Acknowledgments

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### Table 1-1
Sources of Hydrocarbon Inputs into the Sea

<table>
<thead>
<tr>
<th>Source</th>
<th>Amount Introduced (metric tons/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Natural Sources</strong></td>
<td></td>
</tr>
<tr>
<td>Marine seeps</td>
<td>0.25</td>
</tr>
<tr>
<td>Sediment erosion</td>
<td>(0.2)</td>
</tr>
<tr>
<td>Offshore Production</td>
<td>0.05</td>
</tr>
<tr>
<td>Transportation</td>
<td>1.47</td>
</tr>
<tr>
<td>Tanker operations</td>
<td>(0.7)</td>
</tr>
<tr>
<td>Dry-docking</td>
<td>(0.03)</td>
</tr>
<tr>
<td>Marine terminals</td>
<td>(0.02)</td>
</tr>
<tr>
<td>Bilge and fuel oils</td>
<td>(0.5)</td>
</tr>
<tr>
<td>Tanker accidents</td>
<td>(0.4)</td>
</tr>
<tr>
<td>Nontanker accidents</td>
<td>(0.02)</td>
</tr>
<tr>
<td>Atmospheric Transport</td>
<td>0.3</td>
</tr>
<tr>
<td>Municipal and Industrial</td>
<td>1.18</td>
</tr>
<tr>
<td>Municipal wastes</td>
<td>(0.7)</td>
</tr>
<tr>
<td>Refineries</td>
<td>(0.1)</td>
</tr>
<tr>
<td>Nonrefining industrial wastes</td>
<td>(0.2)</td>
</tr>
<tr>
<td>Urban runoff</td>
<td>(0.12)</td>
</tr>
<tr>
<td>River runoff</td>
<td>(0.04)</td>
</tr>
<tr>
<td>Ocean dumping</td>
<td>(0.02)</td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td>3.2</td>
</tr>
</tbody>
</table>

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by tankers. Oil production from offshore platforms contributes less than 2% of the total amount of oil entering the sea.

### 1.1.2 Environmental Impact of Wastes

The primary measure of the environmental impact of petroleum wastes is their toxicity to exposed organisms. The toxicity of a substance is most commonly reported as its concentration in water that results in the death of half of the exposed organisms within a given length of time. Exposure times for toxicity tests are typically 96 hours,
although other times have been used. Common test organisms include mysid shrimp or sheephead minnows for marine waters and fathead minnows or rainbow trout for fresh waters.

The concentration that is lethal to half of the exposed population during the test is called LC\textsubscript{50}. High values of LC\textsubscript{50} mean that high concentrations of the substance are required for lethal effects to be observed, and this indicates a low toxicity. A related measure of toxicity is the concentration at which half of the exposed organisms exhibit sublethal effects; this concentration is called EC\textsubscript{50}. Another measure of toxicity is the no observable effect concentration (NOEC), the concentration below which no effects are observed.

The environmental impact of hydrocarbons in water varies considerably (National Research Council, 1985). The toxicity of aromatic hydrocarbons is relatively high, while that of straight-chain paraffins is relatively low. LC\textsubscript{50} values for the most commonly found aromatic hydrocarbons found in the petroleum industry (benzene, toluene, xylene, and ethylbenzene) are on the order of 10 ppm. Hydrocarbon concentrations of less than 1 mg/l in water have been shown to have a sublethal impact on some marine organisms. High molecular weight paraffins, on the other hand, are essentially nontoxic. Chronic exposures of entire ecosystems to hydrocarbons, either from natural seeps or from petroleum facilities, have shown no long- or intermediate-term impact; the ecosystems have all recovered when the source of hydrocarbons was removed. No evidence of irrevocable damage to marine resources on a broad oceanic scale, by either chronic inputs or occasional major oil spills, has been observed. Although there are short-term impacts from major spills, the marine resources can and do recover.

Other effects of hydrocarbons include stunted plant growth if the hydrocarbon concentration in contaminated soil is above about 1% by weight. Lower concentrations, however, can enhance plant growth (Deuel, 1990). Hydrocarbons can also impact higher organisms that may become exposed following an accidental release. Marine animals that use hair or feathers for insulation can die of hypothermia if coated with oil. Coated animals can also ingest fatal quantities of hydrocarbons during washing and grooming activities.

The high dissolved salt concentration of most produced water can also impact the environment. Typical dissolved salt concentrations for produced water range between 50,000 and 150,000 ppm. By comparison, the salt concentration in seawater is about 35,000 ppm. Dissolved
salt affects the ability of plants to absorb water and nutrients from soil. It can also alter the mechanical structure of the soil, which disrupts the transport of air and water to root systems. Water with dissolved salt concentrations below about 2,500 mg/l have minimal impact on most plants (Deuel, 1990). LC\textsubscript{50} values for dissolved salt concentrations for freshwater organisms are on the order of 1,000 ppm (Mount et al., 1993).

The toxicity of drilling muds varies considerably, depending on their composition. Toxicities (LC\textsubscript{50}) of water-based muds containing small percentages of hydrocarbons can be a few thousand ppm. The LC\textsubscript{50}s of polymer muds, however, can exceed one million, which means that fewer than 50% of a test species will have died during the test period.

The toxicity of heavy metals found in the upstream petroleum industry varies widely. The toxicity of many heavy metals lies in their interference with the action of enzymes, which limits or stops normal biochemical processes in cells. General effects include damage to the liver, kidney, or reproductive, blood forming, or nervous systems. With some metals, these effects may also include mutations or tumors. Heavy metal concentrations allowed in drinking water vary for each metal, but are generally below about 0.01 mg/L. The heavy metals in offshore drilling fluid discharges normally combine quickly with the naturally abundant sulfates in seawater to form insoluble sulfates and precipitates that settle to the sea floor. This process renders the heavy metals inaccessible for bioaccumulation or consumption.

Nuclear radiation from NORM can disrupt cellular chemistry and alter the genetic structure of cells. In most cases, however, radiation exposure from NORM is significantly lower than that from other natural and man-made sources of radiation and does not represent a serious health hazard (Snively, 1989).

The various chemicals used during production activities can also affect the environment. Their toxicities vary considerably, from highly toxic to essentially nontoxic. In most cases, however, the concentrations of chemicals actually encountered in the field are below toxic levels (Hudgins, 1992).

The primary environmental consequences of air pollutants are respiratory difficulties in humans and animals, damage to vegetation, and soil acidification. Releases of hydrogen sulfide, of course, can be fatal to those exposed.
minimize or eliminate their environmental risks. Unfortunately, many of those options are expensive and may not be economically possible.

One of the keys to producing oil in environmentally responsible ways is to be aware of any potential hazards and to plan effective ways to minimize those hazards before a particular project begins. The first step in this process is education. Petroleum engineers, geologists, and managers must understand the place their industry occupies in society. All companies, including oil companies, exist by the grace and will of the people in society. If society does not want an industry to exist, that industry can be shut down, either through legislation, litigation, or economic boycotts. Unfortunately, the social pressures imposed on an industry are not necessarily based on accurate scientific information. Many existing regulations are politically based and do little to protect human health and the environment, yet they add considerable costs to businesses that must comply.

The environmental movement that has been under the past few decades has resulted in regulations that have had a profound effect on the operations of the upstream petroleum industry. These regulations have been imposed because the public no longer believes that the industry can regulate itself and still protect the environment. Some of this loss of confidence has been earned, but some is the result of deliberate misinformation spread by environmental extremists and a media willing to misrepresent the truth to sell copy.

Regardless of why the public lacks confidence in the ability of the petroleum industry to operate in an environmentally responsible manner, the industry must adapt and learn to live within the increasingly tight environmental regulations in order to survive. The fundamental shift in attitude toward proactive environmental protection that has begun must continue—the past ways of doing business are gone and will not return. It is not enough just to comply with whatever the current regulations might be; there must be a serious commitment toward protecting the environment in all activities, regardless of the regulations.

The key to effective regulations that protect the environment is for the regulations to be based on accurate scientific information. If an industry has lost its credibility with the public regarding environmental concerns due to its past behavior, then any accurate scientific information about the environmental impact of its current operations will also lack credibility. This results in regulations that are very costly to the industry, but do little to protect the environment.
In the upstream petroleum industry, there are two major operations that can potentially impact the environment: drilling and production. Both operations generate a significant volume of wastes. Environmentally responsible actions require an understanding of these wastes and how they are generated. From this understanding, improved operations that minimize or eliminate any adverse environmental impacts can be developed.

Drilling is the process in which a hole is made in the ground to allow subsurface hydrocarbons to flow to the surface. The wastes generated during drilling are the rock removed to make the hole (as cuttings), the fluid used to lift the cuttings, and various materials added to the fluid to change its properties to make it more suitable for use and to condition the hole.

Production is the process by which hydrocarbons flow to the surface to be treated and used. Water is often produced with hydrocarbons and contains a variety of contaminants. These contaminants include dissolved and suspended hydrocarbons and other organic materials, as well as dissolved and suspended solids. A variety of chemicals are also used during production to ensure efficient operations.

During both drilling and production activities, a variety of air pollutants are emitted. The primary source of air pollutants are the emissions from internal combustion engines, with lesser amounts from other operations, fugitive emissions, and site remediation activities.

2.1 DRILLING

The process of drilling oil and gas wells generates a variety of different types of wastes. Some of these wastes are natural byproducts
further fluid loss. In most cases, the clay particles added to control the viscosity of a drilling fluid are successful in controlling fluid loss to the formation.

In some formations, however, the pore sizes may be so large that the clay particles are unable to bridge the pores and build a filter cake. Such formations may include those having natural or induced fractures, very high permeability sands, or vugs. To limit fluid loss in such formations, larger solids can be added to the drilling fluid. A mudcake of clay particles is then built on the bridge created by those solids. Solids that are commonly used for this application include mica, cane fibers, ground nutshells, plastic, sulfur, perlite, cellophane, cottonseed hulls, and sawdust.

If solids cannot be used to build a filter cake, the viscosity of the drilling fluid can be increased to limit fluid loss. Water-soluble polymers like starch, sodium polyacrylate, and sodium carboxymethylcellulose can be used.

pH Control

A high mud pH between 9.5 and 10.5 is almost always desired in drilling operations. A high pH suppresses the corrosion rate of drilling equipment, minimizes hydrogen embrittlement of steel if hydrogen sulfide enters the mud, lowers the solubility of calcium and magnesium to minimize their dissolution, and increases the solubility of lignosulfonate and lignite additives. A high pH is also beneficial for many new organic viscosity control additives. To keep the pH in the desired range, caustic (sodium hydroxide) is normally added to the mud. Some of the new polymer muds, however, have better shale stabilization properties at a lower pH (Clark, 1994).

Lubricants

During drilling, a considerable amount of friction can be generated between the drill bit and formation and between the drill string and wellbore walls, particularly for deviated and horizontal wells. To reduce this friction, lubricants are sometimes added to drilling fluids. These lubricants speed drilling and help maintain the integrity of the well. Common lubricants include diesel oil, mineral/vegetable oils, glass beads, plastic beads, wool grease, graphite, esthers, and glycerols.
Table 2-2
Composition of Alaskan North Slope Soils and Gravels

<table>
<thead>
<tr>
<th>Element</th>
<th>Mean Level (mg/kg dry)</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>7,050</td>
<td>6,180</td>
</tr>
<tr>
<td>Arsenic</td>
<td>1.83</td>
<td>215</td>
</tr>
<tr>
<td>Barium</td>
<td>397</td>
<td>802</td>
</tr>
<tr>
<td>Boron</td>
<td>29.4</td>
<td>27.4</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.153</td>
<td>0.185</td>
</tr>
<tr>
<td>Calcium</td>
<td>46,700</td>
<td>65,500</td>
</tr>
<tr>
<td>Chromium</td>
<td>11</td>
<td>16</td>
</tr>
<tr>
<td>Copper</td>
<td>14</td>
<td>11</td>
</tr>
<tr>
<td>Iron</td>
<td>19,600</td>
<td>15,800</td>
</tr>
<tr>
<td>Lead</td>
<td>4.24</td>
<td>5.06</td>
</tr>
<tr>
<td>Magnesium</td>
<td>14.1</td>
<td>2.886</td>
</tr>
<tr>
<td>Manganese</td>
<td>484</td>
<td>1.040</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.268</td>
<td>0.289</td>
</tr>
<tr>
<td>Nickel</td>
<td>21.3</td>
<td>14.8</td>
</tr>
<tr>
<td>Potassium</td>
<td>699</td>
<td>810</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.267</td>
<td>0.187</td>
</tr>
<tr>
<td>Silicon</td>
<td>1,640</td>
<td>6,230</td>
</tr>
<tr>
<td>Silver</td>
<td>0.26</td>
<td>0.177</td>
</tr>
<tr>
<td>Sodium</td>
<td>529</td>
<td>672</td>
</tr>
<tr>
<td>Strontium</td>
<td>93.4</td>
<td>140</td>
</tr>
<tr>
<td>Vanadium</td>
<td>29.9</td>
<td>140</td>
</tr>
<tr>
<td>Zinc</td>
<td>74.6</td>
<td>46.1</td>
</tr>
</tbody>
</table>

Source: from Schumacher et al., 1991.
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of pipe dope contained as much as 60% metals by weight, primarily lead, zinc, copper, or combinations of these metals (McDonald, 1993). These metals are malleable and deform within the threads without fracturing, forming both a seal and lubricant for the threads. These metals, however, can leach out of the pipe dope and contaminate the drilling fluid, particularly if an excess of pipe dope is used.

Another source of heavy metals in drilling fluid is from crude oil. Crude oil naturally contains widely varying concentrations of various
2.1.4 Reserves Pits

The most common method for the disposal of drilling wastes for onshore wells is in on-site reserves pits. The contents of reserves pits vary, depending on the drilling mud and the types of formations drilled. Reserves pits, however, can cause local environmental impact, particularly older pits that contain materials that are currently banned from such disposal or that were not constructed according to current regulations. The environmental impact of modern reserves pits are minimal.

The composition of the fluid in a reserves pit may be different from that of the original drilling fluid. Chemical and physical alterations of drilling fluids can occur during and after drilling from the heat and pressure encountered during drilling or from the addition of formation materials. Other materials may also be added to the pit before closure, either deliberately or inadvertently. Such materials include caustic soda, rig wash, diesel fuel, waste oil from machinery, metal and plastic containers, and other refuse (Powter, 1990). Bad storage and disposal practices associated with reserves pits have lead to their being a source of benzene, lead, arsenic, and fluoride, even when these components were not detected in the active mud system (Wojtanowicz, 1991).

The heavy metals and other dissolved solids contents in both the water and mud (sludge) phases of 125 reserves pits scattered around the United States were measured in one study, and the total and water-soluble (leachable) concentrations were determined (Leuterman et al., 1988). The mean metals concentrations of all of the pits varied significantly with species, with mean concentrations on the order of a few tens of mg/L. These data are summarized in Table 2-3. It was found that the metals concentrations in the mud phase were generally higher than in the water phase, indicating that most of the metals were probably bound to the organic and clay particles and were not readily available for leaching.

In separate studies, the heavy metals contents of reserves pits in the U.S. Gulf Coast were also analyzed and found to vary significantly (Wojtanowicz et al., 1989 and Deuel and Holliday, 1990). In the latter study, the pit contents were analyzed by the U.S. Environmental Protection Agency, the American Petroleum Institute, and in a private study under Louisiana State guidelines. The analysis protocols and procedures differed in the three studies and yielded somewhat different results. The results are summarized in Tables 2-4 and 2-5.
The heavy metals found in pits are not uniformly distributed in the pits. Heavy metals are often bound to coarse particulates and tend to accumulate near the point of discharge. The nonuniform distribution of metals in a pit needs to be considered when sampling the pit for metals concentration (Deuel and Holliday, 1990). Other studies, however, reveal no preferential distribution of metals in reserves pits (Wojtanowicz et al., 1989). Because the migration rate of chromium out of unlined pits is only a few feet per decade (Campbell and Akers, 1990), reserves pits are not expected to be a major source of chromium contamination for the environment.
potential source of contamination through surface runoff and wind
dispersion to adjoining land. Bromacil and tebuthiuron have commonly
been used as sterilization chemicals. These herbicides can become inactive
by applying charcoal to the site at abandonment (Powter, 1990).

2.2 PRODUCTION

The production of oil and gas generates a variety of wastes. The
largest waste stream is produced water, with its associated constituents.
This section reviews both the production process and the wastes that
are generated during production.

2.2.1 Overview of Production Processes

For the oil (or gas) to be produced, a pressure gradient must be
established in the formation on the pore level. This pressure gradient
then forces oil from one pore to the next and ultimately to the
production well. There are two basic ways for such a pressure gradient
to be established. First is to have a production well with a lower
pressure than that of the surrounding formation. This will cause oil
to flow to the well, where it can be produced. Second is to increase
the pressure in some parts of the formation by injecting fluids. This
will force oil to flow away from the injection wells to lower pressure
production wells. In many reservoirs, a combination of low pressure
at the production well coupled with a high pressure at an injection
well are used.

During production, both water and formation solids are commonly
produced with oil and gas. The produced materials are passed through
separation equipment, where the density differences between the
produced materials are used to separate them.

The first stage of separation normally occurs in a free water knock-
out. This consists of a large tank that allows time for the bulk oil,
gas, and water phases to separate. These tanks are also called wash
tanks, settling tanks, and gun barrels. The output streams from this
equipment consists primarily of gas, water with some oil, and oil with
some water. Solids either settle to the bottom of the tank or are carried
along with the water stream. The performance of these separators has
been reviewed by Powers (1990 and 1993) and the American Petro-
leum Institute (1990a).
Sodium chromate, however, adds chromium to the produced water. Sodium hexametaphosphate (Na$_6$P$_6$O$_{18}$) is used in cooling and boiling water treatment. Zinc salts of organic phosphonic acids and sodium molybdate (Na$_2$MoO$_4$) have also been used for corrosion control. Zinc-based inhibitors are less toxic than chromates and should be used if possible. Organic anionic inhibitors, such as sodium sulfonates and sodium phosphonates, are also used in cooling waters and antifreeze. Current regulations may limit the use of some corrosion inhibitors.

Hydrogen sulfide can be removed from produced fluids with a zinc scavenger. Zinc carbonate (ZnCO$_3$-Zn[OH]$_2$) is widely used. This chemical reacts with hydrogen sulfide, producing insoluble zinc sulfide (ZnS).

For water injection systems, oxygen causes the largest problem with corrosion. Oxygen can be removed from water by stripping it with an inert gas, such as natural gas, steam, or flue gas, by vacuum deaeration, or by chemical treatment. Oxygen scavengers include sodium sulfite (Na$_2$SO$_3$), sodium bisulfite (NaHSO$_3$), ammonium bisulfite (NH$_4$HSO$_3$), sulfur dioxide (SO$_2$), sodium hydrosulfite (Na$_2$S$_2$O$_4$), and hydrazine (N$_2$H$_2$).

Cathodic protection can be used for external corrosion of casing and pipes and for internal corrosion of tanks. Both internal and external surfaces of surface equipment can sometimes be protected with liners to prevent corrosion. These liners can be hydrocarbon, plastic, metal, ceramic, or cement based.

**Scale Inhibitors**

The dissolved solids in produced water are normally in thermodynamic chemical equilibrium with the downhole conditions. As water is produced, however, its temperature and pressure are lowered, altering the chemical equilibrium. One common result of this altered chemical equilibrium is the precipitation of inorganic salts in production equipment, i.e., scale. Scale can plug production equipment, rendering it useless. Scale is commonly composed of calcium, strontium, and barium sulfates, as well as calcium carbonate. A more complete discussion of scaling is given by Jones (1988).

Scale can be inhibited by organic phosphate esters of amino-alcohols, phosphonates, or acrylic acid type polymers (sodium polyacrylate polymers). These chemicals adsorb onto the crystal nuclei when scale first
Coagulants commonly include polyamines and polyamine quaternary ammonium salts.

**Foam Breakers**

Some crude oils generate a foam during production. This foam inhibits the separation of the oil, water, and solids in the production equipment. Although not commonly needed, foam breakers are available. Foam breakers include silicones, polyglycol esters, and aluminum stearate.

**Surfactants**

Surfactants (detergents) are regularly used to wash equipment and decks on offshore rigs. These surfactants commonly include alkyl aryl sulfonates and ethoxylated alkylphenols.

**2.2.4 Well Stimulation**

The oil and gas production rate of many wells is restricted by a low permeability around the wellbore. To increase the production rate, the permeability is often increased by stimulation. The two most common forms of stimulation are acidizing and hydraulic fracturing.

**Acidizing**

Acids are used to dissolve acid-soluble materials around the wellbore to increase the formation’s permeability. These acid-soluble materials can include formation rocks and clays, as well as any materials added during drilling. A variety of inorganic and organic acids can be used, depending on the formation. These acids include hydrochloric, formic, acetic, and hydrofluoric. Additives are also required to optimize the process.

The most widely used acid is hydrochloric acid. Its main application is in low permeability carbonate reservoirs. The major reaction products produced during acidizing are carbon dioxide, calcium chloride, and water. Spent acid returned from a well has a high chloride content. The principal disadvantage of hydrochloric acid is its corrosivity on tubulars, particularly at temperatures above about 250°F.
Table 2-8
Heavy Metal Concentrations
of Produced Solids

<table>
<thead>
<tr>
<th>Metal</th>
<th>Total (ppm, wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Antimony</td>
<td>11</td>
</tr>
<tr>
<td>Arsenic</td>
<td>105</td>
</tr>
<tr>
<td>Barium</td>
<td>326</td>
</tr>
<tr>
<td>Beryllium</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Cadmium</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Chromium</td>
<td>93</td>
</tr>
<tr>
<td>Cobalt</td>
<td>10</td>
</tr>
<tr>
<td>Copper</td>
<td>64</td>
</tr>
<tr>
<td>Lead</td>
<td>16</td>
</tr>
<tr>
<td>Mercury</td>
<td>5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>16</td>
</tr>
<tr>
<td>Nickel</td>
<td>2</td>
</tr>
<tr>
<td>Selenium</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Silver</td>
<td>1</td>
</tr>
<tr>
<td>Thallium</td>
<td>17</td>
</tr>
<tr>
<td>Vanadium</td>
<td>27</td>
</tr>
<tr>
<td>Zinc</td>
<td>214</td>
</tr>
<tr>
<td>Fluoride</td>
<td>76</td>
</tr>
</tbody>
</table>

Source: from Cornwell, 1993.
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water injection wells, and as a component of water-based hydraulic fracturing fluids.

2.2.7 Radioactive Materials

Many drilling sites and production facilities have radioactive materials associated with them. Some of these radioactive materials, primarily radioactive tracers or logging tools, are deliberately brought to the site for use, while other materials are naturally occurring and are called naturally occurring radioactive materials (NORM).

Radioactive Sources and Tracers

Radioactive sources are used primarily during logging with wire-line tools. Both gamma ray and neutron sources are available. These


CHAPTER 3

The Impact of Drilling and Production Operations

Many of the materials and wastes associated with drilling and production activities have the potential to impact the environment. The potential impact depends primarily on the material, its concentration after release, and the biotic community that is exposed. Some environmental risks may be significant, while others are very low.

The most common measure of the potential environmental impact of a material is its toxicity. Toxicity occurs when a material causes a deleterious effect on an organism, population, or community. These effects can range from temporary disorientation to lethality. This chapter reviews how toxicity is measured and then summarizes many of the toxicities measured for materials associated with drilling and production activities.

3.1 MEASURING TOXICITY

The toxicity of a substance is a measure of how it impairs the life and health of living organisms following exposure to the substance. In most cases, the effects of the substance on human life and health is of primary importance. Toxicity is determined through bioassays by exposing laboratory animals to different amounts of the substance in question. The resulting effects on the health of the animals are observed. For petroleum industry wastes, common test species used for marine waters are the mysid shrimp (Mysisopsis bahia) and sheepshead minnow (Cyrinodon variegatus), while fathead minnow
3. List of hazardous ingredients, with exposure limits.
4. Physical and chemical characteristics, including boiling point, melting point, density, solubility in water, appearance, odor, vapor density, and vapor pressure.
5. Fire and explosion hazard data, including flash point, flammability limits, extinguishing media, special firefighting procedures, and unusual fire and explosion hazards.
6. Reactivity data, including chemical stability, incompatibility with other chemicals and materials, hazards of decomposition or byproducts, and whether the material polymerizes.
7. Health hazard data, including exposure routes (inhalation, skin, or ingestion), acute and chronic health hazards, toxicity data, carcinogenicity, signs and symptoms of exposure, medical conditions aggravated by exposure, and emergency procedures (including first aid).
8. Precautions for safe handling and use, including steps to be taken if the material is spilled or released, first-aid procedures for exposure, method for disposal, and precautions for handling and storage.

One limitation to MSDS data is that it is often incomplete; normally, it only summarizes existing information from the literature. The manufacturer, in many cases, is not required to conduct additional research on the material. Such research is generally very costly and time-consuming. Because of this, the quality of MSDS data can vary considerably from chemical to chemical and from vendor to vendor. Even though manufacturers may not be required to conduct bioassays on the materials they offer for sale, bioassays are often required before a permit to discharge a material to the environment can be obtained.

### 3.2 HYDROCARBONS

Crude oil contains thousands of different types of hydrocarbon molecules. The toxicities and potential environmental impacts of the different molecules vary considerably. Numerous studies have been conducted on the environmental impact of hydrocarbon exposure. In this section, the major types (families) of hydrocarbons and their toxicities are discussed, and related environmental impact studies are reviewed.
hydrocarbons has been found to vary considerably and generalizations cannot be easily made. Factors that affect toxicity include molecular weight, hydrocarbon family, the organism exposed to the hydrocarbon, and life-cycle stage of the organism exposed (egg, larva, juvenile, or adult). For mixtures of hydrocarbons, such as crude oil, the toxicity also depends on the history of the exposure.

For hydrocarbons of a similar type (the same family), the toxicity tends to increase with decreasing molecular weight. Smaller molecules tend to be more toxic than large molecules. Light crude oils and refined products tend to be more toxic than those of heavy crude oils, because heavy crude oils have a higher average molecular weight. For similar molecular weight hydrocarbons, the toxicity varies with family. The toxicity of hydrocarbon families generally increases in the following order: alkanes, alkenes, cycloparaffins, aromatics, and polyaromatic hydrocarbons.

Some of the least toxic hydrocarbons include dodecane and higher paraffins. In fact, these high molecular weight paraffins are used in cooking, food preparation, and candles. The most toxic hydrocarbons are the low-boiling-point aromatics, particularly benzene, toluene, ethylbenzene, and xylene. Because of their similar properties, these four aromatic molecules are commonly referred to as BTEX. The most toxic hydrocarbons also tend to have a high solubility in water. A high solubility makes a molecule more accessible for uptake by plants and animals.

The toxicity of a given hydrocarbon varies considerably with the organism exposed. Factors that also affect the toxicity to a particular organism include the general health of the organism and whether the organism is already stressed. Stress factors include water salinity, temperature, and food abundance. The toxicity of crude oil to some fish can be twice as high in seawater as in fresh water. The toxicity of a particular hydrocarbon also appears to increase with decreasing temperature. Synergistic effects from the presence of other toxins can also significantly alter the toxicity of specific hydrocarbons.

The toxicities (LC$_{50}$) for a variety of aromatic and polyaromatic hydrocarbons are shown in Tables 3-4a and 3-4b (National Research Council, 1985). The LC$_{50}$ values for many aromatic hydrocarbons are less than about 5 ppm, although some have values as high as 28 ppm. From these tables, it can also be seen that the toxicity is higher (lower LC$_{50}$) for higher molecular weight polyaromatic
Table 3-4b
Summary of Bioassay Tests on Marine Organisms

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Test Species</th>
<th>Test Duration (hr)</th>
<th>LC$_{50}$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylnaphthalene</td>
<td><em>Palaemonetes</em></td>
<td>96</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td><em>Cancer</em></td>
<td>96</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td><em>Penaeus aztecus</em></td>
<td>24</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td><em>Copepod</em></td>
<td>24</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td><em>Cyprinodon</em></td>
<td>24</td>
<td>1</td>
</tr>
<tr>
<td>Trimethylnaphthalene</td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td><em>Cancer</em></td>
<td>96</td>
<td>0.5</td>
</tr>
<tr>
<td>Fluorene</td>
<td><em>Palaemonetes</em></td>
<td>96</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td><em>Cyprinodon</em></td>
<td>96</td>
<td>1.5</td>
</tr>
<tr>
<td>Dibenzothiophene</td>
<td><em>Palaemonetes</em></td>
<td>96</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td><em>Cyprinodon</em></td>
<td>96</td>
<td>3</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td><em>Palaemonetes</em></td>
<td>24</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>0.5</td>
</tr>
<tr>
<td>Methylphenanthrene</td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>0.25</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td><em>Neanthes</em></td>
<td>96</td>
<td>0.5</td>
</tr>
</tbody>
</table>

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hydrocarbons than the single ring aromatics of benzene, toluene, ethylbenzene, and xylene (BTEX).

The high toxicity of aromatic hydrocarbons relative to other hydrocarbons can be seen by comparing the 96-hour mysid shrimp toxicity for drilling muds using diesel oil to that using mineral oils. Diesel oil contains as much as 60% aromatic components, while some mineral oils contain less than 1%. LC$_{50}$ values for diesel are around 2,000 ppm, while those for some mineral oils are greater than 1,000,000 ppm, in which case less than 50% of the test species died during the test period (Derkics and Souders, 1993). As discussed below in the section on drilling fluids, the mysid shrimp test protocol dilutes the oil with sea water by a factor of nine before the test is conducted. Thus, these
exposure to hydrocarbons than the young. For all of the species included in this table, however, the LC50 values are below 10 ppm, indicating a high toxicity at all life-cycle stages.

An important factor affecting the toxicity of crude oils is their history before any organisms are exposed. Because the most toxic hydrocarbons are also the most volatile, they rapidly evaporate from a release site. Within a few days after a crude oil release, only higher molecular weight hydrocarbons remain, so the toxicity of the remaining crude oil is lower. Hydrocarbons in water also tend to adsorb onto suspended sediments, making them much less bioavailable to marine organisms than hydrocarbons in solution or dispersion in water. This further lowers the toxicity of released crude oil. If the sediments accumulate on the bottom of the sea, they can accumulate in estuarine organisms. The accumulation and metabolism of these compounds, however, vary with species (American Petroleum Institute, 1989e).

**Impact of Crude Oil on Marine Animals**

The actual impact of hydrocarbon exposure on marine animals is more complex than simple bioassay tests reveal. Oil at sublethal concentrations can significantly alter the behavior and development of marine organisms. These effects, however, are difficult to quantify. The problem of determining sublethal toxicity is further compounded because different species have different reactions and there is mixed effect when multiple toxins are present. Although there is a tremendous amount of scatter in the data, most threshold concentrations of crude oil in water for effects to be observed for eggs, embryos, and larvae of marine fish are between 0.01 and 5 mg/l (National Research Council, 1985).

Behavioral changes from exposure to hydrocarbons are primarily those involving motility, while in higher organisms, changes affect avoidance, burrowing, feeding, and reproductive activities. Behavioral changes in feeding have been observed at hydrocarbon concentrations as low as a few microgram/l. Other measures of sublethal effects include changes in respiration, the ratio of oxygen consumed to nitrogen excreted, biochemical enzyme assays, and cellular activity. The respiratory rate following exposure is usually reduced, although in some cases, it is increased. The level of exposure for respiratory impact for fish and planktonic crustaceans in the laboratory is less than 1 mg/l.
have been observed in coniferous forest growth following blowouts at distances as great as 2 km from the wellhead (Baker, 1991).

3.3 SALT

Salt (sodium chloride) in low concentrations is essential to the health of plants and animals. At concentrations different from the naturally occurring levels found in a given ecosystem, however, salt can cause an adverse impact.

3.3.1 Impact on Plants

The impact of salt on plants arises primarily from an excess salt concentration in the cellular fluids of the plants or from alteration in the soil structure in which the plants grow. The primary impact of an abnormal salt concentration in cellular fluids is the disruption of the fluid chemistry balance within cells. This disruption inhibits cellular growth, water uptake, and the overall health of the plants. Growth of nonmarine plants is impaired at total dissolved salt concentrations between about 1,500 and 2,500 mg/l, although this threshold level varies significantly with plant type, how the water is applied, and whether the soil is kept saturated. Salt concentrations below about 1,000 mg/l seem to improve some plant growth (Vickers, 1990).

When salt was spread over soil in the form of salty drilling muds, the yield of brome grass was reduced when the concentration of chloride exceeded about 1,000 kg Cl/hectare for potassium and sodium chloride, and about 50 kg Cl/hectare for a freshwater gel. The plant yield for intermediate chloride application levels was higher than that of control plots (Macyk et al., 1990).

Salt can indirectly impact plant growth by altering the physical properties of soil. When saline water is discharged on land, it can alter the pore structure of the soil by causing compaction, limiting the access of air and water to the plant roots. The impact varies, however, with salinity level and plant type. If the total dissolved solids content is above about 2,800 mg/l, salt can build up in the soil (Vickers, 1990).

Excess sodium in soil can also cause clays to disperse, lowering the permeability of the soil. This can form an impenetrable surface crust that hinders the emergence of seedlings and limits the availability of nutrients such as iron, manganese, calcium, and magnesium to the
membranes, erosion of teeth, and aggravation of respiratory conditions such as asthma. Little aquatic toxicity data are available for acids.

Pesticides vary in toxicity. Prolonged or repeated exposure may cause various systemic effects, including damage to the nervous and muscular systems. Some pesticides are carcinogenic. Exposure to some pesticides can be fatal.

Glycol can be fatal if ingested in quantities of about 100 ml. Lower doses may be irritating to the mouth, throat, and stomach and can cause disorders of or damage to the digestive tract. Repeated exposure can cause kidney, brain, or liver damage. Blood chemistry and blood cells can also be affected.

Bioassays have been conducted for a variety of production chemicals using different freshwater and saltwater organisms. Table 3-10 summarizes the typical concentrations of some chemicals used for different types of applications. The information includes typical ranges of chemical concentrations when used, concentrations when discharged for disposal, and the LC$_{50}$ values (Hudgins, 1992). From this table, it can be seen that the toxicities of production chemicals vary widely.

More detailed toxicity data are summarized for scale inhibitors in Table 3-11, for biocides in Tables 3-12a and 3-12b, reverse emulsion breakers in Table 3-13, emulsion breakers in Table 3-14, corrosion inhibitors in Table 3-15, paraffin inhibitors in Table 3-16, surfactants in Tables 3-17a through 3-17e, coagulants in Table 3-18, foam breakers in Table 3-19, and gas treatment chemicals in Table 3-20. Because of varying test protocols, a direct comparison of the toxicities of these chemicals may not be valid.

3.6 DRILLING FLUIDS

Two methods have been used to evaluate the environmental impact of drilling fluids. First are bioassays conducted using various organisms placed in different concentrations of drilling fluids. Second are direct measurements of environmental impact following disposal of drilling fluids, either in reserves pits or by offshore dumping.

3.6.1 Bioassays of Drilling Fluids

Bioassays using mysid shrimp (Mysidopsis bahia) are currently required for the offshore discharge of drilling fluids in the United
### Table 3-11
**Acute Toxicity of Scale Inhibitors (96-hr LC\(_{50}\), mg/L)**

<table>
<thead>
<tr>
<th>Generic Chemical Type</th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine phosphate ester</td>
<td>&gt;1,000</td>
<td>&gt;4,309</td>
</tr>
<tr>
<td>Phosphonate</td>
<td>3,700–&gt;10,125</td>
<td>1,676–&gt;10,125</td>
</tr>
</tbody>
</table>

*Source: after Hudgins, 1992. Copyright SPE, with permission.*

### Table 3-12a
**Acute Toxicity of Biocides (LC\(_{50}\), mg/L)**

<table>
<thead>
<tr>
<th>Generic Type</th>
<th>Generic Chemical Type</th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aldehydes</td>
<td>Glutaraldehyde (25%)</td>
<td>16.9–43</td>
<td>2.1–1,100</td>
</tr>
<tr>
<td></td>
<td>Glutaraldehyde (50%)</td>
<td>11.5–23.7</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Formaldehyde</td>
<td>18–64</td>
<td>23–1,000</td>
</tr>
<tr>
<td>Formaldehyde mixtures</td>
<td>With heterocyclic polyamine</td>
<td>41.4–73.3</td>
<td>2.9–1,000</td>
</tr>
<tr>
<td></td>
<td>With alkyldimethyl benzyl quaternary</td>
<td>1.79–2.24</td>
<td>12–290</td>
</tr>
<tr>
<td>Quaternary</td>
<td>Ethoxy quaternary</td>
<td>0.35–1.32</td>
<td>174–1,000</td>
</tr>
<tr>
<td></td>
<td>Dicocoamine</td>
<td>0.42–1.7</td>
<td>0.4–34</td>
</tr>
<tr>
<td>Amine salt</td>
<td>Cocodiamine acetate</td>
<td>0.22–1.6</td>
<td>0.719–965</td>
</tr>
<tr>
<td></td>
<td>Cocodiamine fatty acids</td>
<td>0.73–0.92</td>
<td>0.22–670</td>
</tr>
<tr>
<td></td>
<td>Others</td>
<td>0.09–1.62</td>
<td>24–922</td>
</tr>
<tr>
<td>Amine</td>
<td>Alkyl propylene diamine+ 2 ethylhexanol</td>
<td>0.75–0.78</td>
<td>0.49–49</td>
</tr>
<tr>
<td>Others</td>
<td>Metronidazole</td>
<td>&gt;100</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>2,2-dibromo-3-nitrilopropionamide</td>
<td>4.5–8.15</td>
<td>2.8–&gt;1,000</td>
</tr>
<tr>
<td></td>
<td>Dithiocarbamates</td>
<td>1.29</td>
<td>1.38</td>
</tr>
<tr>
<td></td>
<td>Isothiazalin</td>
<td>40.6</td>
<td>66.1–4,000</td>
</tr>
<tr>
<td></td>
<td>2,4,5-trichlorophenate</td>
<td>0.86–1.26</td>
<td>—</td>
</tr>
<tr>
<td></td>
<td>Toxaphene pesticide</td>
<td>0.036–0.042</td>
<td></td>
</tr>
</tbody>
</table>

*Test lengths are for either 48 or 96 hours.*

*Source: after Hudgins, 1992. Copyright SPE, with permission.*
## Table 3-15
Toxicity of Corrosion Inhibitors (96-hr LC<sub>50</sub>, mg/L)

<table>
<thead>
<tr>
<th>Generic Chemical Type</th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amide/imadizoline</td>
<td>0.26–75</td>
<td>2.12–261</td>
</tr>
<tr>
<td>Amide/imadizoline + quaternary</td>
<td>1.2–1.3</td>
<td>1–5</td>
</tr>
<tr>
<td>Quaternary</td>
<td>1.5–2.8</td>
<td>—</td>
</tr>
<tr>
<td>Ammonium salts</td>
<td>—</td>
<td>5.96–116</td>
</tr>
<tr>
<td>Amines</td>
<td>0.86</td>
<td>1.98–710</td>
</tr>
<tr>
<td>Sulfonate</td>
<td>—</td>
<td>220</td>
</tr>
<tr>
<td>Phenanthradine</td>
<td>6.1</td>
<td>—</td>
</tr>
<tr>
<td>Pyridine salt + quaternary</td>
<td>2.26</td>
<td>—</td>
</tr>
<tr>
<td>Alkyl morpholines</td>
<td>—</td>
<td>8.0–1,055</td>
</tr>
<tr>
<td>Ammonium bisulfite</td>
<td>75–126</td>
<td>77–88</td>
</tr>
<tr>
<td>Sodium sulfite</td>
<td>7,600</td>
<td>—</td>
</tr>
</tbody>
</table>


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## Table 3-16
Acute Toxicity of Paraffin Inhibitors (96-hr LC<sub>50</sub>, mg/L)

<table>
<thead>
<tr>
<th>Generic Chemical Type</th>
<th>Fresh Water</th>
<th>Salt Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vinyl polymer</td>
<td>42</td>
<td>2.7</td>
</tr>
<tr>
<td>Sulfonate salt</td>
<td>17–25.1</td>
<td>37.4</td>
</tr>
<tr>
<td>Alkyl polyether + aryl polyether</td>
<td>—</td>
<td>1.55</td>
</tr>
<tr>
<td>Other</td>
<td>17–44</td>
<td>13.3–37.4</td>
</tr>
</tbody>
</table>


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Branch, R. T., Artiola, J., and Crawley, W. W., “Determination of Soil Conditions that Adversely Affect the Solubility of Barium in Nonhazardous...
Environmental Control in Petroleum Engineering


CHAPTER 4

Environmental Transport of Petroleum Wastes

The environmental impact of most releases of petroleum industry wastes would be minimal if the wastes remained at their points of release. Unfortunately, wastes can migrate away from a release point by a number of pathways. These pathways include transport along the surface of the earth or along the surface of a body of water, transport through the soil through the pore structure, and transport through the air. These migration pathways are briefly discussed below.

4.1 SURFACE PATHS

Surface pathways of transport are those where the released material travels along either the soil or open water surface. Surface transport of petroleum wastes from releases on land occurs primarily when high volumes of liquid wastes are discharged onto the ground or when stormwater sweeps through a site. These liquids then flow down topographical drainage features until they either mix with existing surface waters, evaporate, or enter the pore network of the earth they flow over. Dikes and diversion trenches can be used to control such surface migration.

Surface transport of petroleum wastes on open water can occur with hydrocarbons because they are lighter than water. This transport of hydrocarbons will be controlled by natural water currents and wind. Because virtually all natural water currents are parallel to the shoreline, the primary direction of transport will be parallel to the
1. Determine compliance with applicable regulations.
2. Identify activities where improvements in operations are needed to minimize risk, liability, and potential environmental impacts or to lower operating costs.
3. Improve decision-making ability of facility personnel regarding environmental issues.
4. Provide an early warning device for impending problems and reduce "surprises" or repeated patterns of shortcomings in environmental performance.
5. Increase awareness among supervisors and operators of the regulatory requirements.
6. Reinforce top management’s commitment to environmental protection.
7. Identify areas where environmental training is needed.
8. Establish and quantify measures for risk reduction.
9. Confirm effective communications between environmental staff and field personnel.
10. Increase confidence of management that environmental activities are a sound investment.
11. Determine how knowledgeable employees are about company policies regarding environmental issues.
12. Improve relationship with regulatory agencies and the public in regard to activities conducted by the company.

Normally, the first steps in conducting an environmental audit are to review records of the site, to interview knowledgeable people about the site and its activities, and to conduct a physical inspection of the site. If obvious problems exist or if insufficient information to evaluate the potential for future liability of the property is available, then a more detailed study involving sampling and detailed engineering analysis may be required (Curtis and Kirchof, 1993). The information that can be obtained during an audit includes records of all materials entering the area, including those produced from the wells, created in surface facilities, and brought into the area by service companies. These materials include all solids, sludges, liquids, gases, and mixtures. The volume of each of these materials and their ultimate disposition must be identified. Naturally occurring radioactive materials (NORM) generated during production must also be considered.
and reduce the amount of water produced with the oil. The water produced from the water zone must also be disposed of (reinjection), but it should contain essentially no oil (Wojtanowicz, 1991). Polymers, gels, or cement can be used to plug water production zones if they are separate from oil producing zones.

Since many drilling and production operations are conducted by contractors, they should be carefully reviewed and selected. Contractors should have a good environmental track record. When conducting the bidding process for selecting equipment to be used, a visual inspection of the equipment is advised to determine its general condition, particularly drilling rigs. Contractors should have properly functioning equipment, with drip pans and splash guards.

Any contracts should specify activities that are prohibited while the contractor is on site. Such activities can include unnecessary rig washing, painting of the contractor’s equipment, or changing lube oil during downtime. This will minimize the possibility that excess water, painting wastes, or used oil gets dumped into reserves pits. An environmental activity review should be conducted with all contractor crews just prior to the start of activities. This review should include waste handling and minimization procedures.

Materials Substitution

Another important method for minimizing the amount of potentially toxic wastes generated is to use less toxic materials for the various operational processes. A number of studies of material substitutions have been presented (Derkics and Souders, 1993; Freidheim and Shinnie, 1991; Peresich et al., 1991; Savage, 1993; Thurber, 1992; Wojtanowicz, 1991).

Drilling muds represent a significant opportunity for toxic waste reduction by materials substitution. When substituting materials, however, it is important to ensure that the substituted materials yield a drilling mud that still has acceptable properties.

One of the best opportunities for materials substitution is in wells where oil-based muds are needed. Two alternatives to the use of diesel oil as a base fluid are being studied: using a less toxic oil-based mud and using a water-based mud with an improved additives package. These alternative mud systems, however, are considerably more expensive than traditional muds. Unfortunately, the use and discharge of
to the vendor for refilling. Oily rags can be cleaned and reused. Used drilling mud can also be used to make cement. Waste acids can be used to neutralize caustic wastes, and vice versa.

Many wastes can be used as feedstock by other companies. Materials exchanges are available in numerous locations to assist companies in finding other companies that may be interested in obtaining wastes. These exchanges should be contacted to see exactly what materials can be recycled in each area. Care should be taken, however, that the recycler is reputable and in compliance with all regulations. Transfer of a waste to a waste exchange does not necessarily relieve the waste generator of future liability for what the waste exchange does with the waste. A list of some of the major waste exchanges in the United States is given in Appendix C (Quan, 1989).

In some cases, only part of a particular waste stream contains valuable materials that can be reused. It may be possible to recover or reclaim the valuable materials, reducing the net volume of waste. For example, crude oil tank bottoms, oily sludges, and emulsions can be treated to recover their hydrocarbons. Oily materials can also be burned for their energy content. Gravel and cuttings can be washed and used in construction of roads and other sites.

Companies can take proactive action to assist employees in finding suitable opportunities for recycling. For example, funds generated from recycling can be placed in an employee fund for use at employee discretion to encourage recycling. Emphasis can also be placed on purchasing recycled goods to increase the market for them.

5.3.3 Treatment and Disposal

Wastes that cannot be eliminated must be treated and disposed. Treatment is used to reduce the volume and/or toxicity of wastes and/or put it in a form suitable for final disposal. A number of treatment and disposal options are available for the wastes generated in the petroleum industry. These options are discussed in Chapters 6 and 7, respectively.

5.4 CERTIFICATION OF DISPOSAL PROCESSES

One option for waste management is to ship wastes to an off-site, commercial waste disposal facility. Paying a disposal facility to take


to bacterial colonies that degrade the hydrocarbons. (American Petroleum Institute, 1986a). The application of biological processes to other waste streams will be discussed below.

### 6.1.2 Removal of Dissolved Hydrocarbons

In addition to suspended hydrocarbons, most produced water also contains varying amounts of dissolved hydrocarbons. A variety of methods are available to remove these dissolved hydrocarbons from the water.

#### Adsorption

An effective way to remove low levels of dissolved hydrocarbons is to adsorb it onto a solid medium. The most widely used medium is activated carbon. The pH and temperature of the system impacts the effectiveness of activated carbon on removing different hydrocarbon compounds. All free oil must be removed prior to the use of activated carbon to prevent the oil from clogging the carbon. In some cases, coal may also be used as an adsorption media. Natural and synthetic resins have also been developed that have proven effective in removing dissolved hydrocarbons from water.

#### Volatilization

Volatile organic carbon compounds (VOCs) can be removed from water by lowering the partial pressure of the compound in the vapor in contact with the water. When the partial pressure of the dissolved VOCs in the water exceeds that of its vapor pressure, the compounds will come out of solution and enter the vapor phase.

A variety of methods can be used to volatilize VOCs. Perhaps the most common is air stripping. In this process, air and water are passed through a containment vessel in countercurrent flow where VOCs evaporate into the air. The removal of VOCs can be enhanced by heating the air or by using steam, because higher temperatures increase their vapor pressure. Volatilization can also be enhanced by pulling a vacuum on the water, lowering the total system pressure.

One limitation to volatilization is that it transfers the VOCs from water to a vapor phase, yielding a contaminated vapor stream that must then be handled. If air is used, the oxygen will dissolve into the water,
In most cases, no special attempt has been made to limit leaching of metals or hydrocarbons from reserves pits or evaporation ponds. If leaching is a problem, the pit can be constructed with an impermeable liner and a leachate collection system with monitoring wells and enhanced evaporation features (sprinkler recirculation to increase the surface-to-volume ratio of the water). Lined pits are now required in some areas for oil-based or salty drilling mud systems. Any suspended or dissolved solids in the water will be concentrated as the water evaporates. If the pond has completely dried, these materials will be converted into a sludge, which may require further treatment before disposal.

Before dewatering and closure of reserves pits, the pit contents can segregate into layers. These layers can include a layer of free oil floating on a layer of water. The water normally contains a high concentration of dissolved solids. At the bottom is a layer of sludge that contains most of the settled solids. As the oil layer is weathered, a surface crust can also form. These top layers inhibit the evaporation of water, delaying the natural dewatering of the pits.

**Percolation**

In some arid areas where the water table is very deep, aqueous wastes can be placed in percolation ponds. These ponds have permeable sides and bottoms, allowing the water to percolate into the surrounding soil, leaving the solids at the bottom of the pond. The use of these ponds is highly restricted, however, because they allow dissolved solids in the water to spread into the surrounding soil.

**Mechanical Methods**

In many cases, evaporation is too slow to remove water from solid wastes. A number of mechanical methods are available to dewater solids. Preliminary separation of free liquids from the solids should be made with shale shakers, settling ponds, or hydrocyclones.

To further reduce the free water content of sludges, more advanced (and expensive) technologies can be used. These technologies include high-pressure filter presses, centrifuges, and vacuum filtering. Polymer conditioning of sludges can also be used to enhance dewatering. The low water content of the high-pressure filter presses can significantly
pollutant mobility and improves handling characteristics. Two types of solidification have been used: adding materials to absorb free liquids and adding materials to chemically bind and encapsulate the contaminants. Most off-site disposal sites use solidification to treat the wastes for final disposal by burial (Jones, 1990; Roberts and Johnson, 1990).

Absorbants are typically used to dewater reserves pits in areas where the evaporation rate is low. Materials that have been added to the pits to absorb free water include straw, dirt, fly ash, clays, kiln dust, fly ash, and polymers.

The best solidification methods, however, are those that chemically bind the contaminants. These methods are based primarily on portland cement, calcium silicate, or alumino-silicate reactions (Cai et al., 1989; Nahm et al., 1993). These materials, unlike fly ash or kiln dust, can reduce the leachability of toxic heavy metals, asbestos, oils, and salts. The mobility of metals from these solidification can be reduced by 80-90%, while that of organics can be reduced by 50-99% (U.S. Environmental Protection Agency, 1990).

Vitrification by heating the solids to a high enough temperature to melt silica has also been proposed (Buelt and Farnsworth, 1991), but is likely to be too expensive for applications in the petroleum industry.

6.3 TREATMENT OF AIR EMISSIONS

During drilling and production activities, a substantial volume of air pollutants can be generated and emitted. These pollutants include hydrocarbons, sulfur oxides, nitrogen oxides, and particulates. A variety of treatment methods are available, but their effectiveness varies considerably with the pollutant being treated.

6.3.1 Hydrocarbons

The primary source of hydrocarbon emissions is from the exhaust of internal combustion engines. Unfortunately, there is little that can be done to treat these emissions other than to operate the engines within their design specifications.

The vapor space in production tanks can collect volatile hydrocarbon vapors. These vapors can be collected and treated with vapor recovery systems (Webb, 1993). Casing gas from thermal enhanced oil recovery operations may also contain high levels of hydrocarbon


Waste Disposal Methods

The upstream petroleum industry generates a significant volume of wastes, primarily produced water and drill cuttings. No matter how effective a waste management plan or waste treatment program may be, wastes will remain that must be disposed of. In some cases, the final disposal can be on-site, while in other cases, the wastes must be shipped for disposal off-site.

Ultimately, petroleum industry wastes can be disposed of above or below the surface of either land or water. The suitability of these disposal locations varies with the wastes being disposed.

7.1 SURFACE DISPOSAL

The easiest and least expensive method of waste disposal is to discharge the wastes onto the ground or into surface waterways. Although this has historically been a common disposal method for many wastes, its use and misuse has been a major factor in the increase in environmental regulations governing the petroleum industry. Nevertheless, various forms of surface disposal are still appropriate for many treated wastes.

7.1.1 Disposal of Water

Wastewater can be discharged directly into local streams, rivers, or the ocean as long as its quality meets regulatory standards, i.e., its concentration of suspended and dissolved solids, chemicals, and hydrocarbons is sufficiently low. Surface discharge is regulated in most areas, however, and permits for such discharge are required.
When wastewater is discharged offshore, the water is typically treated to remove only the hydrocarbons. Although the dissolved solids (salt) concentrations of most produced waters are high enough to be toxic to even marine life, the rapid mixing and dilution of the discharged water makes the resulting environmental impact negligible.

For near-shore discharges in shallow water, there is less opportunity for mixing and dilution of the discharged water, and a toxic plume can exist for some distance away from the discharge point. Such toxic plumes are of particular concern when discharging a dense, high-saline, oxygen-deficient brine because it can be trapped in subsurface topographic low areas. Because this trapped brine can significantly impact the local marine life, permits to discharge high-salinity brines near the shore may be difficult to obtain, even if the hydrocarbon content is low.

When wastewater is discharged into onshore freshwater locations, both the hydrocarbon and dissolved solids concentrations must be low. Because of the high cost of removing dissolved solids, surface discharge of wastewater is generally possible only if the initial dissolved solids concentration of the water is low. Surface discharge into dry stream beds is a common way to dispose of treated water in arid areas like Wyoming. Surface discharge into percolation ponds is also used in some areas. In percolation ponds, the water is allowed to percolate into the undersaturated (vadose) zone, where it eventually evaporates back into the atmosphere. Because of the lack of control over where the water goes, this disposal method is being phased out. Discharge into evaporation ponds is also an option in many arid areas, particularly if a liner is used to prevent leaching of dissolved solids.

### 7.1.2 Disposal of Solids

Waste solids can be discharged directly onto the ground or into the ocean as long as their quality meets regulatory standards, i.e., the concentration of contaminants like hydrocarbons and heavy metals is sufficiently low. Because such discharges are regulated, permits are required in most areas.

**Offshore Discharges**

Offshore discharges of treated solids, such as drill cuttings and produced solids, are permitted in some areas. Offshore discharges,


Past environmental practices by segments of the petroleum industry have lead to the loss of public confidence that the industry is able to regulate itself and still protect the environment. Because of this, a large number of environmentally-related laws have been passed, and more are under consideration.

Regulations vary significantly from country to country, state to state, and locality to locality. In most areas, there are multiple, overlapping regulatory agencies that govern various aspects of oil and gas exploration and production. Because these regulations are rapidly changing, any summary of them can be quickly outdated.

Many environmental regulations impose both civil and criminal penalties, with fines and jail terms for violators. Civil penalties can be imposed on both companies and individuals for violations, regardless of intent. Criminal penalties can be imposed on individuals for deliberate violations of the regulations. It is the individual’s responsibility to ensure that their actions are in compliance with all existing regulations. The courts in the United States have generally held that supervisors and managers “know” what their employees are doing and thus can be held liable for their employees’ actions.

Most environmental laws in the United States are based on the concept of strict liability. Strict liability means that neither negligence nor wrongful intent are necessary for liability to be imposed. The company or person that violated the law will be held responsible, no matter what mitigating circumstances may be present, including sabotage or natural disaster.

Good communications between industry, legislators, and regulatory agencies are needed in developing meaningful regulations. Input from
when ignited, burns so vigorously that it creates a hazard; or if it is an ignitable compressed gas or an oxidizer as defined under U.S. Department of Transportation regulations. Examples of ignitable wastes include acetone, isopropanol, hexane, and methanol.

- **Corrosivity.** A waste is considered corrosive if it is able to deteriorate standard containers, damage human tissue, and/or dissolve toxic components of other wastes. An aqueous waste is considered corrosive if it has a pH less than or equal to 2 or greater than or equal to 12.5. A nonaqueous liquid is corrosive if it corrodes SAE 1020 steel at a rate greater than 0.25 inches per year at a temperature of 130°F. Although there is no provision for corrosivity of solids, many states require that a sample be placed in distilled water and the resulting pH be measured. Examples of corrosive wastes include sodium hydroxide, potassium hydroxide, and acids.

- **Reactivity.** A waste is considered reactive if it has a tendency to become chemically unstable under normal management conditions or react violently when exposed to air or mixed with water, or if it can generate toxic gases. Specific regulatory definitions for reactivity have not been developed. Examples of reactive wastes include cyanide or sulfide solutions, water-reactive metals, and picric acid.

- **Toxicity.** A waste is considered toxic if it can leach toxic components in excess of specified regulatory levels upon contact with water. A list of materials and the level above which they would be considered toxic under RCRA is shown in Table A-2. The test procedure to be used, called toxicity characteristic leaching procedure (TCLP), is carefully specified under the regulations and is very expensive to conduct. A summary of the TCLP procedure as it applies to the petroleum industry has been prepared by the American Petroleum Institute (American Petroleum Institute, 1990a).

If a waste is considered to be hazardous under RCRA, “cradle-to-grave” management and tracking of the waste is then required, including waste generation, transportation, treatment, storage, and disposal. The generator of the waste can be held liable for the waste, no matter who it has been passed on to or how long ago the waste was disposed.

After an extensive review of wastes generated by the upstream petroleum industry, it was determined that those wastes were not
RCRA: Subtitle C Exempt Wastes

Produced Water.

Drilling Fluids.

Drill Cuttings.

Rigwash.

Drilling fluids and cuttings from offshore operations disposed of onshore.

Well completion, treatment, and stimulation fluids.

Basic sediment and water and other tank bottoms from storage facilities that hold product and exempt waste.

Accumulated materials like hydrocarbons, solids, sand, and emulsions from production separators, fluid treating vessels, and production impoundments.

Pit sludges and contaminated bottoms from source or disposal of exempt wastes.

Workover wastes.

Gas plant dehydration wastes, including glycol-based compounds, glycol filters, filter media, backwash, and molecular sieves.

Gas plant sweetening wastes for sulfur removal, including amine, amine filters, amine filter media, backwash, precipitated amine sludge, iron sponge, hydrogen sulfide, scrubber liquids and sludges.

Cooling tower blowdown.

Spent filters, filter media, and backwash (assuming the filter itself is not hazardous and the residue in it is from an exempt waste stream).

Packing fluids.

Produced sand.

Pipe scale, hydrocarbon solids, hydrates, and other deposits removed from piping and equipment prior to transportation. Scale formed in boilers is nonexempt, however.

Hydrocarbon-bearing soil.

Pigging wastes from gathering lines.

(continued on next page)
Petroleum products, such as crude oil, crude oil fractions, and some refined products like gasoline, are currently exempt from being considered hazardous wastes under CERCLA. However, other wastes that are exempt from RCRA: Subtitle C may be considered hazardous under CERCLA, including some drilling muds and production chemicals. In fact, several oilfield waste disposal sites that accepted RCRA: Subtitle C exempt wastes have become Superfund (CERCLA) sites because the sites were not managed properly (Fitzpatrick, 1990; Campbell and Akers, 1990).

Under CERCLA, it is a crime to fail to notify the appropriate federal agency of a release of a hazardous substance into the environment and to fail to notify the EPA of the existence of an unpermitted hazardous waste disposal site. Fines of up to $10,000 and one year of imprisonment can be imposed per violation. Penalties of $20,000 and one year of imprisonment can be imposed for knowingly destroying or falsifying records required under CERCLA.

Superfund Amendments and Reauthorization Act (SARA)

In 1986, the Superfund Amendments and Reauthorization Act of 1986 (SARA: Title III) was passed, and added an emergency planning and community right-to-know provision to CERCLA. SARA requires owners and operators of facilities that store, use, or release hazardous materials in volumes above a specified threshold to report information about those materials to state and local authorities. This information includes a list of all hazardous chemicals, their volumes, and Material Safety Data Sheets (MSDS). The purpose of this information is to assist local authorities in preparing for emergency responses. SARA also requires releases of these chemicals above a certain amount be reported to the appropriate agencies.

SARA was targeted primarily at industrial sites that maintain large quantities of on-site chemicals over long periods of time. At drilling and production facilities, however, many chemicals, such as drilling or workover chemicals, are present for only a few days a year and not present at any other time. Normal operations make it very difficult to identify the times that specific chemicals are present at any given location.

To simplify the reporting requirements under SARA for the upstream petroleum industry, a generic hazardous chemical category list
Service to determine whether the proposed action is likely to jeopardize a threatened or endangered species.

Second is the taking provision, where any actions that adversely impact a threatened or endangered species is prohibited. A species is considered to be “taken” if it is harmed, harassed, pursued, hunted, wounded, trapped, captured, collected, or any action is undertaken to conduct those activities. The concept of “harm” includes any actions that significantly disrupt essential behavioral patterns.

Third is an incidental take permit, where a low level of “incidental taking” is allowed in exchange for the development of a Habitat Conservation Plan. A Habitat Conservation Plan specifies the impact of the allowed level of taking, steps to minimize or mitigate taking impacts, alternatives considered, and other measures that may be required by the permitting agency.

Violations of the Endangered Species Act can result in a $50,000 fine per offense. Willful violations can result in criminal penalties.

**Marine Mammal Protection Act**

The Marine Mammal Protection Act of 1972, amended in 1988, prohibits the taking and harassing of marine mammals. This act regulates the use of explosives for removing offshore platforms.

**Comprehensive Wetlands Conservation and Management Act**


**Hazard Communication Standard**

The Hazard Communication Standard (under the U.S. Occupational Safety and Health Administration, or OSHA) requires all employers to identify and list chemical hazards at their facilities. The employers are also required to provide health and safety information about those chemicals and to educate all employees through warning labels, Material Safety Data Sheets, and training programs.
National Environmental Policy Act (NEPA)

The National Environmental Policy Act (NEPA) was adopted in 1969 to ensure that the potential environmental impact from any proposed actions of the federal government or of the private sector that receive federal permits have been considered. This act requires detailed environmental reviews for major actions that may affect the quality of the human environment. These reviews may include extensive environmental impact statements. The impact of actions on threatened and endangered species must be included in the environmental reviews.

STATE REGULATIONS

In addition to the federal regulations discussed above, many states have imposed additional regulations on exploration and production activities for the oil and gas industry. These regulations vary considerably from state to state. A more complete discussion of the regulations of individual states is found in the literature (Interstate Oil Compact Commission, 1990; Boyer, 1990; Crist, 1990; Lynn, 1990; Wascom, 1990; Sarathi, 1991; Smith et al., 1993).

LOCAL REGULATIONS

Local agencies—counties, cities, groups of counties—may also regulate petroleum exploration and production activities. Typical local regulations include those involving noise and dust (particulate) levels at a site. However, air and water pollution, including visual and esthetic impacts, can also be regulated in cooperation with state and federal governments.

REGULATIONS IN OTHER COUNTRIES

Most countries regulate oil and gas activities to minimize their environmental impact. These regulations, however, may be different from those in the United States and can vary considerably from country to country. Many of the regulations of other countries have been discussed by a variety of authors, as indicated in Table A-3.


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