constituents, particularly vanadium, nickel, iron, and copper). The hydrocarbons found in petroleum are classified into the following types (Chapter 2):

1. *Paraffins*, saturated hydrocarbons with straight or branched chains but without a ring structure.
2. *Cycloparaffins* (*naphthenes*), saturated hydrocarbons containing one or more rings, each of which may have one or more paraffinic side chains (more correctly known as *alicyclic hydrocarbons*).
3. *Aromatics*, hydrocarbons containing one or more aromatic nuclei, such as benzene, naphthalene, or phenanthrene ring systems, that may be linked up with (substituted) naphthalene rings and/or paraffinic side chains.

On this basis, petroleum may have some value in the crude state but, when refined, provides fuel gas, petrochemical gas (methane, ethane, propane, and butane), transportation fuel (gasoline, diesel fuel, aviation fuel), solvents, lubricants, asphalt, and many other products. In addition to the hydrocarbon constituents, petroleum does contain heteroatomic (nonhydrocarbon) species, but they are in the minority compared to the number of carbon and hydrogen atoms. They do, nevertheless, impose a major influence on the behavior of petroleum and petroleum products as well as on the refining processes (Speight and Ozum, 2002).

A widely used classification of petroleum distinguishes between crude oils either on a *paraffin base* or on an *asphalt base* and arose because paraffin wax separates from some crude oils on cooling, whereas other oils show no separation of paraffin wax on cooling. The terms *paraffin base* and *asphalt base* were introduced and have remained in common use (van Nes and van Westen, 1951).

The presence of paraffin wax is usually reflected in the paraffinic nature of the constituent fractions, and a high asphaltic content corresponds with the naphthenic properties of the fractions. As a result, the misconception has arisen that paraffin-base crude oils consist mainly of paraffins and asphalt-base crude oils mainly of cyclic (or *naphthenic*) hydrocarbons. In addition to paraffin- and asphalt-base oils, a mixed base had to be introduced for those oils that leave a mixture of bitumen and paraffin wax as a residue by nondestructive distillation.

1.3.2. Correlation Index

An early attempt to give the classification system a quantitative basis suggested that a crude should be called asphaltic if the distillation residue contained less than 2% wax and paraffinic if it contained more than 5%. A division according to the chemical composition of the 250 to 300°C (480 to 570°F) fraction has also been suggested (Speight, 1999, and references cited therein). Difficulties arise in using such a classification because in fractions boiling above 200°C (390°F), the molecules can no longer be placed in a single group because most of them are of a typically mixed nature. Purely naphthenic or aromatic molecules occur very seldom; cyclic compounds generally contain paraffinic side chains, and often even aromatic and naphthenic rings side by side. More direct chemical information is often desirable and can be supplied by means of the correlation index (CI).

The correlation index, developed by the U.S. Bureau of Mines, is based on a plot of specific gravity versus the reciprocal of the boiling point in kelvin ($K = {}^\circ\mathrm{C} + 273$). For pure hydrocarbons, the line described by the constants of the individual members of the normal paraffin series is given the value CI = 0, and a parallel line passing through the point for the values of benzene is given as CI = 100; thus,

$$\mathrm{CI} = 473.7d - 456.8 + \frac{48{,}640}{K}$$

where K for a petroleum fraction is the average boiling point determined by the standard Bureau of Mines distillation method and d is the specific gravity.

Values for the index between 0 and 15 indicate a predominance of paraffinic hydrocarbons in the fraction. A value from 15 to 50 indicates a predominance of either naphthenes or of mixtures of paraffins, naphthenes, and aromatics. An index value above 50 indicates a predominance of aromatic species.

1.3.3. Density

Since the early years of the industry, density (specific gravity) has been, the principal and often the only specification of crude oil products and was taken as an index of the proportion of gasoline and, particularly, kerosene present. As long as only one type of petroleum was in use, the relations were approximately true, but as crude oils having other properties were discovered and came into use, the significance of density measurements disappeared. Nevertheless, crude oils of particular types are still rated by gravity, as are gasoline and naphtha within certain limits of other properties. The use of density values has been advocated for quantitative application using a scheme based on the American Petroleum Institute (API) gravity of the 250 to 275°C (480 to 525°F, 1760 mm) and 275 to 300°C (525 to 570°F, 40 mm) distillation fractions (Speight, 1999, and references cited therein). Indeed, investigation of crude oils from worldwide sources showed that 85% fell into one of the three classes: paraffin, intermediate, or naphthene base.

It has also been proposed to classify heavy oils according to *characterization gravity*. This is defined as the arithmetic average of the instantaneous specific gravity of the distillates boiling at 177°C (350°F), 232°C (450°F), and 288°C (550°F) vapor line temperature at 25 mm pressure in a true boiling-point distillation.

In addition, a method of petroleum classification based on other properties as well as the density of selective fractions has been developed. The method consists of a preliminary examination of the aromatic content of the fraction boiling up to 145°C (295°F), as well as that of the asphaltene content, followed by a more detailed examination of the chemical composition of the naphtha (bp $< 200^\circ\mathrm{C}$ $< 390^\circ\mathrm{F}$). For this examination a graph is used that is a composite of curves expressing the relation among the percentage distillate from the naphtha, aniline point, refractive index, specific gravity, and boiling point. The aniline point after acid extraction is included to estimate the paraffin-to-naphthene ratio.

1.3.4. Carbon Distribution

A method for the classification of crude oils can only be efficient (1) if it indicates the distribution of components according to volatility, and (2) if it indicates one or more characteristic properties of the various distillate fractions. The distribution according to volatility has been considered the main property of petroleum, and any fractionating column with a sufficient number of theoretical plates may be used for recording a curve in which the boiling point of each fraction is plotted against the percentage by weight.

However, for characterization of the various fractions of petroleum, use of the n–d–M method (n = refractive index, d = density, M = molecular weight) is suggested. This method enables determination of the carbon distribution and thus indicates the percentage of carbon in aromatic structure ($\%C_A$), the percentage of carbon in naphthenic structure ($\%C_N$), and the percentage of carbon in paraffinic structure ($\%C_P$). The yields over the various boiling ranges can also be estimated; for example, in the lubricating oil fractions the percentage of carbon in paraffinic structure can be divided into two parts, giving the percentage of carbon in normal paraffins ($\%C_{nP}$) and the percentage of carbon in paraffinic side chains. The percentage of normal paraffins present in lubricating oil fractions can be calculated from the percentage of normal paraffinic carbon ($\%C_{nP}$) by multiplication by a factor that depends on the hydrogen content of the fractions.

It is also possible to extrapolate the carbon distribution to the gasoline range on the one hand and to the residue on the other hand. A high value of $\%C_A$ at 500°C (930°F) boiling point usually indicates a high content of asphaltenes in the residue, whereas a high value of $\%C_{nP}$ at a 500°C (930°F) boiling point usually indicates a waxy residue.

1.3.5. Viscosity–Gravity Constant

The viscosity–gravity constant and the Universal Oil Products characterization factor have been used to some extent as a means of classifying crude oils. Both parameters are generally employed to give an indication of the paraffinic character of the crude oil, and both have been used, if a subtle differentiation can be made, as a means of petroleum characterization rather than for petroleum classification.

Nevertheless, the viscosity–gravity constant (VGC) was one of the early indexes proposed to characterize (or classify) oil types:

$$\mathrm{VGC} = 10d - \frac{1.0752\log(v - 38)}{10 - \log(v - 38)}$$

where d is the specific gravity 60/60°F and v is the Saybolt viscosity at 39°C (100°F). For heavy oil, where the low-temperature viscosity is difficult to measure, an alternative formula,

$$\mathrm{VGC} = d - 0.24 - \frac{0.022 \log(v - 35.5)}{0.755}$$

has been proposed in which the 99°C (210°F) Saybolt viscosity is used. The two do not agree well for low-viscosity oils. However, the viscosity–gravity constant is of particular value in indicating a predominantly paraffinic or cyclic composition. The lower the index number, the more paraffinic is the stock; for example, naphthenic lubricating oil distillates have VGC = 0.876, and the raffinate obtained by solvent extraction of lubricating oil distillate has VGC ∼ 0.840.

1.3.6. UOP Characterization Factor

The UOP characterization factor is perhaps one of the more widely used derived characterization or classification factors and is defined by the formula

$$K = \sqrt[3]{\frac{T_B}{d}}$$

where T_B is the average boiling point in degrees Rankine (°F + 460) and d is the specific gravity 60°/60°F. This factor has been shown to be additive on a weight basis. It was devised originally to show the thermal cracking characteristics of heavy oils; thus, highly paraffinic oils have $K \sim 12.5$ to 13.0, and cyclic (naphthenic) oils have $K \sim 10.5$ to 12.5.

1.4. PETROLEUM PRODUCTS

Petroleum is rarely used in the form produced at the well, but is converted in refineries into a wide range of products, such as gasoline, kerosene, diesel fuel, jet fuel, and domestic and industrial fuel oils, together with petrochemical feedstocks such as ethylene, propylene, butene, butadiene, and isoprene. Petroleum is refined, that is, it is separated into useful products (Figure 1.1; Chapter 3).

Unless properties dictate otherwise (Speight, 1999; Speight and Ozum, 2002), refining consists of initially dividing the petroleum into fractions of different boiling ranges by distillation. Other forms of treatment are utilized during the refining process to remove undesirable components of the crude oil. The fractions themselves are often distilled further to produce the desired commercial product. A variety of additives may be incorporated into some of the refined products to adjust the octane ratings or improve engine performance characteristics.

The lowest-boiling (lightest) constituents of petroleum are gases at room temperature, which are collected and used as heating gas mixtures and in the petrochemical industry or as a refinery fuel. The next-lightest hydrocarbons, which occur in molecules that contain four to nine carbon atoms and have a boiling range (also known as the light and heavy naphtha fraction), are used in

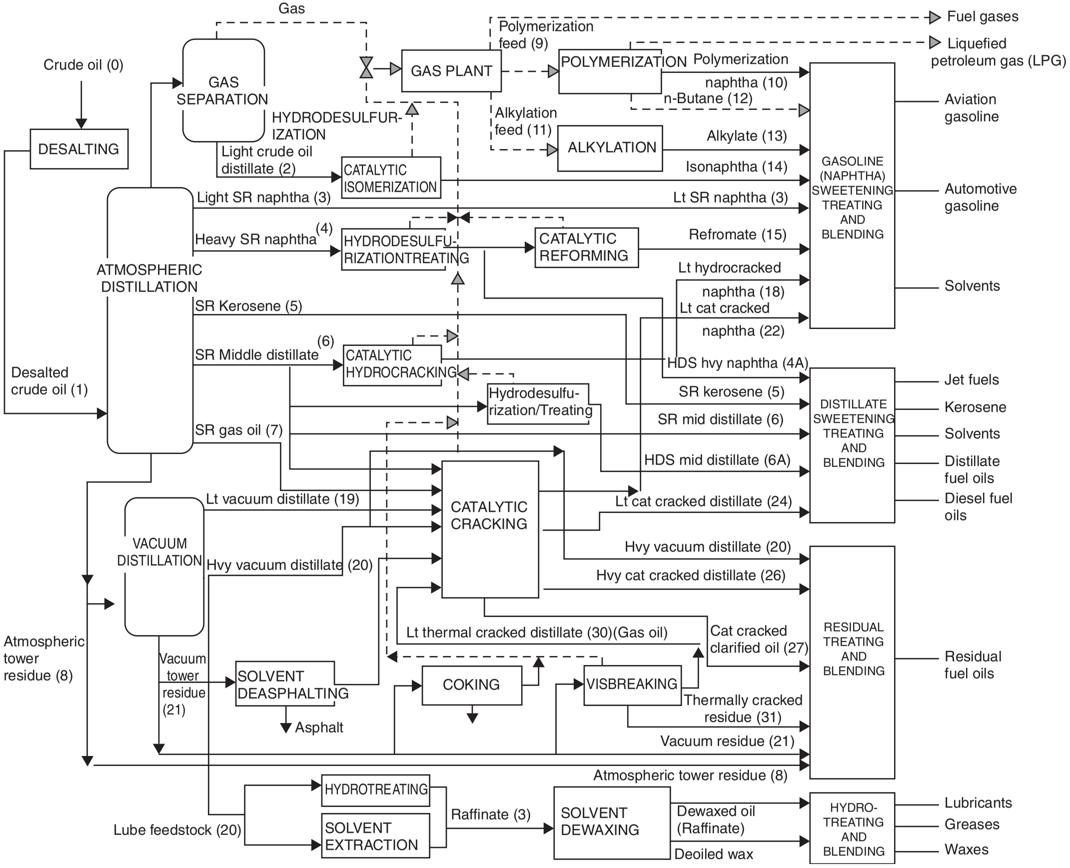

Figure 1.1. General layout of a petroleum refinery.

gasoline formulation. Constituents boiling in the middle ranges, *middle distillates*, are used for the production of kerosene diesel fuel, jet fuel, and fuel oil. These fuels contain paraffins (alkanes), cycloparaffins (cycloalkanes), aromatics, and olefins from approximately the nine- to 20-carbon molecular range.

The highest-boiling molecular-weight compounds that do not distill under refinery conditions or vaporize at all are asphalts or paraffins, depending on the source of the crude oil. The highest-boiling fractions are high-molecular-weight hydrocarbons suitable for lubricants and heating oil. Lubricants may contain hydrocarbons ranging from 18 to 25 carbon atoms per molecule. Paraffin wax and petroleum jelly typically contain 28 to 38 carbon atoms per molecule. Other petroleum products include a wide variety of solvents that can have a considerable influence on living organisms, particularly the human organism (Table 1.3). Refined oils may also have a number of additives, such as gelling inhibitors, which are added to diesel fuels during cold weather. Certain additives may be of special concern in an injury assessment, either because they are toxic themselves or because they significantly change the behavior of the oil products.

Petroleum products have a vast array of uses. In approximate order of importance the uses are: as fuels for vehicles and industry, as heating oils, as lubricants, as raw materials in manufacturing petrochemicals and pharmaceuticals, and as solvents. By a wide margin, most products derived from petroleum find use as fossil fuels to run vehicles, to produce electricity, and to heat homes and business. About 65% of the petroleum used as fuel is consumed as gasoline in automobiles. Thus, petroleum products are ubiquitous in the modern environment, which leads to contamination problems for both the environment and in sampling activities.

Table 1.3. Effects of Organic Solvents

Solvent	Affected Parts of Human Body
Aliphatic hydrocarbons	
Pentanes, hexanes, heptanes, octanes	Central nervous system and liver
Halogenated aliphatic hydrocarbons	
Methylene chloride	Central nervous system, respiratory system
Chloroform	Liver
Carbon tetrachloride	Liver and kidneys
Aromatic hydrocarbons	
Benzene	Blood, immune system
Toluene	Central nervous system
Xylene	Central nervous system
Alcohols	
Methyl alcohol (methanol and toxic metabolites)	Optic nerve
Isopropyl alcohol	Central nervous system
Glycols	
Ethylene glycol (and toxic metabolites)	Central nervous system

1.4.1. Boiling Range

There are several ways to classify or group various petroleum products. Refined oils are sometimes characterized by the approximate boiling-point range, which corresponds with the size (such as the number of carbon atoms) of the petroleum hydrocarbons in the refined oil:

1. 1 to 205°C (32 to 400°F): *naphtha* or *straight-run gasoline* (meaning, not produced through catalytic decomposition).
2. 205-345°C (400 to 655°F): *middle distillates*, including kerosene, jet fuel, heating oil, and diesel fuel.
3. 345 to 565°C (655 to 1050°F): *gas oil*, including lubricating (lube) oil and wax.
4. 565°C+ (1050°F+): residuum, which may be cut with lighter oil to produce bunker oil and other fuel oil.

1.4.2. Environmental Behavior

Another way to describe or characterize petroleum products is by generalized spill cleanup categories, and the following categories are in use by the National Oceanic and Atmospheric Administration (NOAA) to identify cleanup options:

1. *Gasoline products* are highly volatile products that evaporate quickly (often completely) within one or two days. They are narrow cut fractions with no residue and low viscosity, which spread rapidly to a thin sheen on water or onto the land. They are highly toxic to biota, will penetrate the substrate, and are nonadhesive.
2. *Diesel-like products* (jet fuel, diesel, No. 2 fuel oil, kerosene) are moderately volatile products that can evaporate with no residue. They have a low-to-moderate viscosity, spread rapidly into thin slicks, and form stable emulsions. They have a moderate-to-high (usually, high) toxicity to biota, and the specific toxicity is often related to type and concentration of aromatic compounds. They have the ability to penetrate substrate, but fresh (unoxidized) spills are nonadhesive.
3. *Intermediate products* (No. 4 fuel oil, lube oil) are products that are loss volatile than the two previous categories; up to one-third will evaporate within 24 hours. They have a moderate-to-high viscosity and a variable toxicity that depends on the amount of the lower-boiling components. These products may penetrate the substrate, and therefore cleanup is most effective if conducted quickly.
4. *Low-API fuel oil* (heavy industrial fuel oil) is a medium-viscosity product that are highly variable and often blended with lower-boiling products. The blends may be unstable and the oil may separate when spilled onto the ground or onto a waterway. The oil may be buoyant or sink in water,

depending on water density. The sunken oil has little potential for evaporation and may accumulate on the bottom (of the waterway) under calm conditions. However, the sunken oil may be resuspended during storm events, providing shoreline oiling (contamination). These products weather (oxidize) slowly.

5. *Residual products* (No. 6 fuel oil, bunker C oil): these products have little (usually, no) ability to evaporate. When spilled, persistent surface and intertidal area contamination is likely with long-term contamination of the sediment. The products are very viscous to semisolid and often become less viscous when warmed. They weather (oxidize) slowly and may form tar balls that can sink in waterways (depending on product density and water density). They are highly adhesive to soil. Heavy oil, a viscous petroleum, and bitumen from tar sand deposits also come into this category of contaminant.

1.5. REFINERY WASTE

The pollution of ecosystems, either inadvertently or deliberately, has been a fact of life for millennia (Pickering and Owen, 1994). In recent times, the evolution of industrial operations has led to issues related to the disposal of a wide variety of chemical contaminants (Easterbrook, 1995). Chemical wastes that were once exotic have become commonplace and hazardous (Tedder and Pohland, 1993). Recognition of this makes it all the more necessary that steps be taken to terminate the pollution, preferably at the source or before it is discharged into the environment. It is also essential that the necessary tests be designed to detect the pollution and its effect on living forms.

Any chemical substance, if improperly managed or disposed of, may pose a danger to living organisms, materials, structures, or the environment, by explosion or fire hazards, corrosion, toxicity to organisms, or other detrimental effects. In addition, when released to the environment, many chemical substances can be classified as hazardous or nonhazardous. Consideration must be given to the distribution of chemical wastes on land systems, in water systems, and in the atmosphere.

In general terms, the origin of chemical wastes refers to their points of entry into the environment. Point-source leaks and spills (i.e., sources that release emissions) through a confined vent (stack) or opening and non-point-source emissions have resulted in environmental contamination from petroleum and petroleum products. Spills of crude oil and fuels have caused wide-ranging damage in marine and freshwater environments. Oil slicks and tars in shore areas and beaches can ruin the aesthetic value of entire regions. Other sources of environmental leakage as it affects the petroleum industry may consist of (1) deliberate addition to soil, water, or air by humans: for example, the disposal of used engine oil; (2) evaporation or wind erosion from emissions into the atmosphere; (3) leaching from waste dumps into groundwater, streams, and bodies of water; (4) leakage, such as from underground storage tanks or pipelines;

(5) accidents, such as fire or explosion; and (6) emissions waste treatment or storage facilities.

In terms of waste definition, there are three basic approaches (as it pertains to petroleum, petroleum products, and nonpetroleum chemicals) to defining petroleum or a petroleum product as hazardous: (1) a qualitative description of the waste by origin, type, and constituents; (2) classification by characteristics based on testing procedures; and (3) classification as a result of the concentration of specific chemical substances.

However, various countries use different definitions of chemical waste and there are often several inconsistencies in the definitions. Usually, the definition involves qualification of whether or not the material is hazardous. For example, in some countries, a hazardous waste is any material that is especially hazardous to human health, air, or water, or which is explosive, flammable, or may cause disease. Poisonous waste is material that is poisonous, noxious, or polluting and whose presence on the land is liable to give rise to an environmental hazard. But in more general terms (in any country), hazardous waste is waste material that is unsuitable for treatment or disposal in municipal treatment systems, incinerators, or landfills and which therefore requires special treatment.

Moreover, and somewhat paradoxically, measures taken to reduce air and water pollution may actually increase the production of chemical wastes. As examples, disposal of petroleum wastes by water treatment processes can yield a chemical sludge or concentrated liquor that requires stabilization and disposal (Cheremisinoff, 1995). Scrubbing to remove hydrogen sulfide, sulfur oxides, and low-boiling organic sulfides as well as carbon dioxide (gas cleaning) are not immune to process waste, even though the chemistry of the cleaning processes is, in theory, reversible (Speight, 1993). Sludge is often produced and the disposal of this material became a major environmental issue that cannot be ignored. In addition, electrostatic precipitators, used to remove metals from flue gases (Speight, 1993), also yield significant quantities of solid by-products, some of which are hazardous.

1.5.1. Chemical Characteristics

A chemical waste is considered hazardous if it exhibits one or more of the following characteristics: *ignitability, corrosivity, reactivity*, and *toxicity*. Under the authority of the Resource Conservation and Recovery Act (RCRA) and the U.S. Environmental Protection Agency (EPA), a hazardous substance has one or more of the foregoing characteristics.

Briefly, *ignitability* is that characteristic of chemicals that are volatile liquids and the vapors are prone to ignition in the presence of an ignition sources. Nonliquids that may catch fire from friction or contact with water and which burn vigorously or are persistently ignitable compressed gases and oxidizers also fall under the mantle of ignitable chemicals. Examples include solvents, friction-sensitive substances, and pyrophoric solids that may include catalysts and metals isolated from various refining processes. Organic solvents are indigenous to the petroleum industry and release to the atmosphere as vapor and can

Table 1.4. Flammability of Selected Organic Liquids

Liquid	Flash Point (°C)[a]	Volume Percent in Air[b]	
		LFL	UFL
Diethyl ether	−43	1.9	36
Pentane	−40	1.5	7.8
Acetone	−20	2.6	13
Toluene	4	1.3	7.1
Methanol	12	6.0	37
Gasoline (2,2,4-trimethyl-pentane)	—	1.4	7.6
Naphthalene	157	0.9	5.9

[a] Closed-cup flash point test.

[b] LFL, lower flammability limit; UFL, upper flammability limit at 25°C (77°F).

pose a significant inhalation hazard. Improper storage, use, and disposal can result in the contamination of land systems as well as groundwater and drinking water (Barcelona et al., 1990).

Often, the term *ignitable chemical* (i.e., naphtha or gasoline) is used in the same sense as the term *flammable chemical* (Table 1.4) insofar as it is a chemical that will burn readily, but a *combustible chemical* (any higher-boiling hydrocarbon product of refining but which can include naphtha or gasoline) often requires relatively more persuasion to burn (i.e., the chemical is less flammable). Most petroleum products that are likely to burn accidentally are low-boiling liquids that form vapors that are usually denser than air and thus tend to settle in low spots. The tendency of a liquid to ignite is measured by a test in which the liquid is heated and exposed to a flame periodically until the mixture of vapor and air ignites at the liquid's surface. The temperature at which this occurs is called the *flash point*.

There are several standard tests for determining the flammability of materials (ASTM, 2004). For example, the upper and lower concentration limits for the *flammability* of chemicals and waste can be determined by standard test methods (ASTM D4982, E681), as can the *combustibility* and the *flash point* (ASTM D1310, E176, E502). With these definitions in mind it is possible to divide ignitable materials into two subclasses:

1. A *flammable solid* is a solid that can ignite from friction or from heat remaining from its manufacture, or which may cause a serious hazard if ignited. Explosive materials are not included in this classification.
2. *A flammable liquid* is a liquid having a flash point below 37.8°C (100°F) (ASTM D92, D1310). A *combustible liquid* has a flash point in excess of 37.8°C (100°F) but below 93.3°C (200°F). Gases are substances that exist

> entirely in the gaseous phase at 0°C (32°F) and 1 atm pressure (14.7 psi) pressure. A *flammable compressed gas* [such as liquefied petroleum gas (LPG), or any liquefied hydrocarbon gas or petroleum product] meets specified criteria for lower flammability limit, flammability range, and flame projection.

In considering the ignition of vapors, two important concepts are *flammability limit* and *flammability range*. Values of the vapor/air ratio below which ignition cannot occur because of insufficient fuel define the lower flammability limit. Similarly, values of the vapor/air ratio above which ignition cannot occur because of insufficient air define the upper flammability limit. The difference between upper and lower flammability limits at a specified temperature is the flammability range.

Dust explosions (ASTM E789) that can occur during catalytic reactor shutdown and cleaning are due to the production of finely divided solids through attrition. Many catalyst dusts can burn explosively in air. Thus, control of dust generated by catalyst attrition is essential (Mody and Jakhete, 1988).

Substances that catch fire spontaneously in air without an ignition source are called *pyrophoric*. These include phosphorus, the alkali metals and powdered forms of magnesium, calcium, cobalt, manganese, iron, zirconium, and aluminum—all of which may occur at one time or another at a refinery site. Moisture in air is often a factor in *spontaneous ignition*.

Corrosivity is that characteristic of chemicals that exhibits extremes of acidity or basicity or a tendency to corrode steel. Such chemicals, used in various refining (treating) processes, are acidic and are capable of corroding metal such as tanks, containers, drums, and barrels. On the other hand, *reactivity* is a violent chemical change (an explosive substance is an obvious example) that can result in pollution and/or harm to indigenous flora and fauna. Such wastes are unstable under ambient conditions insofar as they can create explosions, toxic fumes, gases, or vapors when mixed with water.

Finally, *toxicity* (defined in terms of a standard extraction procedure followed by chemical analysis for specific substances) is a characteristic of all chemicals, whether petroleum or nonpetroleum in origin. Toxic wastes are harmful or fatal when ingested or absorbed, and when such wastes are disposed of on land, the chemicals may drain (leach) from the waste and pollute groundwater. Leaching of such chemicals from contaminated soil may be particularly evident when the area is exposed to acid rain. The acidic nature of the water may impart mobility to the waste by changing the chemical character of the waste or the character of the minerals to which the waste species are adsorbed.

As with flammability, there are many tests that can be used to determine corrosivity (ASTM D1838, D2251). Most corrosive substances belong to at least one of the following four chemical classes: strong acids, strong bases, oxidants, or dehydrating agents (Table 1.5). All are used in the refining industry. For example, sulfuric acid is a prime example of a corrosive substance (ASTM C694). As well as being a strong acid (ASTM E1011), concentrated sulfuric acid is also a

Table 1.5. Examples of Corrosive Substances

Name (Formula)	Properties and Effects
Nitric acid (HNO_3)	Strong acid, strong oxidizer, corrodes metals, reacts with protein in tissue
Hydrochloric acid (HCl)	Strong acid, corrodes metals, HCl gas damages respiratory tract
Hydrofluoric acid (HF)	Corrodes metals, dissolves glass, causes bad burns
Alkali metal hydroxides (e.g., NaOH)	Corrode zinc, lead, and NaOH and KOH; dissolve tissue; cause severe burns
Hydrogen peroxide (H_2O_2)	Causes severe burns
Interhalogen compounds	Corrosive irritants, dehydrate tissue
Halogen oxides (OF_2, Cl_2O, Cl_2O_7)	Corrosive irritants, dehydrate tissue
Halogens (F_2, Cl_2, Br_2)	Corrosive to mucous membranes, strong irritants

dehydrating agent and oxidant. The heat generated when water and concentrated sulfuric acid are mixed illustrates the high affinity of sulfuric acid for water. If this is done incorrectly by adding water to the acid, localized boiling and spattering can occur and result in personal injury. The major destructive effect of sulfuric acid on skin tissue is the removal of water with an accompanying release of heat. Contact of sulfuric acid with tissue results in tissue destruction at the point of contact. Inhalation of sulfuric acid fumes or mists damages tissues in the upper respiratory tract and eyes. Long-term exposure to sulfuric acid fumes or mists has caused erosion of teeth as well as destruction of other parts of the body!

Reactive chemicals are those that tend to undergo rapid or violent reactions under certain conditions. Such substances include those that react violently or form potentially explosive mixtures with water, such as some of the common oxidizing agents (Table 1.6). Explosives (Sudweeks et al., 1983; Austin, 1984) constitute another class of reactive chemicals. For regulatory purposes, those substances are also classified as reactive that react with water, acid, or base to produce toxic fumes, particularly hydrogen sulfide or hydrogen cyanide.

Heat and temperature are usually very important factors in reactivity since many reactions require energy of activation to get them started. The rates of most reactions tend to increase sharply with increasing temperature, and most chemical reactions give off heat. Therefore, once a reaction is started in a reactive mixture lacking an effective means of heat dissipation, the rate will increase exponentially with time (doubling with every 10° rise in temperature), leading to an uncontrollable event. Other factors that may affect the reaction rate include the physical form of reactants, the rate and degree of mixing of reactants, the degree of dilution with a nonreactive medium (e.g., an inert solvent), the presence of a catalyst, and pressure.

Toxicity is of the utmost concern in dealing with chemicals and their disposal (ASTM D4447). This includes both long-term chronic effects from continual or

Table 1.6. Common Oxidizing Agents

Name	Formula	Gas/Liquid/Solid
Ammonium nitrate	NH_4NO_3	Solid
Ammonium perchlorate	NH_4ClO_4	Solid
Bromine	Br_2	Liquid
Chlorine	Cl_2	Gas (stored as liquid)
Fluorine	F_2	Gas
Hydrogen peroxide	H_2O_2	Solution in water
Nitric acid	HNO_3	Concentrated solution
Nitrous oxide	N_2O	Gas (stored as liquid)
Ozone	O_3	Gas
Perchloric acid	$HClO_4$	Concentrated solution
Potassium permanganate	$KMnO_4$	Solid
Sodium dichromate	$Na_2Cr_2O_7$	Solid

periodic exposures to low levels of toxic chemicals and acute effects from a single large exposure (Zakrzewski, 1991). Not all toxins are immediately apparent. For example, living organisms require certain metals for physiological processes. When present at concentrations above the level of homeostatic regulation, these metals can be toxic (ASTM E1302). In addition, there are metals that are chemically similar to, but higher in molecular weight than, the essential metals (heavy metals). Metals can exert toxic effects by direct irritant activity, blocking functional groups in enzymes, altering the conformation of biomolecules, or displacing essential metals in a metalloenzyme.

1.5.2. Environmental Behavior

In addition to the classification of petroleum-related chemicals by the characteristics described above, the U.S. Environmental Protection Agency designates more than 450 chemicals or chemical wastes that are specific substances or classes of substances known to be hazardous. Each such chemical or waste is assigned a hazardous waste number in the format of a letter followed by three numerals, where a different letter is assigned to substances from each of the following list:

1. F-type: chemicals or chemical wastes from nonspecific sources (Table 1.7)
2. K-type: chemicals or chemical wastes from specific sources (Table 1.8)
3. P-type: chemicals or chemical wastes that are hazardous and that are mostly specific chemical species such as fluorine
4. U-type: generally hazardous chemicals or chemical wastes that are predominantly specific compounds

Table 1.7. Chemical Wastes Designated as F-Category Wastes

Number	Waste Material
F001	Spent halogenated solvents chlorinated fluorocarbons; sludge from solvent recovery processes
F004	Spent nonhalogenated solvents (cresols, nitrobenzene); still bottoms from solvent recovery operations
F007	Spent solution from electroplating operations
F010	Sludge from metal heat-treating operations

Table 1.8. Chemical Wastes Designated as K-Category Wastes

Number	Waste Material
K001	Sediment/sludge from wastewater treatment from wood-preserving processes (especially creosote and pentachlorophenol sediment/sludge)
K002	Wastewater treatment sludge from chrome yellow and orange pigments
K020	Residue from vinyl chloride distillation
K034	2,6-Dichlorophenol waste
K047	Pink/red water from trichloroethane manufacture
K049	Waste oil/emulsion/solids from petroleum refining
K060	Ammonia lime still sludge
K067	Electrolytic sludge from zinc production

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) gives a broader definition of hazardous substances, which includes the following:

1. Any element, compound, mixture, solution, or substance whose release may substantially endanger public health, public welfare, or the environment
2. Any element, compound, mixture, solution, or substance in reportable quantities designated by CERCLA Section 102
3. Certain substances or toxic pollutants designated by the Water Pollution Control Act.
4. Any hazardous air pollutant listed under Section 112 of the Clean Air Act

5. Any imminently hazardous chemical substance or mixture that has been the subject of government action under Section 7 of the Toxic Substances Control Act (TSCA)
6. Any hazardous chemical or chemical waste listed or having characteristics identified by the Resource Conservation Recovery Act, with the exception of those suspended by Congress under the Solid Waste Disposal Act

In terms of quantity by weight, more wastes than all others combined are those from categories designated by hazardous waste numbers preceded by F and K. The F categories are those wastes from nonspecific sources (Table 1.7). K-type hazardous wastes are those from specific sources produced by industries, such as the manufacture of inorganic pigments, organic chemicals, pesticides, explosives, iron and steel, and nonferrous metals, and from processes such as petroleum refining or wood preservation (Table 1.8).

Some refinery wastes that might exhibit a degree of hazard are exempt from the Resource Conservation Recovery Act regulation by legislation and include the following:

1. Ash and scrubber sludge from thermal generation or power generation by utilities
2. Oil and gas field drilling mud
3. By-product brine from petroleum production
4. Catalyst dust

Eventual reclassification of these types of low-hazard wastes could increase the quantities of regulated wastes severalfold.

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