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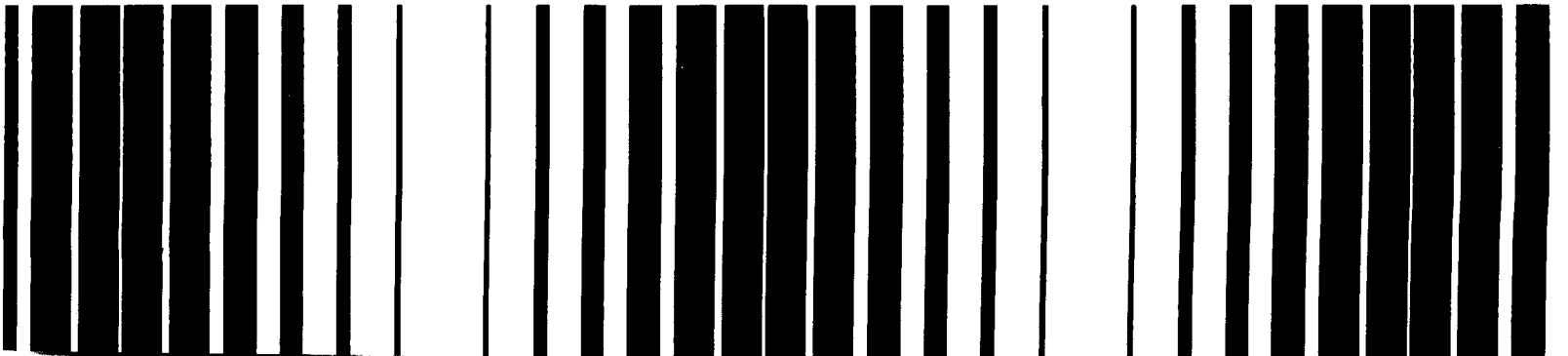
Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste

A Reference Guide

Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste:

A Reference Guide

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Acknowledgments

Contents

Table of Contents (Continued)

Chapter   **Page**

List of Tables

List of Tables (Continued)

List of Figures

List of Figures (Continued)

Figure   **Page**

PREFACE

The geochemical fate of deep-well-injected wastes must be thoroughly understood to help avoid problems when incompatibility between the injected wastes and the injection-zone formation is a possibility. An understanding of geochemical fate also will be useful when a geochemical no-migration demonstration must be made. This reference guide was written to address both of these needs by presenting state-of-the-art information on the geochemical fate of hazardous deep-well-injected wastes. Furthermore, operators of any new industrial-waste injection well who must consider the possibility of incompatibility will find this guide helpful in identifying geochemical reactions of potential concern and methods for testing incompatibility.

U.S. EPA regulations (53 *Federal Register* 28118-28157, July 26, 1988) stipulate that deep-well injection of hazardous wastes is allowed only if either of two no-migration standards is met (40 CFR 148.20[a][1]):

1) Fluid movement conditions are such that the injected fluids will not migrate within 10,000 years: vertically upward out of the injection zone; or laterally within the injection zone to a point of discharge or interface with an Underground Source of Drinking Water (USDW) as defined in 40 CFR Part 146.

2) Before the injected fluids migrate out of the injection zone or to a point of discharge or interface with USDW, the fluid will no longer be hazardous because of attenuation, transformation, or immobilization of hazardous constituents within the injection zone by hydrolysis, chemical interactions, or other means.

The state of the art of fluid-transport modeling is considerably more advanced than that of geochemical-fate and transport modeling. Consequently, geochemical-fate modeling is most likely to be used if a fluid-flow no-migration standard cannot be met. Geochemical-fate/transport modeling of deep-well-injected hazardous wastes is in very early stages of development, and its use in meeting current EPA Underground Injection Control regulations is unbroken ground. However, where the no-migration standard must be considered, this reference guide can help determine whether geochemical-fate/transport modeling of a specific waste is even feasible, and what approaches might be taken.

Organization

This reference guide follows the format of its companion volume (*Assessing the Geochemical Fate of Hazardous Wastes: Summaries of Recent Research*). The contents and organization of each chapter are:

Chapter One (Overview of Deep-Well Injection of Hazardous Wastes in the United States) discusses the identification and properties of significant wastes (Section 1.1). The sources, amounts, and compositions of deep-well-injected wastes are summarized in Section 1.2, and the geographic distribution in industrial injection wells is covered in Section 1.3. The chapter concludes with a discussion of the design and construction of such wells (Section 1.4).

Chapter Two (Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes) begins with an overview of influences on the geochemical fate of injected wastes (Section 2.1). This section discusses key characteristics of chemical systems, fate-influencing processes (partition, transformation, and transport), and interactions between hazardous waste and deep-well reservoirs. Subsequent sections examine partition (Section 2.2), transformation (Section 2.3), and transport processes (Section 2.4) in more detail. Chapter Two concludes with a discussion of the interactions among partition, transformation, and transport processes in the deep-well environment (Section 2.5).

Chapter Three (Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes) examines the environmental factors that determine what types of processes may occur and their outcomes. Section 3.1 discusses specific environmental factors (pH, redox potential, salinity, reservoir matrix, temperature, and pressure). Section 3.2 reviews brines and the major types of rocks in injection zones (carbonates and sandstones) and confining beds. Section 3.3 assesses the implications of these environmental factors for well plugging, confining formation failure, and well blowout. Finally,

Section 3.4 evaluates the influence of deep-well conditions on biodegradation.

Chapter Four (Geochemical Characteristics of Hazardous Wastes) begins with a general discussion of inorganic and organic hazardous wastes (Section 4.1) followed by more detailed information on inorganic wastes (Section 4.2) and organic wastes (Section 4.3). Section 4.4 contains suggestions on how to locate additional data on a substance of interest.

Chapter Five (Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes) covers basic approaches (Section 5.1) and specific methods and models (Section 5.2). The latter section discusses computer codes for both aqueous and solution geochemistry (Section 5.2.1), adsorption (Section 5.2.2), biodegradation (Section 5.2.3), hydrolysis (Section 5.2.4), and chemical transport (Section 5.2.5).

Chapter Six (Field Sampling and Laboratory Procedures and Protocols) summarizes specific laboratory procedures for geochemical-fate assessment. This chapter includes a discussion of how to select sampling methods and laboratory procedures (Section 6.1.2); methods for characterizing the waste to be injected and the injection reservoir (Section 6.2); types of waste-reservoir interaction tests (Section 6.3); procedures for measuring adsorption isotherms, hydrolysis rate constants, and biodegradation (Section 6.4); and a brief discussion of quality-control/assurance procedures (Section 6.5). The chapter concludes with an annotated bibliography of laboratory and field geochemical studies of deep-well waste injection and references related to laboratory procedures and protocols (Section 6.6).

Chapter Seven (Case Studies of Deep-Well Injection of Industrial Wastes) discusses the methods for field investigation of geochemical fate (Section 7.1) and then describes six cases where geochemical interactions of injected wastes in a variety of deep-well environments have been studied (Sections 7.2 to 7.7). Each case study contains information on (1) the injection facility, including the waste characteristics and history of injection activities, (2) lithology and chemistry of the injection zone and confining layer, and (3) geochemical processes observed or inferred to occur in the injection zone.

How to Use This Reference Guide

Because the study of the geochemical fate of wastes in the deep-well environment involves a range of scientific disciplines, this guide was written so that an expert in a field can quickly find information and references, but that others needing more of an overview of processes, chemistry, modeling techniques, laboratory procedures or other such information can readily gain a deeper knowledge of the subject. Suggestions for using this guide follow.

Information on a specific inorganic hazardous waste. For an inorganic waste, such as lead or chromium, turn to Section 4.2, which identifies relevant processes. You may also want to read the discussion of relevant processes in Chapter Two.

Information on organic hazardous wastes. For an organic waste, such as phenol, turn to the appropriate subsection in Section 4.3 (Monocyclic Aromatics, Section 4.3.3, in the case of phenol). To determine to which organic group the substance belongs, check Appendix A. The tables on the characteristics of each group of compounds (Tables 4-5 through 4-11) list other tables in the handbook containing information on individual compounds. Appendix B contains a list of hazardous organic compounds that have been studied in ground-water contaminant transport studies. Literature citations giving partition coefficients or retardation factors and ground-water biodegradation studies for the particular compound are listed. Again, you may want to read the discussion of relevant processes in Chapter Two, and check the index in Appendix A for other references to the substance. Section 4.4 lists data bases that can be used to perform literature searches for a specific substance.

Information on specific reservoir conditions. Section 3.2 discusses brine characteristics and reservoir-confining rocks. This section also has a reference index (Table 3-9) that includes citations to literature on the geology in areas of the United States where injection is practiced or the feasibility of injection has been assessed.

Information on a specific process, environmental factor, or fate-prediction method or model. Turn to the appropriate sections in Chapters Two (Processes), Three (Environmental Factors), and/or Four (Methods and Models).

Information on laboratory procedures. Turn to Chapter Six. The bibliography in this chapter gives detailed information about all the citations.

CHAPTER ONE

OVERVIEW OF DEEP-WELL INJECTION OF HAZARDOUS WASTES IN THE UNITED STATES

This chapter discusses the characteristics of hazardous wastes typically injected into Class I injection wells. It includes:

■ The properties that define a waste as hazardous (Section 1.1)

■ The sources, amounts, and composition of existing deep-well-injected hazardous wastes (Section 1.2)

■ Trends and distribution of industrial and hazardous waste injection (Section 1.3)

■ The design and construction of deep-injection wells (Section 1.4)

1.1 Identifying Hazardous Wastes

Wastes are defined as hazardous for purposes of regulatory control in 40 CFR Part 261. In this regulation, wastes are classified as hazardous either by being listed in tables within the regulation or by meeting certain specified characteristics. Thus under 40 CFR Part 261 hazardous wastes are known either as **listed** or **characteristic wastes**. Some listed wastestreams, such as *spent halogenated solvents* (listed in 40 CFR 261.31), come from many industries and processes. Other listed wastestreams, such as *API separator sludges from the petroleum-refining industry* (listed in 40 CFR 261.32), come from one particular industry and one process. A characteristic waste is not listed, but is classified as hazardous because it exhibits one or more of the following characteristics:

■ Toxicity to living organisms

■ Reactivity

■ Corrosivity

■ Ignitability

Listed wastes also exhibit one or more of these characteristics.* The significance of each of the characteristics listed above is discussed below and is summarized in Table 1-1. Deep-well-injected wastes commonly contain several components that classify the waste as hazardous, along with other nonhazardous components.

1.1.1 Toxicity
A waste is toxic under 40 CFR Part 261 if the extract from a representative sample of the waste exceeds specified limits for eight elements and four pesticides (arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, methoxychlor, toxaphene, 2,4-D and 2,4,5-TP Silvex—see Table 1, 40 CFR 261.24) using extraction procedure (EP) toxicity test methods. Note that this narrow definition of toxicity relates to whether a waste is defined as hazardous for regulatory purposes; in the context of this reference guide, toxicity has a broader meaning because most deep-well-injected wastes have properties that can be toxic to living organisms.

1.1.2 Reactivity
Reactivity describes a waste's tendency to interact chemically with other substances. Many wastes are reactive, but it is the degree of reactivity that defines a waste as hazardous. Hazardous reactive wastes are those which are normally unstable and readily undergo violent change without detonating, react violently with water, form potentially explosive mixtures with water, generate toxic gases or fumes when combined with water, contain sulfide or cyanide and are exposed to extreme pH conditions, or are explosive. Because deep-well-injected wastestreams are usually dilute (typically less than 1°o

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*Note: Radioactive wastes are not covered by 40 CFR Part 261. They involve environmental and regulatory issues that are beyond the scope of this reference guide.

waste in water) hazardous reactivity is not a significant consideration in deep-well injection, although individual compounds may exhibit this property at higher concentrations than those which exist in the wastestream. Nonhazardous reactivity is, however, an important property in deep-well injection, since when a reactive waste is injected, precipitation reactions that can lead to well plugging may occur (see Section 3.3.1).

1.1.3 Corrosivity

Corrosive wastes are defined as those wastes with a pH $\leq$ 2 $\geq$ 12.5 (i.e., the waste is very acidic or very basic). Beyond its importance in defining a waste as hazardous , the **corrosivity** of wastes is also a property of concern to deep-well injection systems and operations. Corrosive wastes may damage the injection system, typically by electrochemical or microbiological means. Corrosion of injection well pumps, tubing, and other equipment can lead to hazardous waste leaking into strata not intended for injection. For information on various types of electrochemical corrosion relevant to the injection-well system, the reader is referred to Warner and Lehr (1977). Other recommended sources include Langelier (1936), Ryznar (1944), Larson and Buswell (1942), and Stiff and Davis (1952). These sources discuss saturation and stability indexes for predicting the potential for corrosion or scaling (accumulation of carbonate and sulfate precipitates) in injection wells. The Stiff and Davis index is recommended by Warner and Lehr (1977) as most applicable to deep-well injection of hazardous wastes, because it is intended for use with highly saline ground waters. Additionally, Ostroff (1965) provides examples of how to use the index, Watkins (1954) describes procedures that test for corrosion, and Davis (1967) thoroughly discusses microbiological corrosion of metals.

1.1.4 Ignitability

As noted, deep-well-injected wastes are relatively dilute. Therefore, **Ignitability** is not a significant consideration in deep-well injection, although in a concentrated form, individual compounds may exhibit this property. Ignitability has no further implications for the fate of deep-well-injected waste.

1.2 Sources, Amounts, and Composition of Deep-Well-Injected Wastes

The sources, amounts, and composition of injected hazardous wastes are a matter of record, since the Resource Conservation and Recovery Act (RCRA) requires hazardous waste to be manifested (i.e., a record noting the generator of waste, its composition or characteristics, and its volume must follow the

Table 1-1   Typical Physical/Chemical Properties of Hazardous Components in Deep-Well-Injected Wastes

Characteristic	Comment
Hazardous Characteristics	
Toxicity	Has toxic properties that result in classification as a hazardous waste, but specific properties may vary greatly.
Reactivity	Reactivity usually reduced by dilution; actual concentration may affect toxicity and mobility.
Corrosivity	May be a significant consideration in well design and geochemical fate.
Ignitability	Not a significant consideration under injection conditions.
Physical/Chemical Properties	
Normal physical state	Liquids or dissolved solids.
Molecular weight	May affect structure-activity relationships (see Section 4.4.4).
Density/Specific gravity	Must be miscible in water.
Solubility	Must be soluble or miscible in water.
Boiling point	Greater than ambient temperatures.
Melting point	Less than ambient temperatures.
Vapor pressure/Density	Water soluble volatile compounds may be involved, but vapor pressure and vapor density are not significant considerations in deep-well injection.
Flash point/ Autoignition point	Greater than ambient temperatures.

2

waste load from its source to its ultimate disposal site). The sources and amounts of injected hazardous waste can be determined, therefore, based on these records. Table 1-2 shows the estimated volume of deep-well-injected wastes by industrial category for 1983, the most recent year for which data summaries are available. More than 11 billion gallons of hazardous waste were injected in 1983. Organic chemicals (51%) and petroleum-refining and petrochemical products (25%) accounted for three-quarters of the volume of injected wastes that year. The remaining 24% was divided among six other industrial categories: miscellaneous chemical products, agricultural chemical products, inorganic chemical products, commercial disposal, metals and minerals, and aerospace and related industry.

Although the general composition of each shipment of wastes to an injection well may be known, a number of factors makes it difficult to characterize fully the overall composition of industrial wastewaters at any one well. These factors include (1) variations in flow, in concentrations, and in the nature of organic constituents over time; (2) biological activity that may transform constituents over time; and (3) physical inhomogeneity (soluble and insoluble compounds) (Hunter, 1971). Further, the exact composition of the

shipment may *not* be known because of chemical complexity (Hunter, 1971). An example of the complexity of organic wastes is illustrated in Roy et al. (1989), which presents an analysis of an alkaline pesticide-manufacturing waste. This waste contained more than 50 organic compounds, two-fifths of which could not be precisely identified.

Although no systematic data base exists on the exact composition of deep-well-injected wastes in a survey of 209 operating waste-injection wells, Reeder et al. (1977) found that 53% injected one or more chemicals identified in that study as hazardous. The U.S. EPA gathered data for 108 wells (55% of total active wells) that were operated in 1983. Table 1-3 summarizes the total quantity of undiluted waste in six major categories, provides a breakdown of average concentrations of constituents for which data were available, and indicates the number of wells involved. A little more than half the undiluted waste volume was composed of nonhazardous inorganics (52%). Acids were the most important constituent by volume (20%), followed by organics (17%). Heavy metals and other hazardous inorganics made up less than 1% of the total volume in the 108 wells. About a third of the wells injected acidic wastes and about two-thirds injected organic wastes. Although the percentage of heavy metals by volume was low, almost one-fifth of the wells injected wastes containing heavy metals.

An injected wastestream typically is composed of the waste material and a large volume of water. Because the data in Table 1-3 include only 55% of the injection wells that were active in 1983, it is not possible to estimate precisely the percentage of waste to the total volume of injected fluid shown in Table 1-2. However, if the same total proportions apply to all wells, wastes made up of 3.6% of the total volume of injected fluid (36,000 mg/L). This percentage agrees well with an independent estimate for a typical injection ratio of 96% water and 4% waste (Strycker and Collins, 1987).

Table 1-3 also shows that the average concentration of all the acidic wastes exceeded 40,000 mg/L. Concentrations of metals ranged from 1.4 mg/L (chromium) to 5,500 mg/L (unspecified metals, probably containing multiple species). Five of the 18 organic constituents exceeded 10,000 mg/L (total organic carbon, organic acids, formaldehyde, chlorinated organics, and formic acid); four exceeded 1,000 mg/L (oil, isopropyl alcohol, urea nitrogen, and organic peroxides).

Table 1-2   Estimated Volume of Deep-Well-Injected Wastes by Industrial Category, 1983

Industrial Category	Volume (million gal/yr)	Percent of Total
Organic chemical	5,868	50.9
Petroleum refining and petrochemical products	2,888	25.0
Miscellaneous chemical products	687	6.0
Agricultural chemical products	525	4.6
Inorganic chemical products	254	2.2
Commercial disposal	475	4.1
Metals and minerals	672	5.8
Aerospace and related industry	169	1.5
Total[a]	11,539	100.0

[a]Total may not add due to rounding.

Source: U.S. EPA (1985).

Table 1-3	Waste Characteristics of 108 Hazardous Waste Wells Active in 1983 in the United States		
Waste Type/ Components	**Gallons[a]**	**Average Concentration (mg/L)**	**No. of Wells**
Acids	44,140,900 (20.3)[b]		35 (32.4)[b]
Hydrochloric acid		78,573	15
Sulfuric acid		43,000	6
Nitric acid		75,000	2
Formic acid		75,000	2
Acid, unspecified		44,900	12
Heavy Metals	1,517,600 (0.7)		19 (17.6)
Chromium		1.4	11
Nickel		600	5
Metals, unspecified		5,500	2
Metal hydroxides		1,000	1
Hazardous Inorganics	89,600 (<0.1)		4 (3.7)
Selenium		0.3	2
Cyanide		391	2
Organics	39,674,500 (17.4)		71 (65.7)
Total organic carbon (TOC)		11,413	24
Phenol		805	22
Oil		3,062	6
Organic acids		10,000	3
Organic cyanide		400	3
Isopropyl alcohol		1,775	3
Formaldehyde		15,000	2
Acetophenone		650	2
Urea "N"		1,250	2
Chlorinated organics		35,000	2
Formic acid		75,000	2
Organic peroxides		4,950	2
Pentachlorophenol		7.6	2
Acetone		650	2
Nitrile		700	1
Methacrylonitrile		22	1
Ethylene chloride		264	1
Carbon tetrachloride		970	1
Nonhazardous Inorganics	118,679,700 (52.0)	—	50 (46.3)
Other	22,964,600 (9.9)	—	33 (30.5)
Total	228,021,800[c]		108

[a]Gallons of nonaqueous wastes before dilution and injection.
[b]Number in parentheses is the percentage of total.
[c]Excludes overlaps between organics and acids.

Source: U.S. EPA (1985).

1.3 Geographic Distribution of Hazardous Waste Injection Wells

The use of wells for disposal of industrial wastes dates back to the 1930s, but this method was not used extensively until the 1960s, when it was implemented primarily in response to more stringent water pollution control regulations (Warner and Orcutt, 1973). Table 1-4 shows the trend in the number of industrial waste injection wells from 1967 to 1968. Because of slight differences in definitions, precise comparisons cannot be made for the 4 years for which systematic data are available. The 1967 and 1973 data represent all industrial-waste injection and may include wells that would not now be considered Class I wells. The 1984 data, based on a survey by U.S. EPA, include all active Class I hazardous waste injection wells (H); hazardous waste injection wells that have been permitted but not yet drilled, that are under construction and that are completed but not yet active or that have a permit pending (HP); and hazardous waste wells that have been temporarily or permanently abandoned (A). The 1986 data, from a survey by the Illinois State Geological Survey (ISGS), include hazardous waste wells (H), proposed hazardous waste wells (HP), and Class I nonhazardous waste wells (NH). (The proposed categories for the EPA and ISGS surveys may not follow exactly the same criteria, and the ISGS [H] category may include some or all of the abandoned wells in the EPA survey).

Even though the totals in Table 1-4 may not be directly comparable, the number of industrial-waste injection wells more than doubled between 1967 and 1986. The change from 1967 to 1986 is particularly noteworthy. The EPA survey noted that there had been no significant increase in new injection-well construction since 1980 (U.S. EPA, 1985); the ISGS data would appear to indicate a dramatic increase. If the 263-well total is asumed to include all the 41 abandoned wells in the EPA survey, then active wells would total 222, an increase of 27 wells in 2 years, compared with an increase of 7 wells from 1982 to 1984 reported in U.S. EPA (1985). If proposed wells in each survey are added, the net increase becomes 37 wells in 2 years.

The state totals in Table 1-4 show some interesting patterns. Class I injection wells are concentrated in two states, Texas (112 wells) and Louisiana (70 wells), which have a total of 69% of all wells in the 1986 (H) category. The growth from 1984 to 1986 has been concentrated in Texas, with a 38% increase, from 81 (H+HP+A) to 112 (H) wells. The only

other states to show a significant increase from 1984 to 1986 in the H+HP categories are Indiana (13 proposed wells) and California (7 proposed wells). Nine states have had industrial-waste injection wells in the past but did not have any permitted Class I wells in 1986 (Alabama, Colorado, Iowa, Mississippi, Nevada, North Carolina, Pennsylvania, Tennessee, and Wyoming). One state (Washington) had a Class I well in 1986, but no record of industrial wastewater injection before that year. Note that the total of active and proposed injection wells in 1973 was 278, more than the 252 total in the EPA 1984 survey. The states with the largest number of wells in the 1973 survey that may have been planned but not constructed appear to have been Kansas (30) and Michigan (32).

Figure 1-1 shows the number of Class I wells in the 1986 survey by state, divided into EPA regions, and also indicates the regulatory status of such wells in each state as of 1989. A comparison of this map with Figure 3-1 in Chapter Three shows the heavy concentration of hazardous waste injection wells in three geologic basins: Gulf Coast, Illinois Basin, and the Michigan Basin.

1.4 Design and Construction of Deep-injection Wells

The following description of the design and construction of deep-injection wells is adapted from Donaldson (1964), Donaldson et al. (1974), and U.S. EPA (1985).

1.4.1 Surface Equipment Used in Waste Disposal
Figure 1-2 shows the surface equipment used in a typical subsurface waste-disposal system. Detailed discussion of surface treatment methods can be found in Warner and Lehr (1977). The individual elements are:

■ A **sump tank** or an open 30,000- to 50,000-gallon steel tank is commonly used to collect and mix waste streams. An oil layer or, in a closed tank, an inert gas blanket is often used to prevent air contact with the waste. Alternatively, large, shallow, open ponds may provide sufficient detention time to permit sedimentation of particulate matter. Such ponds often are equipped with cascade, spray, or forced-draft aerators to oxidize iron and manganese salts to insoluble forms that precipitate in the aeration ponds.

■ An **oil separator** is used when the waste contains oil because oil tends to plug the disposal formation. The waste is passed through a settling

5

Table 1-4   Historical Trends in the Distribution of Industrial-Waste Injection Wells

State	1967	1973[a]	1984[b] H	1984[b] HP	1984[b] A	1986[b] H	1986[b] HP	1986[b] NH
Alabama	—	5	2	—	1	—	—	2
Alaska	—	—	1	1	—	1	3	—
Arkansas	—	1	4	—	1	7	1	—
California	4	5	2	—	—	3	7	—
Colorado	1	2	—	2	—	—	—	—
Florida	2	6	4	—	—	4	—	51
Illinois	3	7	6	—	—	6	—	3
Indiana	9	13	8	—	5	9	13	—
Iowa	1	1	—	—	—	—	1	—
Kansas	2	30	5	—	2	5	—	51
Kentucky	—	3	2	—	—	2	—	—
Louisiana	24	45	60	6	5	70	—	10
Michigan	21	32	11	—	11	15	1	—
Mississippi	—	1	1	—	—	—	—	6
Nevada	—	1	—	—	—	—	—	—
New Mexico	1	1	—	—	—	1	—	—
New York	—	4	—	—	—	6	—	—
North Carolina	—	4	—	—	4	—	—	—
Ohio	1	9	14	—	1	13	—	2
Oklahoma	1	11	6	1	1	7	—	8
Pennsylvania	5	9	—	—	3	—	—	—
Tennessee	1	—	—	—	—	—	—	—
Texas	32	74	69	5	7	112	—	24
Washington	—	—	—	—	—	1	—	—
West Virginia	2	7	—	—	—	1	—	—
Wyoming	—	1	—	1	—	—	—	8
Total	110	170	195	16	41	263	26	165

[a]State totals include active and proposed wells and total 278; the number of active injection wells was 170 and is shown in the total to facilitate comparison with other years.

[b]Class I wells, H = hazardous, HP = proposed hazardous, A = abandoned or inactive, NH = nonhazardous.

Sources: Warner (1968); Warner and Orcutt (1973); U.S. EPA (1985); Brower et al. (1989).

Figure 1-1   Regulatory Status of Class I Wells in the United States (Adapted from Brower et al., 1989). Well data from 1986 survey by Brower et al. 1989; regulatory status updated with data from U.S. EPA Office of Drinking Water/UIC Branch.

tank equipped with internal baffles to separate the oil from the waste.

■ A **clarifier** removes such particulate matter as polymeric flocs, dirt, oil, and grease. It is often a tank or a pond in which detention time is long enough to allow suspended particles to settle gradually. The process also may be accelerated by adding a flocculating agent such as aluminum sulfate, ferric sulfate, or sodium aluminate. Tank clarifiers are often equipped with a mechanical stirrer, sludge rake, and surface skimmer that continuously remove sludge and oil.

■ A **filter** is used in some cases when coagulation and sedimentation do not completely separate solids from the liquid waste in areas where sand and sandstone formations are susceptible to plugging. Filters with a series of metal screens coated with diatomaceous earth or cartridge filters typically are used. Where limestone

formations with high solution porosity are used for injection, filtration is usually not required.

■ A **chemical treater** is used to inject a bactericide if microorganisms could cause fouling of injection equipment and plugging of the injection reservoir.

■ An unlined steel **clear-waste tank** typically is used to hold clarified waste before injection. The tank is equipped with a float switch designed to start and stop the injection pump at predetermined levels.

■ An **injection pump** is used to force the waste into the injection zone, although in very porous formations, such as cavernous limestone, the hydrostatic pressure of the waste column in the well is sufficient. The type of pump is determined primarily by well-head pressures required, the volume of liquid to be injected, and the corrosiveness of the waste. Single-stage centrifugal pumps are

7

Figure 1-2   Typical Above-Ground Components of a Subsurface Waste Disposal System (Donaldson, 1964).
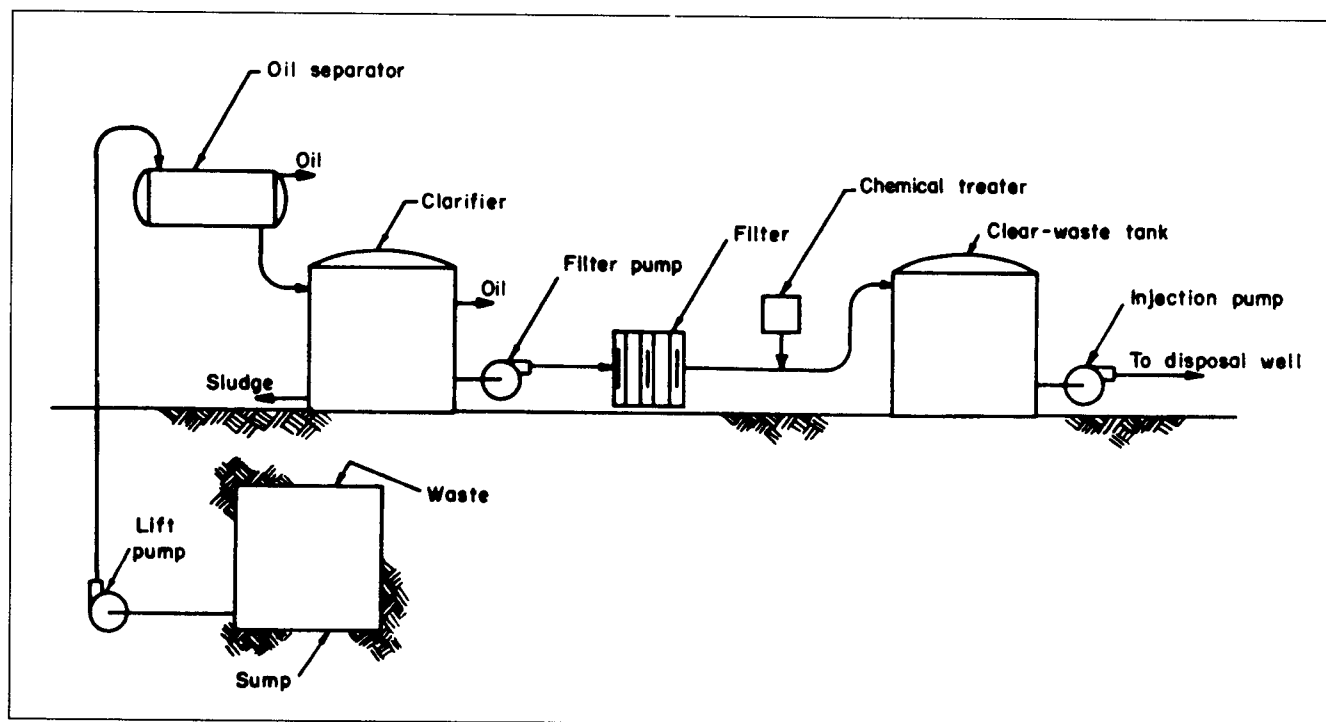
used in systems that require wellhead pressures up to about 150 psi, and multiplex piston pumps are used to achieve higher injection pressures.

1.4.2 Injection-Well Construction

Most injection wells are drilled using the rotary method, although depending on the availability of equipment and other site-specific factors, reverse-rotary or cable-tool drilling may be used. The construction of an injection well incorporates several important elements: (1) bottom-hole and injection-interval completion, (2) casing and tubing, (3) packing and cementing, (4) corrosion control, and (5) mechanical-integrity testing. A detailed discussion of the technical aspects of industrial-waste injection-well construction can be found in Warner and Lehr (1977). U.S. EPA (1985) also presents a survey of well construction methods and materials used for 229 hazardous waste injection wells.

Two types of **injection well completions** are used with hazardous waste injection wells:

■ **Open hole** completion typically is used in competent formations such as limestone, dolomite, and consolidated sandstone that will stand unsupported in a borehole. In 1985, 27% of Class I wells were of this type, with most located in the Illinois Basin.

■ **Gravel pack** and **perforated** completions are used where unconsolidated sands in the injection zone must be supported. In gravel-pack completions the cavity in the injection zone is filled with gravel or, more typically, a screen or liner is placed in the injection-zone cavity before the cavity is filled with gravel. In perforated completions, the casing and cement extend into the injection zone and are then perforated in the most permeable sections. In 1985, 53% of Class I wells were perforated and 17% were screened (U.S. EPA, 1985).

Casing and **tubing** are used to prevent the hole from caving in and to prevent aquifer contamination by confining wastes within the well until they reach the injection zone. Lengths of casing of the same diameter are connected together to form casing strings. Usually two- or three-casing strings are used. The outer casing seals the near-surface portion of the well (preferably to below the point where aquifers containing less than 10,000 mg/L total dissolved solids, potential underground sources of drinking water, are located). The inner casing extends to the injection zone. Tubing is placed inside the inner casing to serve as the conduit for injected wastes, and the space between the tubing and casing is usually filled with kerosene or diesel oil after packing and cementing are completed.

8

Packers are used at or near the end of the injection tubing to plug the space, called the annulus, between the injection tubing and the inner casing. **Cement** is applied to the space between the outer walls of the casing and the borehole or other casing. Portland cement is used most commonly for this purpose, although when acidic wastes are injected, special acid-resistant cements are sometimes used in the portion of the well that passes through the confining layers.

Corrosion control can be handled several ways: (1) by using corrosion-resistant material in constructing the well, (2) by treating the waste stream through neutralization or other measures, and (3) by cathodic protection.

Mechanical integrity testing is required by EPA regulations (40 CFR 146.08[b] and [c]) to ensure that an injection well has been constructed or is operating without (1) significant leakage from the casing, tubing, or packer or (2) upward movement of fluid through vertical channels adjacent to the well

bore. Table 1-5 lists types of mechanical integrity tests and situations in which they might be used. A detailed discussion of mechanical integrity can be found in U.S. EPA (1989).

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*References with more than six authors are cited with "et al."

Table 1-5   Applicability of Tests That May Be Used for Mechanical Integrity Verification

| | Cause of Injection Well Failure | | | | | |
| | Leaks in Casing Tubing or Packer | | Fluid Movement Behind Casing | | Types of Casing | |
Test	Presence	Location	Presence	Location	Metal	PVC
Pressure test	yes	no[a]	no	no	yes	yes
Monitor annulus pressure	yes	no	no	no	yes	yes
Temperature log	yes	yes	yes	yes	yes	yes[b]
Noise log	yes	yes	yes	yes	yes	yes[b]
Radioactive tracer log[c]	yes	yes	yes[d]	yes[d]	yes	yes
Cement bond log[c]	no[e]	no[e]	yes[e]	yes[e]	yes	yes[b]
Caliper log[c]	no[e]	no[e]	no[e]	no[e]	yes	yes
Casing condition log[c]	yes[e]	yes[e]	no[e]	no[e]	yes	no

[a]Can be "yes," if test staged.
[b]Log response may be somewhat dampened—test may not be adequate.
[c]May be used with approval of EPA administrator.
[d]Only if access by tracer can be gained through the casing or beneath casing shoe.
[e]May indicate potential failure site by showing corrosion spots and holes.

Source: U.S. EPA (1985).

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CHAPTER TWO

PROCESSES AFFECTING THE GEOCHEMICAL FATE OF DEEP-WELL-INJECTED WASTES

This chapter examines the major processes that affect the fate of deep-well-injected hazardous wastes. The focus is on processes that (1) are known to occur in the deep-well environment or (2) have not been directly observed but are theoretically possible. Section 2.1 provides an overview of the types and characteristics of chemical processes that affect injected wastes and the chemical interactions that can occur between a reservoir rock and fluids. Subsequent sections in this chapter provide more details on specific partition (Section 2.2), transformation (Section 2.3), and transport processes (Section 2.4), and the combined effects of these processes on the movement of injected wastes (Section 2.5).

2.1 Overview of Fate-influencing Processes in Chemical Systems

The section provides a basic understanding of how chemical systems and geochemical processes operate. Included are:

■ The key characteristics of chemical systems (Section 2.1.1)

■ The three major types of fate-influencing processes that affect wastes in the deep-well environment (Section 2.1.2)

2.1.1 Key Characteristics of Chemical Systems

A chemical system is a mixture of individual components. Chemical systems can be described by interactions that occur within the system and by the effect these processes have on the chemical composition and phases of the system. Interactions that change the chemical structure of system components are called chemical reactions. (Other interactions, such as processes that alter the solubility of system components, change the system without altering chemical structures.) Whether one reaction or a set of reactions occurs and how quickly the reac-

tions proceed are determined by the thermodynamics and kinetics of the system. Section 2.1.1.2 discusses thermodynamics, kinetics, and equilibrium of chemical systems in general; Section 2.1.1.3 discusses the key characteristics of chemical reactions.

2.1.1.1 Phases and Speciation

A substance may exist in one of three phases—solid, liquid or gas. The mobility of a substance in the subsurface is influenced by which of several form or **species** it may take. Species in deep-well injection formations, fall into six main categories:

1. "Free" ions are surrounded only by water molecules and are very mobile in ground water. Acid-base (Section 2.2.1) and dissolution reactions (Section 2.2.3) create free ions.

2. Species with low solubility in water may exist in solid form (such as Ag_2S, $BaSO_4$) or liquid form (such as chlorinated solvents). Precipitation reactions (Section 2.2.3) and immisicible-phase separation (Section 2.2.4) are important processes affecting this type of speciation.

3. Metal/ligand complexes (such as $Al[OH]^{+2}$, Cu-humate) and organic/ligand complexes tend to be mobile in ground water (see Section 2.3.2).

4. Physically adsorbed species are immobile in ground water but may be remobilized if replaced by other species with a stronger affinity to the solid surface (see Section 2.2.2).

5. Species held on a surface by ion exchange (such as calcium ions on clay) are also immobile in ground water. As with physically adsorbed species, they may be replaced by ions with a greater affinity to the solid surface.

6. Species may differ by oxidation state—for example, manganese (II) and (IV); iron (II) and (III); and chromium (III) and (VI). Oxidation state is

influenced by the redox potential (see Section 2.3.4). Mobility is affected because oxidation state influences precipitation-dissolution reactions (Section 2.2.3) and also toxicity in the case of heavy metals.

Dissolved species may be ionic or nonionic. In **ionic** species, an excess or shortage of electrons in the chemical structure creates a net positive or negative charge. In **nonionic** species, all negative and positive charges cancel each other out to form a neutral molecule. **Cations** are positively charged ions (Na^+, Ca^{+2}) and **anions** are negatively charged (SO_4^{-2}). The ability of a neutral substance to dissociate into ionic species is more common with inorganic substances than with organic substances. Acid-base reactions (Section 2.2.1) determine the distribution between ionic and nonionic species.

Neutral species may be nonpolar or polar. In **nonpolar** species, positively charged protons and negatively charged electrons are arranged in the molecular structure so as to create a uniform neutral charge on the molecule's surface. In **polar** species, the molecular structure creates charged poles on the molecule, even though the net charge is zero. Water (H_2O) is a polar molecule with the postive pole on the side of the hydrogen atom and the negative pole on the side of the oxygen atoms. Nonpolar molecules tend to be **hydrophobic** (water-avoiding) for reasons discussed in Section 2.2.2.

2.1.1.2 Thermodynamics, Kinetics, and Equilibrium in Chemical Systems

The thermodynamics of a system relate to the stability of substances within the system, i.e., whether a reaction can occur. Kinetics relates to reaction mechanisms and rate, i.e., how fast reactions can occur. Bedient et al. (1982) review the basic empirical equations defining zero-order, first-order, and second-order kinetic-rate laws.

An equilibrated state implies that as long as there are no significant changes in environmental factors affecting the system, the chemical composition and phases of the system will not change. Equilibrium does not necessarily imply that chemical processes cease. However, it does mean that for every reaction in one direction, a compensating reaction occurs in the opposite direction.

In nonequilibrium systems, chemical processes spontaneously alter the composition and/or phase of the system until equilibrium is attained. Simple systems, such as a mixture of sodium chloride and water, attain equilibrium quickly, whereas complex systems may reach equilibrium only after decades or eons.

The term **steady state** is sometimes use to describe chemical systems where thermodynamically unstable species exist but the rate of conversion to stable species is so slow that a quasi-equilibrated state exists. Because deep-well-injected wastes may be very complex chemical systems, the attainment of true equilibrium is uncertain.

2.1.1.3 Key Characteristics of Chemical Reactions

Chemical reactions may result from interactions among and between the three phases of matter: solid, liquid, and gas. The major interactions that occur in the deep-well environment are those between different liquids (injected waste with reservoir fluids) and those between liquids and solids (injected wastes and reservoir fluids with reservoir rock). Although gases may exist, they are usually dissolved in liquid at normal deep-well pressures (see also Sections 2.2.4 and 3.3.3).

Two chemical properties important in predicting fate in the deep-well environment are **homogeneity** and **reversibility**. Chemical processes can be broadly classified either homogeneous or heterogeneous and either reversible or irreversible. The chemical processes shown in Table 2-1, where relevant to

Table 2-1   Characteristics of Chemical Processes that May Be Significant in the Deep-Well Environment

Characteristic	Types of Reactions
Homogeneous	Acid-base, hydrolysis, hydration, neutralization, oxidation-reduction, polymerization, thermal degradation
Heterogeneous	Adsorption-desorption, precipitation-dissolution, immiscible-phase separation, biodegradation, complexation
Reversible	Acid-base, neutralization, oxidation-reduction (most inorganic and some biologically mediated), adsorption-desorption, precipitation-dissolution, complexation
Irreversible	Hydrolysis, oxidation-reduction (biodegradation of anthropogenic inorganics), immiscible-phase separation

12

deep-well injection, will be discussed in detail in Section 2.2 and Section 2.3.1

Homogeneous reactions in the deep-well environment take place in only one phase (aqueous). These reactions generally occur uniformly throughout the phase and are easier to study and predict than heterogeneous reactions. **Heterogeneous reactions** (for example, adsorption) tend to occur at the interface between phases. Some reactions (such as precipitation) may result in phase changes. Heterogeneous reactions also tend to occur more actively at some locations in the chemical system than at others. Bacterial decomposition of wastes is a heterogeneous process that will be more active in locations with conditions favorable to organisms and less active elsewhere.

The **reversibility** of reactions is another important characteristic in assessing the fate of deep-well-injected wastes. Depending on environmental conditions, reversible reactions readily proceed in either or both directions. Most acid-base reactions exemplify reversible processes. In aqueous solutions, relatively minor changes in such factors as pH or concentration can change the direction of these reactions. Irreversible reactions, typified by hydrolysis, have a strong tendency to go in one direction only.

Table 2-1 lists the reversible and irreversible processes that may be significant in the deep-well environment. The characteristics of the specific wastes (see Chapter Four) and the environmental factors present in a well (see Chapter Three) strongly influence which processes will occur and whether they will be irreversible. Irreversible reactions are particularly important. Waste rendered nontoxic through irreversible reactions may be considered permanently transformed into a non-hazardous state. Rubin (1983) provides a systematic discussion of mathematical modeling of ground-water chemical transport by reaction type.

2.1.2 Fate-Influencing Processes in the Deep-Well Environment

At the simplest level, the processes that most influence geochemical fate can be divided into three groups: **partition, transformation,** and **transport.** Only the first two are primarily geochemical in nature; these will be discussed in detail. Transport is discussed only briefly; a thorough discussion is beyond the scope of this reference guide.

■ **Partition processes** affect the form or state of a specific chemical substance at a given time or under specific environmental conditions, but not its chemical structure or toxicity. Thus, a sub-

stance may be in a solid form or in solution (described by the precipitation-dissolution process), but its toxicity remains unaltered regardless of form. The form or state of a substance, however, influences the transformation and transport processes that can occur. For this reason, partition processes are important to define in a fate assessment.

■ **Transformation processes** alter the chemical structure of a substance. In the deep-well environment, the transformation processes that may occur are largely determined by the conditions created by partition processes and the prevalent environmental factors. Transport processes do not need to be considered if transformation processes irreversibly change a hazardous waste to a nontoxic form.

■ **Transport processes** carry wastes through the subsurface environment and must be considered in a fate assessment if the interaction of partition and transformation processes does not immobilize or alter the hazardous waste. Waste migration can take place either in solution or in solid form (particle migration).

Table 2-2 presents the partition and transformation processes known to occur in the near-surface environment along with the special factors that should be considered when evaluating data in the context of the deep-well environment. Geochemical processes affecting hazardous wastes in deep-well environments have been studied much less than those occurring in near-surface environments (such as soils and shallow aquifers). Consequently, laboratory data and field studies for a particular substance may be available for near-surface conditions, but not for deep-well conditions.

Most of the processes listed in Table 2-2 are discussed in Sections 2.2 and 2.3. Two significant transformation processes that affect many hazardous organic wastes in the near-surface environment but do not occur in deep wells are volatilization (change from liquid to gaseous phase) and photolysis (decomposition in sunlight). Neither of these processes will be explored further in this reference guide.

As Table 2-2 shows, several processes can occur in both the near-surface and deep-well environments. For example, neutralization of acidic or alkaline wastes is a straightforward process, and although temperature differences between the two environments may need to be considered, no other factors make the deep-well setting distinctly different. The same holds true for oxidation-reduction (redox) processes.

13

Table 2-2   Near-Surface Geochemical Processes and Their Relevance to the Deep-Well Environment

Process	Surface Data Applicable to Deep-Well Environment?	Comments
Partition Processes		
Acid-base equilibria	Partly	Near-surface studies tend to investigate fresh or moderately saline water, which creates quite different conditions for acid-base equilibria. Studies of ocean geochemistry come closest to approximating deep-well conditions.
Adsorption-desorption	Partly	Mechanisms for adsorption on similar materials will be similar. Soil-adsorption data generally do not reflect the saturated conditions of the deep-well environment. Organic-matter content is a major factor affecting adsorption in the near-surface; its significance in the deep-well environment is less clear. Fate studies involving artificial recharge are probably useful, but differences between fresh waters and deep brines may reduce relevance.
Precipitation-dissolution	Partly	Higher temperatures, pressures, and salinity of the deep-well environment may result in significant differences between reactions in the two environments.
Immiscible-phase separation	No	Fluids (such as gasoline) that are immiscible in water are a significant consideration in near-surface contamination. Deep-well injection is generally limited to waste streams that are soluble in water. Well blowout from gaseous carbon-dioxide formation is an example of this process that is distinct to the deep-well environment.
Transformation Processes		
Volatilization	No	No atmosphere.
Photolysis	No	No sunlight.
Biodegradation	Partly	Some near-surface bacteria appear capable of entering and surviving in the deep-well environment. However, in general, temperature and pressure conditions in the deep-well environment are unfavorable for microbiota that are adapted to near-surface conditions. Biological transformations are primarily anaerobic.
Complexation	Partly	Humic substances are very significant factors in near-surface complexation processes, probably less so in the deep-well environment. Data on complexation in saline waters are probably most relevant.
Hydrolysis	Partly	Basic processes will be the same. Higher salinity of deep-well environment may affect rate constants.
Neutralization	Partly	Basic process is the same, but some adjustments may be required for pressure/temperature effects.
Oxidation-reduction	Partly	The deep-well environment tends to be more reducing than the near-surface environment, but equally reducing conditions occur in the near-surface. Some adjustments may be required for pressure/temperature effects.

14

The remaining processes, although they occur under both near-surface and deep-well conditions, are less applicable to the latter. Distinct differences between the two environments, however, can lead to significant differences in how the processes affect a specific hazardous substance. Compared with the near-surface environment, the deep-well environment is characterized by (1) higher temperatures, pressures, and salinity, and (2) lower organic matter content and Eh (oxidation-reduction potential—see Section 2.3.4). Chapter Three discusses the significance of these environmental factors.

Table 2-3 lists the partition and transformation processes applicable in the deep-well environment and indicates whether they significantly affect the toxicity and/or mobility of hazardous wastes. None of the partition processes results in detoxification (decomposition to harmless inorganic constituents), but all affect mobility in some way. All transformation processes except complexation can result in detoxification; however, because transformation processes can create new toxic substances, the mobility of the waste can be critical in all processes except neutralization.

Table 2-3 also indicates whether a process is biotic (mediated or initiated by organisms in the environment), abiotic (not involving biological mediation), or both. Biotic processes are limited to environmental conditions that favor growth of mediating organisms. Abiotic processes occur under a wide range of conditions. Adsorption, precipitation, complexation, and neutralization are abiotic; all other processes in Table 2-3 may be either.

2.2 Partition Processes

Partition processes determine how a substance is distributed among the liquid, solid, and gas phases and determine the chemical form, or **species** of a substance (see Section 2.1.1.1).

Partitioning usually does not affect the toxic properties of the substance. Partitioning can, however, affect the mobility of the waste, its compatibility with the injection zone, or other factors that influence fate in the deep-well environment. The major partition processes are:

- Acid-base reactions

- Adsorption-desorption

- Precipitation-dissolution

- Immiscible-phase separation

Table 2-3   Significance of Chemical Processes in the Deep-Well Environment

Process	Detoxification	Mobility	Biotic/Abiotic
Partitioning			
Acid-base equilibrium	No	Yes	Both
Adsorption-desorption	No	Yes	Abiotic
Precipitation-dissolution	No	Yes	Abiotic
Immiscible-phase separation	No	Yes	Both
Transformation			
Biodegradation	Yes	Yes	Biotic
Complexation	No	Yes	Abiotic
Hydrolysis	Yes	Yes	Both
Neutralization	Yes	No	Abiotic
Oxidation-reduction	Yes	Yes	Both

2.2.1 Acid-Base Reactions

Acid-base reactions affect pH (the concentration of hydrogen ions in solution), which is a controlling factor in the type and rate of many other chemical reactions (see Section 3.1.1). Neutralization, a special type of acid-base reaction that functions as a transformation process, is discussed in Section 2.3.1.

Acids dissociate in solution yielding hydrogen ions and anions according to the general reaction:

$$HA \text{ (neutral)} \longleftrightarrow H^+ \text{ (cation)} + A^- \text{ (anion)}$$
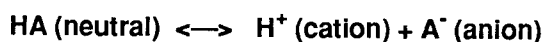
The ionization is reversible. The anion (acting as a weak base) can recombine with the hydrogen ion to re-form neutral HA. Both reactions occur continuously in solution, with the extent of ionization dependent on the strength of the acid. Strong acids, such as HCl, ionize completely in dilute aqueous solution. Thus a 0.01 molar (10^{-2} molar) solution has a pH of 2. Weak acids, such as acetic and other organic acids, ionize only slightly in solution and form solutions with pH from 4 to 6.

In the above example, the anion (A^-) functions as a base when it combines with a hydrogen ion. (By definition, any substance that combines with hydrogen ions is a base. Like strong acids, strong bases ionize completely in a dilute aqueous solution.) Thus NaOH dissolves in water to form hydroxide ions, which in turn function as a base when they combine with hydrogen ions to form water, as shown by the general equation:

$$MOH \longleftrightarrow M^+ + OH^-$$
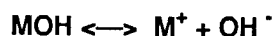
Strong acids (those which ionize completely in solution) are more likely to dissolve solids because charged particles such as hydrogen ions will interact more strongly with solids than will neutral particles. Weak acids do not readily donate hydrogen ions and consequently remain mostly in the neutral form. As a result, weak acids do not dissolve solids as readily as strong acids.

Strong bases (those which most readily extract hydrogen ions from solution) are also found predominantly in ionic forms and are similarly more reactive with solids than weak bases, which remain mostly in neutral form. The extent to which any base will extract hydrogen ions from solution depends on pH and the strength of the base.

Acid-base reactions occur quickly. When the pH of a solution changes, acids and bases readily attain a new equilibrium between neutral and ionic forms. Because toxic organics almost always exist in very low concentrations and tend to be weak acids or weak

bases, they have little, if any, influence on the pH of water. Acid-base equilibrium reactions involving hazardous organic compounds do not affect the toxicity of the waste and, as noted above, do not strongly influence pH. Table 2-4 identifies some acidic and basic hazardous organic wastes. Mills et al. (1985) describe the procedures for calculating the fraction of a toxic organic acid or base that is in nonionic, neutral form. Although this procedure is useful primarily for evaluating the volatilization of organics in near-surface conditions (because only electrically neutral species are directly volatile), it may also be useful when evaluating adsorption behavior in the deep-well environment.

When weak acids and bases ionize in wastestreams, pH is affected very little, but when strong acids and bases ionize in wastestreams, pH is affected dramatically. By definition, wastestreams having a pH ≤ 2 (highly acidic) or a pH ≥ 12.5 (strongly basic) are highly corrosive and are regulated as hazardous. As discussed in Section 2.3.1, acid-base reactions can **neutralize** acidic or basic hazardous waste by raising or lowering its pH.

2.2.2 Adsorption and Desorption

Adsorption is a physicochemical process whereby ionic and nonionic solutes become concentrated from solution at solid-liquid interfaces. Adsorption and desorption are caused by interactions between and among molecules in solution and those in the structure of solid surfaces. Adsorption is a major mechanism affecting the mobility of heavy metals and toxic organic substances and is thus a major consideration when assessing transport. Because adsorption usually is fully or partly reversible (desorption), only rarely can it be considered a

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Table 2-4   Acid-Base Characteristics of Toxic Organics

Acidic	Basic
Phenol	Benzidine
2-Chlorophenol	Dimethylnitrosamine
2,4,-Dichlorophenol	Diphenylnitrosamine
2,4,6-Trichlorophenol	Di-n-propyl nitrosamine
Pentachlorophenol	
2-Nitrophenol	
4-Nitrophenol	
2,4-Dinitrophenol	
2,4-Dimethylphenol	
4,6-Dinitro-o-cresol	

Source: Adapted from Mills et al., (1985).

16

detoxification process for fate-assessment purposes. Although adsorption does not directly affect the toxicity of a substance, the substance may be rendered nontoxic by concurrent transformation processes such as hydrolysis and biodegradation.

Many chemical and physical properties of both aqueous and solid phases affect adsorption, and the physical chemistry of the process itself is complex. For example, adsorption of one ion may result in desorption of another ion (known as ion exchange).

Adsorption is typically exothermic (i.e., releases energy in the process of bonding), but can be endothermic, and can be classified into two groups, based on the energies involved: chemical adsorption and physical adsorption. Chemical adsorption is more significant for heavy metals, either in the form of ion exchange or interactions involving metal complexes. Physical adsorption is more significant for hazardous organic compounds and is discussed in Section 2.2.2.2.

In chemical adsorption (also called chemisorption), chemical bonds are formed between the adsorbate molecule and the adsorbent. These bonds typically involve energies on the order of 7 kcal/mole or greater (Roy et al., 1987). These energies distinguish them from physical bonds, which typically involve energies less than 7 kcal/mole. Ion exchange, ligand exchange, protonation, and hydrogen bonds typically fall in the category of chemical bonds (see Table 2-5). Depending on the classification scheme used, numerous distinct types of chemical bonds have been identified in the laboratory under controlled conditions. Determining bonding mechanisms in the natural environment is much more difficult because of the diversity and complexity of adsorption surfaces. Chemical adsorption bonds are described below.

2.2.2.1 Chemical Bonding Mechanisms
Most interactions between heavy metals and/or organic species and clays involve one or more of three types of chemical bonds (Mortland, 1985): ion exchange, protonation, and hydrogen bonds. Where complex molecules are involved (see Section 2.3.2), ligand exchange may also serve as an important bonding mechanism (Roy et al., 1987). Table 2-5 summarizes the forces, adsorbate characteristics, and energies of these and other less common types of bonds, which are discussed in the following paragraphs.

Ion exchange. Ionic bonds bind metal and organic cations to negative electrical charges on the adsor-

bent surface. The negatively charged sites where ionic adsorption occurs are called exchange sites, and adsorbed cations that may be displaced by other cations are called exchangeable ions. In the deep-well environment, most exchange sites are filled primarily by such cations as Na^+, Ca^{+2}, and Mg^{+2}. Consequently, any ionic chemisorption of injected toxic wastes results from the displacement of these cations already adsorbed. Heavy metals have a strong tendency towards ion exchange. Ion exchange does not occur with nonionic toxic organics and generally is insignificant even for ionizable organic species because most organics ionize only slightly in solution.

Cations that form high-energy bonds will displace those which form lower-energy bonds. Thus, in ion exchange, divalent metal ions (ions with two available electrons) such as Ca^{+2} and Mg^{+2}, which have a stronger charge and thus a stronger attraction to negatively charged sites (see Section 3.1.4.2), will displace monovalent metal ions (ions with one available electron) such as Na^+ and K^+. Similarly, monovalent ions tend to displace organic molecules that adsorb using lower-energy physical forces.

Protonation. Protonation, which may take place without ion exchange, occurs when an acid-base reaction takes place with an exchangeable hydrogen ion located at the adsorption site. A neutral organic molecule that can act as a base may protonate (i.e., add a hydrogen ion to its structure) and become attached to the site where the H^+ ion has already been adsorbed. Protonation may occur with hydrogen ions that have adsorbed directly onto the mineral surface or with those attached to hydrated metal cations that have adsorbed onto the surface.

Hydrogen bonds. The negative pole of a polar organic molecule may be attracted to hydrogen atoms either on the surface of complex molecules (see Section 2.3.2) or on molecules already adsorbed onto the mineral surface. A water bridge may link the polar organic molecule to a water molecule on a hydrated exchangeable metal cation (see also Section 2.3.2). Similarly, a hydrogen atom in an adsorbed organic cation may provide a site for hydrogen bonding. In either case the shared hydrogen atom is more strongly bound to the adsorbed molecule, so hydrogen bonds are weaker than protonation bonds.

Ligand exchange. A ligand bond is formed when an ion or molecule attaches to a central ion to form a complex ion (Hamaker and Thompson, 1972). The ion or molecule attached to the central molecule is called a ligand. Because complex molecules tend to be strongly adsorbed on solid surfaces, if a molecule

(usually a water molecule) replaces a ligand, it becomes part of the already-adsorbed molecule.

Other bonds. The literature describes additional types of bonds that do not appear significant in the deep-well environment. These bonds are described below, with citations to detailed references.

- **Covalent bonds.** Covalent bonding involves the sharing of a pair of electrons by two atoms. Covalent bonding between silicates and organic groupings has been created in the laboratory but the degree to which such reactions occur in soils and sediments is unknown. The relatively high pressures and temperatures in deep-well environments over geologic time may cause some covalent bonding between organic matter and silicates (Mortland, 1970). Covalent bonds have high energies on the order of 100 kcal/mole. Thus, covalent bonding probably would not be a significant process during short-term interactions of organic wastes and reservoir solids, but may be important for metals.

- **Charge transfer.** Charge-transfer bonds result from the transfer of electrons across the surface of the adsorbent or organic molecules (Hamaker and Thompson, 1972). Hydrogen bonding, discussed above, is a special case of this phenomenon.

- **Anionic exchange or adsorption.** Anionic adsorption has been observed on dry clay films in the laboratory. It is not very likely, however, that organic anions will be absorbed on clays in the saturated conditions that exist in the deep-well environment unless they possess other properties. For example, in the case of anionic polymers with large molecular weights, entropy-generating forces (see hydrophobic forces in Section 2.2.2.2) might favor adsorption (Mortland, 1985).

- **Pi bonds.** Pi bonding occurs when the pi electrons of an organic compound are donated to a metal. This bond has been observed in the laboratory between benzene, xylene, toluene, and chlorobenzene and Cu(II) saturated montmorillonite clay (Doner and Mortland, 1969), but it does not seem likely to be significant in the deep-well environment.

2.2.2.2 Physical Adsorption Forces

Several physical forces influence adsorption. However, only two—**van der Waals** and **hydrophobic** (water-avoiding) forces—are significant in the deep-well environment.

Table 2-5 summarizes key information about these forces, which with two forces of lesser importance are discussed below.

Van der Waals forces. These are physical forces that operate between and among all atoms, ions, and molecules. They are relatively weak and decrease rapidly with distance. Van der Waals interactions are additive and can become significant when large-molecular-weight organic compounds are present. They also tend to be the most significant forces affecting adsorption of nonpolar organic molecules. The term *van der Waals-London* is also used to describe this kind of bonding.

Hydrophobic forces. Hydrophobic forces cause water molecules to be displaced when organic molecules interact with the surface of an adsorbent. This force does not result primarily from the attraction between the adsorbing surface and the organic molecule. Rather, it occurs because the structure of water is less stable when mixed with nonpolar organic molecules (neutral molecules in which the electrons are uniformly distributed on the surface). The hydrophobic interactions of nonpolar organic molecules with water tend to "push" the organic molecules to nearby mineral surfaces where van der Waals forces can cause adsorption, displacement of water molecules, and an increase in entropy. The term *entropy generation* has also been used for this type of adsorption (Mortland, 1970; Jury, 1986). The net effect is that the system is thermodynamically more stable when nonpolar molecules displace water molecules at the solid surface (Hamaker and Thompson, 1972).

Dipole-dipole interactions. Ion-dipole and dipole-dipole interactions occur between polar organic molecules and electrically charged or polar-adsorbing surfaces. Adsorbed metal cations have the greatest potential for providing bonding sites in the deep-well environment. Polar organic molecules must compete with more abundant water molecules, which are also polar; therefore dipole-dipole interactions are probably not major processes in ground-water systems (Mortland, 1985).

Magnetic forces. Ring structures containing conjugated double bonds create magnetic currents; thus, magnetic forces between large molecules and those between organic humic substances with conjugated double bonds may be significant (Hamaker and Thompson, 1972). But such conditions, if occurring at all in the deep-well environment, would be rare.

| Table 2-5 | Major Intermolecular Interactions Involved in Adsorption in the Deep-Well Environment |

Type of Interaction	Forces	Adsorbate	Energy (kcal/mole)	Sources
Primarily Chemical Bonds (>7 kcal/mole)				
Ion exchange	Electrostatic	Metal cations	up to 50	Hamaker and Thompson, 1972
		Organic acid/ Cation		
Ligand exchange	Electrostatic	Complex ion	1.9-19.3	Roy et al., 1987
Protonation	Electrostatic	Organic bases, metals	up to 35	Mortland, 1970
Hydrogen	Electrostatic	Polar organic	0.5-15 1.9-10	Hamaker and Thompson, 1972 Roy et al., 1987
Primarily Physical Adsorption Forces				
Van der Waals	Electrostatic	Small molecules	1-2 0.03-1.9	Hamaker and Thompson, 1972 Roy et al., 1987
		Large molecules	11+	Hamaker and Thompson, 1972
Hydrophobic	Entropy generation	Nonpolar organic	~1	*ibid.*
Dipole	Electrostatic	Polar organic	0.6 <1.9	*ibid.* Roy et al., 1987
Magnetic	Magnetic	—	—	

2.2.2.3 Reversibility of Adsorption

Adsorption is often fully reversible, as can be seen in an adsorption-desorption cycle. First, a mineral is exposed to a solution with a known concentration of a compound until equilibrium is reached. Then the same mineral is exposed to the same solution (but without the added solute) until no further desorption is noted. If adsorption is a fully thermodynamic process, the amount of the compound adsorbed will equal the amount that is desorbed; that is, all adsorbed material is desorbed.

A number of investigators of adsorption-desorption behavior of pesticides on soil have observed, however, apparent irreversibility (Van Genuchten et al., 1974). Rao and Davidson (1980) have identified three major causes of irreversibility in laboratory experiments involving adsorption:

■ **Artifacts created by some aspect of the laboratory method.** For example, desorption experiments typically involve repeated use of a centrifuge to separate "equilibrated" solutions from the solids, and then follow with agitation and resuspension of solids in the solution. This procedure may break down soil particles, thus increasing the number of adsorption sites during the desorption phase.

■ **Failure to establish complete equilibrium during adsorption.** For example, slow solvent action of the aqueous solution might unmask new adsorption sites. Also, a pseudo-equilibrium (appearance of a steady state before true equilibrium is attained) may result when clays or organic matter have adsorption sites within the particles that are reached only after slow diffusion.

■ **Chemical transformations of the adsorbed substance.** These transformations result in a chemical structure that is more strongly bound to the solid surface, or they result from microbial degradation. Since the total amount of the substance in the system is reduced, desorption results in concentrations that are lower than the beginning concentration.

In spite of considerable research in this area, the physicochemical basis for "irreversible" adsorption is not well understood (Rao and Davidson, 1980). For example, in flow-through adsorption experiments involving phenol interacting on a Frio sandstone core under simulated deep-well temperatures and pressures, Collins and Crocker (1988) observed **no** desorption when the core was flushed with brines that did not contain phenol.

2.2.3 Precipitation and Dissolution

Precipitation is a phase-partitioning process whereby solids separate from a solution. Dissolution involves movement from the solid or gaseous phase to the aqueous phase. Solids dissolve into ions, whereas gases retain their original chemical structure when dissolved. The solubility of a compound (its tendency to dissolve in water or other solutions) is the main property affecting the precipitation-dissolution process. This section examines the solubility characteristics of hazardous wastes and the significance of precipitation and dissolution processes in the deep-well environment.

The concentration of a compound in water is controlled by its **equilibrium solubility** or **solubility constant** (the maximum amount of a compound that will dissolve in a solution at a specified temperature and pressure). Equilibrium solubility will change with environmental parameters such as temperature, pressure, and pH; for example, the solubility of most organic compounds triples when temperature rises from $0°C$ to $30°C$. Each type of waste has a specific equilibrium solubility at a given temperature and pressure. The solubility of toxic organic compounds is generally much lower than that of inorganic salts. This characteristic is particularly true of nonpolar compounds because of their hydrophobic character (see Section 2.2.2.2).

Precipitation usually occurs when the concentration of a compound in solution exceeds the equilibrium solubility, although slow reaction kinetics may result in "supersaturated" solutions. For organic wastes in the deep-well environment, precipitation is not generally a significant partitioning process; in certain circumstances, however, it may need to be considered. For example, pentachlorophenol precipitates

out of solution when the solution has a pH < 5 (Choi and Aomine, 1974a, 1974b), and polychlorophenols form insoluble precipitates in water high in Mg^{+2} and Ca^{+2} ions (Davis, 1967). Also, organic anions react with such elements as Ca^{+2}, Fe^{+2}, and Al^{+3} to form slowly soluble to nearly insoluble compounds.

Precipitation may be significant for heavy metals and other inorganic constituents in injected wastes. For example, sulfide ions have a strong affinity for metal ions, precipitating as metal sulfides. The dissolved constituents in injected wastes and reservoir fluids would not be in equilibrium with the in situ brines because of the fluids' different temperature, pH, and Eh (oxidation-reduction potential; see Section 3.6.2). When the fluids are mixed, precipitation reactions can lead to injection-well plugging. Section 3.3.1.3 (Well Plugging) examines specific inorganic precipitation reactions that may cause problems during injection.

Coprecipitation is a partitioning process whereby toxic heavy metals precipitate from the aqueous phase even if the equilibrium solubility has not been exceeded. This process occurs when heavy metals are incorporated into the structure of silicon, aluminum, and iron oxides when these latter compounds precipitate out of solution (Fisher et al., 1974, as cited by Scrivner et al., 1986). Iron hydroxide collects more toxic heavy metals (chromium, nickel, arsenic, selenium, cadmium, and thorium) during precipitation than aluminum hydroxide (Bunshah, 1970). Coprecipitation is considered to remove effectively trace amounts of lead and chromium from solution in injected wastes at New Johnsonville, Tennessee (Scrivner et al., 1986). Coprecipitation with carbonate minerals may be an important mechanism for cobalt, lead, zinc and cadmium (Förstner and Wittmann, 1979).

Dissolution of carbonates (acidic wastes), sand (alkaline wastes), and clays (both acidic and alkaline wastes) can neutralize deep-well-injected wastes (Scrivner et al., 1986). Neutralization is discussed in Section 2.3.1. Because precipitation-dissolution reactions are highly dependent on environmental factors such as pH and Eh, changes in one or more factors as a result of changes in injected-waste characteristics, or varying percentages of injected waste and reservoir fluids concentrations, may result in re-solution or reprecipitation of earlier reaction products. This sensitivity to environmental factors increases the complexity of predicting precipitation-dissolution reactions because different equilibrium solubilities of a compound may exist in different parts of the injection zone depending on the proportions

of waste and reservoir fluid. Similarly, a sequence of precipitation and dissolution reactions may take place at a given location of the injection zone as the concentration of injected wastes increases.

2.2.4 Immiscible-Phase Separation

An insoluble liquid or gas will separate from water, resulting in immiscible-phase separation. The behavior of nonaqueous-phase liquids (NAPLs) that may be lighter (LNAPLs) or denser (DNAPLs) than water is important in near-surface ground-water contamination studies (Palmer and Johnson, 1989). However, aqueous-phase separation generally is not an issue in the deep-well environment because injected hazardous wastes are usually dilute. Failure to remove immiscible oily fluids from injected wastes potentially may cause plugging in the injection zone. Density and viscosity differences between injected and reservoir fluids, however, may need to be considered in transport modeling (see Section 2.4.4). Generally, pressures are high enough in the deep-well environment to keep gases such as carbon dioxide, generated as products of waste-reservoir interactions, in solution. Under certain conditions of high temperature and high waste concentrations, however, injected hydrochloric acid can cause carbon dioxide to separate from the liquid and produce a well blowout. This reaction is discussed further in Section 3.3.3 (Well Blowout) and in the case study described in Section 7.6.

2.3 Transformation Processes

Transformation processes change the chemical structure of a compound. Because not all transformation processes convert hazardous wastes to nonhazardous compounds, geochemical fate assessment must consider both the full range of transformation processes that may occur and the toxicity and mobility of the resulting products. For deep-well-injected wastes, transformation processes and subsequent reactions may lead to one or more of the following:

- Detoxification

- Transtoxification

- Toxification

Detoxification is an irreversible change in a substance from toxic to nontoxic form. For example, when an organic substance breaks down into its inorganic constituents, detoxification has taken place. **Transtoxification** occurs when one toxic compound is converted into another toxic compound. **Toxification** is the conversion of a nontoxic compound to a toxic substance. Table 2-6 lists some examples of each. Transformation processes that may be significant in deep-well-injection fate assessments are:

- Neutralization

- Complexation

- Hydrolysis

- Oxidation-reduction

- Catalysis

- Polymerization

- Thermal degradation

- Biodegradation

Two other processes that may transform hazardous wastes are photolysis and volatilization, but they are not covered here because they do not occur in the deep-well environment (see Section 2.1.2).

2.3.1 Neutralization

Acidic wastes with a pH $\leq$ 2.0 and alkaline wastes with a pH $\geq$ 12.5 are defined as hazardous (40 CFR Part 261). To meet the regulatory definition of non-hazardous, acidic wastes must be neutralized to a pH > 2.0 by reducing the hydrogen ion concentration, and alkaline wastes must be neutralized to a pH > 12.5 by increasing the hydrogen ion concentration.

Carbonates (limestone and dolomite) will dissolve in and neutralize acidic wastes. The process is:

$$CaCO_3 \longrightarrow Ca^{+2} + CO_3^{-2} \text{ (dissolution)}$$

$$CO_3^{-2} + 2H^+ \longrightarrow CO_2 + H_2O \text{ (neutralization)}$$
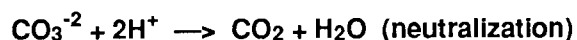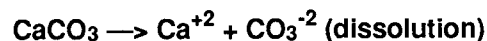
When calcium carbonate goes into solution, it releases basic carbonate ions (CO_3^{-2}), which react with hydrogen ions to form carbon dioxide (which will normally remain in solution at deep-well-injection pressures) and water. Removal of hydrogen ions raises the pH of the solution. However, aqueous carbon dioxide serves to buffer the solution (i.e., re-forms carbonic acid in reaction with water to add H$^+$ ions to solution). Consequently, the buffering capacity of the solution must be exceeded before complete neutralization will take place. Buffering capacity and the specific chemical reaction involving carbon dioxide, water, and carbonic acid are discussed in more detail in Section 3.1.1. Nitric acid can react with certain alcohols and ketones under increased pressure to increase the pH of the solution,

21

Table 2-6   Examples of the Effects of Transformation Processes on the Toxicity of Substances

Type of Transformation	Process	Source
Detoxification		
Cyanide —> Amide —> Acids + Ammonia	Hydrolysis	Scrivner et al., 1986
Cyanide —> Sulfate + Carbon + Nitrogen	Biooxidation	Mudder and Whittlock, 1983
Nitrile —> Amide —> Acids + Ammonia	Hydrolysis	Scrivner et al., 1986
Alkyl halide —> Alcohol + Halide ion	Hydrolysis	Valentine, 1986
Chlorobenzene —> CO_2 + Cl^- + H_2O	Biooxidation	Bouwer and McCarty, 1984
1,3-Dichlorobenzene —> CO_2 + Cl^- + H_2O	Biooxidation	ibid.
1,4-Dichlorobenzene —> CO_2 + Cl^- + H_2O	Biooxidation	ibid.
Vinyl chloride —> CO_2 + Cl^- + H_2O	Bioreduction	Vogel and McCarty, 1987
Transtoxification		
2,4-D ester —> 2,4-D acid (increased)	Hydrolysis	Mills et al., 1985
Phenol + Formaldehyde —> Phenolic resins	Polymerization	Strycker and Collins, 1987
Aldrin —> Dieldrin	Oxidation	Crosby, 1973
DDT —> DDD	Reduction	Glass, 1973
o-Xylene —> o-Toluic acid	Co-metabolism	Horvath, 1972
Benzene —> Phenol	Biooxidation	Gibson, 1972
Carbon tetrachloride —> Chloroform —> Methylene chloride	Bioreduction	Wood et al., 1985
Ethylbenzene —> Phenylacetic acid	Co-metabolism	Horvath, 1972
1,1,1-Trichloroethane —> 1,1-Dichloroethane —> Chloroethane	Bioreduction	Wood et al., 1985
Tetrachloroethylene —> Trichloroethylene —> Various Dichloroethenes —> Vinyl chloride	Bioreduction	ibid.
1,2-Dichloroethane —> Vinyl chloride	Hydrolysis	Ellington et al., 1988
Inorganic mercury —> Methyl mercury	Bioreduction	Reeder et al., 1977
Nitrilotriacetate —> Nitrosamines	Bioreduction	ibid.
Toxification		
Amines —> Nitrosamines	Biooxidation	Alexander, 1981

and this reaction was proposed by Goolsby (1971) to explain the lower-than-expected level of calcium ions in backflowed waste at the Monsanto waste injection facility in Florida (see Section 7.2).

Quartz (SiO_2) and other silicates are generally stable in acidic solutions but will dissolve in highly alkaline waste solutions, decreasing the pH of the waste. The process by which this reaction occurs is complicated because it creates complex mixtures of nonionic and ionic species of silica. Scrivner et al. (1986) discusses these reactions in some detail. They observe that the silicates in solution buffer the liquid. Also, laboratory experiments in which alkaline wastes have been mixed with sandstone have shown relatively small reductions in pH. At near-surface temperature and pressure conditions, an alkaline waste remains hazardous, but at simulated subsurface temperatures and pressures, the waste is rendered nonhazardous, ranging in pH from 11.5 to 12.4 in the experiments performed by Roy et al. (1989). However, the pH of the sandstone-waste mixture remained above 12.5 in other investigations, possibly because a higher solid:liquid ratio (less sandstone per volume of liquid) is used (personal communication, May 10, 1990, W. R. Roy, Illinois State Geological Survey, Champaign, Illinois).

Reactions with clay minerals can neutralize both low-pH and high-pH solutions. Neutralization of acids occurs when hydrogen ions replace Al, Mg, and Fe. In alkaline solutions, neutralization is more complex and may involve cation exchange, clay dissolution, and reaction of cations with hydroxide ions to form new minerals called zeolites (Scrivner et al., 1986).

2.3.2 Complexation
A complex ion is one that contains more than one ion. Because of its effect on mobility, **complexation**, the process by which complex ions form in solution, is very important for heavy metals and may be significant for organic wastes. Heavy metals are particularly prone to complexation because their atomic structure (specifically the presence of unfilled d orbitals) favors the formation of strong bonds with polar molecules, such as water and ammonia (NH_3), and anions, such as chloride (Cl^-) and cyanide (CN^-). Depending on the chemistry of an injected waste and existing conditions, complexation can increase or decrease the waste's mobility.

Complexation is more likely in solutions with high ionic strength (which is typical of fluids found in the deep-well-injection environment—see Section 3.1.3). This is true because the large number of ions present in solution increases the number of chemical species that can form (Langmuir, 1972). Many variables affect the stability of a complex ion relative to ions and metals that can serve as potential ligands to the central metal, the most important of which is the valence (charge) of the central cation and its radius. As a rule, the stability of complexes formed with a given ligand increases with cation charge and decreases with cation radius (Langmuir, 1979).

The solubility of most metals is much higher when they exist as organometallic complexes (Strycker and Collins, 1987). Naturally occurring chemicals that can partially complex with metal compounds and increase the solubility of the metal include aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols. Several complexation processes, including chelation and hydration, can occur in the deep-well environment.

2.3.2.1 Chelation
Chelation is the process of forming complex ions with organic ligands that have more than one site able to bond to the central metal ion in the complex. The complex ion formed by this process is called a **chelate**. The ligands in chelates are classified according to the number of binding sites in the molecule: monodentate (one site), bidentate (two sites), etc. Metal solubility (i.e., mobility) is greatly increased when chelation occurs, and metal-chelate compounds are very stable when the metal ion is chelated by a heterocyclic ring of an organic molecule. Although most simple organic-metal complexes will dissociate if solutions become more dilute, chelated complexes do not tend to dissociate (Martell, 1971). Even adsorbed metals may be remobilized into solution by organic chelates. For example, the synthetic chelate nitrilotriacetic acid (NTA), used as an alternative to polyphosphate in detergents, has been observed to remobilize adsorbed heavy metals in the near-surface environment (Förstner and Wittmann, 1979). Although remobilization of heavy metals by chelation has not been reported in the published literature on deep-well injection, the possibility should be considered if the waste contains chelates.

2.3.2.2 Hydration
Metal ions in solution readily form complex ions by the process of **hydration** (bonding to water molecules). Because of the polar nature of water molecules, the negative poles are attracted to the positively charged metal ion, usually by ion-dipole bonding. Covalent bonding may also occur (see Section 2.2.2 for discussion of ion-dipole and covalent bonding).

Hydration tends to increase the complexity of chemical reactions because hydrated polyvalent metal ions may form multiple associations with other metals to create complex polynuclear ions. Hydration may also reduce mobility of metal ions through physical adsorption, even when ion-exchange reactions are completed in a solution. Reduction of mobility can also be caused by dehydration when organic ligands replace water molecules in complex ions. Polynuclear metal ions and large organic complexes can be readily adsorbed onto mineral surfaces because of their large molecular weights, which enhance physical adsorption (see Section 2.2.2). Metal complexes may also serve as catalysts for a number of other chemical transformation reactions. These reactions are discussed in Section 2.3.5.

2.3.3 Hydrolysis

Hydrolysis occurs when a compound reacts chemically with water (i.e., new chemical species are formed by the reaction), and can be a significant transformation process for certain hazardous wastes in the deep-well environment (see Table 2-7). Hydrolysis reactions fall into two major categories: **replacement** and **addition**. Each is discussed in Section 2.3.3.1. The rates at which these reactions occur are also significant in a fate assessment because some take so long to occur that they will not take place during the analytical time frame (10,000 years).

2.3.3.1 Types of Hydrolysis

Replacement and addition are essentially irreversible transformation processes. Both can be significant in detoxifying some types of organic hazardous wastes. In replacement, the most common hydrolysis reaction, one functional group is replaced by an -OH (hydroxide ion) originating from a water molecule. For example, an hydroxide ion can replace the halide ion in an alkyl halide to form an alcohol, leaving the halide ion in solution. Alcohols can also form by addition of water to a carbon-carbon double bond.

Hydrolysis reactions can produce intermediate compounds subject to further hydrolysis (e.g., nitriles to amides to acids). Whether hydrolysis results in detoxification, transtoxification, or toxification depends on the toxicity of the most stable end product of any series of hydrolysis reactions.

2.3.3.2 Hydrolysis Rates

Detoxification by hydrolysis is significant in fate assessments only if the rate is fast enough to reduce concentrations to acceptable levels at subsurface locations of regulatory concern. Hydrolysis rates are commonly reported in terms of half-life (i.e., the number of days or years for half of the original concentra-

Table 2-7 Listed Hazardous Organic Wastes for which Hydrolysis May Be a Significant Transformation Process in the Deep-Well Environment

Group/Compound	Half-life[a]
Pesticides	
DDT	81-4,400[b]
Dieldrin	3,800
Endosulfan/Endosulfan sulfate	21
Heptachlor	1
Halogenated Aliphatic Hydrocarbons	
Chloroethane (ethyl chloride)	38
1,2-Dichloropropane	180-700[c]
1,3-Dichloropropene	~60[c]
Hexachlorocyclopentadiene	14
Bromomethane (methyl bromide)	20
Bromodichloromethane	5,000
Halogenated Ethers	
bis(Chloromethyl) ether	<1
2-Chloroethyl vinyl ether	1,800
Monocyclic Aromatics	
Pentachlorophenol	200
Phthalate Esters	
Dimethyl phthalate	1,200
Diethyl phthalate	3,700
Di-n-butyl phthalate	7,600
Di-n-octyl phthalate	4,900[d]

[a]Unless otherwise indicated, half-life is measured in days at pH = 7 and ambient temperature.
[b]Callahan et al. (1979) report lower value for pH 9 and upper value for pH 3 to 5.
[c]Estimated values in Callahan et al. (1979); not based on actual measurements.
[d]Ellington et al. (1988) report a value of 107 years (39,000 days).

Sources: Callahan et al. (1979), Mills et al. (1985), Schwarzenbach and Giger (1985), Ellington et al. (1988).

tion of the substance to be hydrolyzed). Predicted hydrolysis half-lives of various hazardous organic compounds range from days to thousands of years. Such factors as pH, temperature, and the presence of other ions affect the rate of hydrolysis of organic compounds. Strycker and Collins (1987) speculate that deep-well environments may lead to shorter half-lives because of increased temperatures, pressures, and Eh changes. Hydrolysis reaction rates do increase with increasing temperatures, but predicting rates in the deep-well environment is

complicated because the influence of temperature on hydrolysis is not always known precisely. The effects of ionic strength on hydrolysis reactions are also difficult to predict and can lead to either acceleration or retardation of rates, depending on the substrate, the salts, and their concentrations (Mabey and Mill, 1978). The high ionic concentrations of reservoir brines in the deep-well environment make this factor important in fate assessment.

A number of alkaline-earth and heavy-metal ions catalyze hydrolysis of a variety of organic esters; however, this reaction does not appear to be a major contributor to hydrolysis under near-surface conditions (Mabey and Mill, 1978). Consequently, hydrolysis of susceptible compounds may be enhanced in the deep-well environment where concentrations of both alkali metal and heavy metals in reservoir fluids and injected wastes are much higher than those in typical near-surface environments.

Hydrolysis rates greatly depend on pH and vary widely for an individual compound under acidic to basic conditions. Chloromethane, which shows no significant change in hydrolysis rate from a pH of 3 to 9, is an exception (Mills et al., 1985). Hydrogen cyanide illustrates the strong effect that pH can have on hydrolysis rates. Cyanides hydrolyze to amides, which then hydrolyze to acids and ammonia. At pH> 10, this reaction has a half-life of about 10 years. At pH 4, however, the reaction may take more than 10,000 years (Scrivner et al., 1986). Furthermore, metal-cyanide complexes do not hydrolyze readily and can reduce the concentration of free cyanide in solution, increasing the time needed for the total cyanide concentration to decrease from hydrolysis (Scrivner et al., 1986).

Many classes of organic compounds hydrolyze in aqueous solutions, whereas others are resistant. Table 2-8 summarizes organic functional groups that are potentially susceptible to hydrolysis and those which are generally resistant. Only 8 out of 129 priority pollutants have half-lives on the order of 105 days or less in near-surface aquatic environments (see Table 2-7).

At near-surface conditions, hydrolysis half-lives on the order of hundreds of days may not be acceptable (i.e., the reaction rate is too slow to reduce concentrations to standards). However, the 10,000-year no-migration standard for deep-well-injected wastes in EPA regulations (40 CFR 148.20) implies that half-lives of hundreds and perhaps thousands of days may result in significant reductions in waste concentrations before the waste has migrated sig-

Table 2-8 Amenability of Organic Functional Groups to Hydrolysis

Potentially Susceptible	Generally Resistant[a]
Alkyl halides	Alkanes
Amides	Alkenes
Amines	Alkynes
Carbamates	Benzenes/biphenyls
Carboxylic acid esters	Polycyclic aromatic
Epoxides	hydrocarbons
Nitriles	Heterocyclic polycyclic
Phosphonic acid esters	aromatic hydrocarbons
Phosphoric acid esters	Halogenated aromatics/PCBs
Sulfonic acid esters	Dieldrin/Aldrin and related
Sulfuric acid esters	halogenated hydrocarbon
	pesticides
	Aromatic nitro compounds
	Aromatic amines
	Alcohols
	Phenols
	Glycols
	Ethers
	Aldehydes
	Ketones
	Carboxylic acids
	Sulfonic acids

[a]Multifunctional organic compounds in these categories may be hydrolytically reactive if they contain other functional group(s) that are hydrolyzable.

Source: Guswa et al. (1984), adapted from Harris (1982).

nificantly. Half-lives on the order of hundreds of days (10^3) would go through at least 3,650 decay periods in 10,000 years; half-lives on the order of magnitude of thousands of days (10^4) would go through at least 365 periods in the same time. In other words, in the course of 10,000 years, the concentration of a compound with a half-life of 9,999 days would be reduced by half, 365 times, which would almost certainly reduce concentrations to below any laboratory detection limits. Table 2-7 lists 10 hazardous compounds with hydrolysis half-lives on the order of hundreds to thousands of days.

2.3.4 Oxidation-Reduction

Oxidation-reduction (redox) reactions involve the loss of electrons and increase in oxidation number (oxidation) by one substance or system with an associated gain of electrons and decrease in oxidation number (reduction) by another substance or system. Thus for every oxidation there must be a reduction. The **oxidation number** of an atom represents the hypothetical

charge an atom would have if the ion or molecule were to dissociate.

Because redox reactions involve the transfer of electrons, the intensity of redox reactions is measured by electrical potential differences, termed Eh (redox potential). Highly oxidizing conditions will have an Eh of about 0.8 volts; highly reducing conditions, an Eh of about -0.4 volts. Eh as an environmental factor is discussed in Section 3.1.2. Eh is difficult to measure accurately, and ground-water systems are often not in equilibrium with respect to redox reactions. Consequently, the Eh of a chemical system indicates the types of redox reactions that may occur rather than predicting the specific reactions that are occuring. In inorganic chemical systems, redox reactions tend to be reversible, whereas microbiologically mediated redox reactions involving hydrocarbons tend to be irreversible. Therefore, inorganic oxidation-reduction equilibria are somewhat analogous to acid-base equilibria.

2.3.4.1 Redox Reactions Involving Simple Hydrocarbons

The simplest oxidation reaction of an organic compound is the transformation of a simple hydrocarbon (such as a straight-chained compound) to carbon dioxide and water in the presence of oxygen:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$
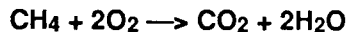
This type of reaction is called **aerobic respiration**, and without biological mediation it is irreversible.

As discussed in Section 2.2.1, acid-base reactions change proportions of neutral and ionic species in response to changes in pH (an analog of Eh) without the intervention of transformation processes. In contrast, changes in Eh in ground-water systems changes the type of oxidation-reduction that takes place. Aerobic respiration quickly depletes dissolved oxygen, and unless a continual supply of oxygen is available, a sequence of reducing reactions is initiated.

Table 2-9 shows the sequence of reducing reactions involving formaldehyde that will occur after oxygen is depleted in a closed ground-water system (i.e., when there is no source of oxygen replenishment). Except in unusual circumstances, when wastes contain significant amounts of a strong oxidant such as chromium (VI), reducing conditions will predominate in deep-well injection zones. For example, conditions favoring sulfate-reduction and methane-fermentation reactions are most likely to occur in injection zones (see case studies in Sections 7.2, 7.3, 7.4, and 7.5).

2.3.4.2 Redox Reactions Involving Complex Organic Compounds

Oxidation reactions involving cyclic hydrocarbons and hydrocarbon derivatives are more complex than those for simple hydrocarbons, and it is not always obvious how to classify such reactions in redox terms. In organic redox reactions, atoms, not electrons, usually are transferred. Oxidation frequently involves a gain in oxygen and a loss in hydrogen atoms, whereas reduction involves the reverse. Organic functional groups can be ranked by increasing oxidation state

Table 2-9   Redox Reactions in a Closed Ground-Water System

Reaction	Equation
1. Aerobic respiration	$CH_2O + O_2 = CO_2 + H_2O$
2. Denitrification	$5CH_2O + $ Nitrate $(4NO_3^-)+4H^+ = $ Nitrogen $(2N_2) + 5CO_2 + 7H_2O$
3. Mn(IV) reduction	$CH_2O + 2MnO_2 + 4H^+ = 2Mn^{+2} + CO_2 + 3H_2O$
4. Fe(III) reduction	$CH_2O + 8H^+ + 4Fe(OH)_3 = 4Fe^{+2} + CO_2 + 11H_2O$
5. Sulfate reduction	$2CH_2O + $ Sulfate $(SO_4^{-2}) + H^+ = HS^- + 2CO_2 + 2H_2O$
6. Methane fermentation	$2CH_2O + CO_2 = $ Methane $(CH_4) + 2CO_2$
7. Nitrogen fixation	$3CH_2O + 3H_2O + 2N_2 + 4H^+ = $ Ammonia $(4NH_4^+) + 3CO_2$

Note: Reactions will tend to go to completion in sequence from top to bottom.

Source: Adapted from Champ et al. (1979).

to facilitate classification of reactions as either oxidation or reduction. Table 2-10 summarizes relative oxidation states of several major functional groups. A functional group is considered oxidized if it is converted into a functional group at a higher oxidation state. Reduction is conversion to a group at a lower state.

Table 2-10 Relative Oxidation States of Organic Functional Groups

Functional Group Oxidation State				
-4	-2	0	+2	+4
Least Oxidized			Most Oxidized	
RH	ROH	RC(O)R	RCOOH	CO_2
	RCl	$(R)_2CCl_2$	$RC(O)NH_2$	CCl_4
	RNH_2		$RCCl_3$	
	C = C	-C≡C-		

Source: Adapted by Valentine (1986) from March (1977).

Table 2-11 lists some organic compounds according to their susceptibility to oxidation. Oxidation reactions are more common in the near-surface environment, where oxygen is abundant and sunlight may provide additional energy for reactions to take place. Oxidation is usually not a significant process in the deep-well environment except, perhaps, when strong oxidants such as Cr (VI) or permanganate are part of the injected waste (Strycker and Collins, 1987).

In general, the importance of redox reactions involving organic compounds in soil and water is not well-documented (Callahan et al., 1979; Valentine, 1986).

Table 2-11 Susceptibility of Organic Compounds to Oxidation In Water

Most-Susceptible	Least-Susceptible
Phenols	Alkenes
Aromatic amines	Haloalkanes
Olefins and dienes (electron-rich)	Alcohols
Alkyl sulfides	Esters
Enamines	Ketones

Source: Mill (1980).

In anaerobic environments, typical of deep-well-injection zones, reduction of chemicals by both biological and nonbiological processes can occur. Reduction of organochlorine compounds (such as DDT and toxaphene), in which a chlorine atom is replaced by a hydrogen atom, is the most frequently reported example of this type of reaction (Callahan et al., 1979).

2.3.5 Catalysis

The rates of many reactions increase in the presence of a **catalyst**, which itself remains unchanged in quantity and composition afterward. Although the catalyst itself is not transformed, the catalyst speeds up reactions that would occur naturally or promotes reactions that would not occur otherwise. For example, metal ions catalyze the hydrolysis and oxidation reactions in biochemical systems (Martell, 1971). Phenol and phenol derivatives are normally resistant to oxidation in wastewaters, but the reaction can be accomplished by metal-ion catalysis when Fe^{+2}, Mn^{+2}, Cu^{+2}, and Co^{+2} are combined with chelating agents (Martell, 1971). The reactions involved in destroying the aromatic ring in these compounds are complex and more likely to occur during waste pretreatment than as a result of processes in the deep-well environment. Certain metals in the presence of clays can also catalyze the polymerization of phenols and benzenes (see Section 2.3.6). Laszlo (1987) reviews organic reactions that are catalyzed by clay minerals.

2.3.6 Polymerization

Polymerization is the formation of large molecules (polymers) by the bonding together of many smaller molecules. For example, styrene polymerizes to form polystyrene. Polymerization can enhance the tendency of a substance to be adsorbed on mineral surfaces by increasing the molecular weight but is not likely to result in detoxification of hazardous wastes.

Polar organic compounds such as amino acids normally do not polymerize in water because of dipole-dipole interactions. However, polymerization of amino acids to peptides may occur on clay surfaces. For example, Degens and Metheja (1971) found kaolinite to serve as a catalyst for the polymerization of amino acids to peptides.

Adsorption of phenol and benzene as a result of polymerization at the clay surface has also been observed in the laboratory on smectite clay (in the montmorillonite group) when exchangeable sites were occupied by Fe^{+3} or Cu^{+2} cations (Mortland and Halloran, 1976). In natural systems, Cu^{+2} is not very likely to exist in significant enough concentrations. However, Fe^{+3} may be present in the deep-

well environment in sufficient amounts to enhance the adsorption of phenol, benzene, and related aromatics. Wastes from resin manufacturing facilities, food processing plants, pharmaceutical plants, and other types of chemical plants occasionally contain resin-like materials that may polymerize to form solids at deep-well-injection pressures and temperatures (Selm and Hulse, 1960).

2.3.7 Thermal Degradation

Thermal degradation occurs when heat causes compounds to undergo structural changes, leading to formation of simpler species. For example, many organophosphorus esters isomerize when heated and break down into component molecules (Crosby, 1973). Temperatures and pressures common in the deep-well environment are normally too low to initiate high-temperature reactions, but if the right chemicals (not necessarily hazardous) are present, thermal degradation might be initiated (Strycker and Collins, 1987). For example, thermal decarboxylation is probably the mechanism of acetate degradation in oilfield waters where temperatures exceed 200°C (Carothers and Kharaka, 1978; Kharaka et al., 1983); however, injection zones usually do not reach this temperature. At a depth of 900 meters (approximately 3,000 ft) temperatures range from 50° to 100°C (Roy et al., 1989).

Smith and Raptis (1986) have suggested using the deep-well environment as a wet-oxidation reactor for liquid organic wastes. This process, however, does not involve deep-well injection of wastes but rather uses temperatures and pressures in the subsurface to increase the oxidation rate of organic wastes, which are then returned to the surface.

2.3.8 Biodegradation

Biotransformation is the alteration of a compound as a result of the influence of organisms. It is one of the most prevalent processes causing the breakdown of organic compounds in the near-surface environment. **Biodegradation** is a more specific term used to describe the biologically mediated change of a chemical into simpler products. The term includes, and sometimes obscures, a series of distinctive processes of toxicological significance in natural ecosystems. Biodegradation is probably more significant in the decomposition of the nonhazardous components of deep-well-injected organic wastes (see Case Studies, Sections 7.2, 7.3, 7.4 and 7.5), although a few hazardous compounds, such as acrylonitrile (see Case Study, Section 7.3) and some monocyclic aromatic hydrocarbons and halogenated aliphatics, may be subject to biodegradation in the deep-well environment (see Section 3.4).

Microorganisms are by far the most significant group of organisms involved in biodegradation (Scow, 1982). They can mineralize (convert to CO_2 and H_2O) many complex organic molecules that higher organisms, such as vertebrates, cannot metabolize. They are often the first agents in biodegradation, converting compounds into the simpler forms required by higher organisms. Most biodegradation in near-surface environments is carried out by **heterotrophic** bacteria (microorganisms that require organic matter for energy and oxygen).

Biodegradation in deep-well environments is performed predominantly by anaerobic microorganisms, which do not consume oxygen and are either **obligate** (oxygen is toxic to the organism) or **facultative** (the organism can live with or without oxygen or prefers a reducing environment). The two main types of anaerobic bacteria, **methanogenic** (methane-producing) and **sulfate-reducing,** do not degrade the same compounds (Strycker and Collins, 1987). The by-products of sulfate reduction are hydrogen sulfide, carbon dioxide, and water (see Equation 5, Table 2-9). Methanogenic bacteria produce methane and carbon dioxide (see Equation 6, Table 2-9). The extent to which either type proliferates is strongly influenced by pH. As a group, anaerobic organisms are more sensitive and susceptible to inhibition than aerobic bacteria (Scow, 1982). Typically, aerobic degradation also is more efficient than anaerobic degradation, and high temperatures are not as limiting for aerobes as for anaerobes (Strycker and Collins, 1987).

Alexander (1980) identifies six major kinds of biodegradation:

■ Mineralization

■ Co-metabolism

■ Detoxification

■ Transtoxification

■ Activation

■ Defusing

Table 2-12 describes each of these processes and gives examples.

For several reasons, mineralization (decomposition to inorganic constituents) is generally a more effective form of biodegradation than co-metabolism (conversion to another compound without using the original compound for energy or growth). First, detoxification is

28

Table 2-12   Summary Descriptions of the Major Types of Biological Transformation Processes

Process	Description
Mineralization	The complete conversion of an organic compound to inorganic constituents (water, carbon dioxide). Generally results in complete detoxification unless one of the products is of environmental concern, such as nitrates and sulfides under certain conditions.
Co-metabolism	Conversion of an organic compound to another organic compound without the microorganism using the compound as a nutrient. Resulting compounds may be as toxic (DDT to DDE or DDD) or less toxic (xylenes to toluic acid).
Detoxification	Conversion of a toxic organic compound to a nontoxic organic compound. The pesticide 2,4-D can be detoxified microbially to 2,4-dichlorophenol.
Transtoxification	Conversion of a toxic compound to another toxic compound with similar, increased, or reduced toxicity.
Activation	Conversion of a nontoxic molecule to one that is toxic, or a molecule with low potency to one that is more potent. Examples include the formation of the phenoxy herbicide 2,4-D from the corresponding butyrate, formation of nitrosamines, and methylation of arsenicals to trimethylarsine.
Defusing	Conversion of a compound capable of becoming hazardous to another nonhazardous compound by circumventing the hazardous intermediate. This has been observed in the laboratory, but not identified in the environment. An example is the direct formation of 2,4-dichlorophenol from the corresponding butyrate of 2,4-D.

Sources: Alexander (1980) and Horvath (1972).

more likely to occur during mineralization. Second, mineralizing populations will increase until the compound is completely degraded, because they use the compound as a source of energy. In contrast, co-metabolized compounds tend to change slowly, and the original compound and its reaction products tend to remain in the environment because the co-metabolized compounds are not used for energy. These differences are illustrated in Figure 2-1.

Almost all the specific chemical reactions in biodegradation can be classified as **oxidation-reduction, hydrolysis,** or **conjugation.** Hydrolysis and oxidation-reduction have been discussed in Section 2.3.3 and Section 2.3.4. Conjugation involves the addition of functional groups or a hydrocarbon moiety to an organic molecule or inorganic species. For example, conjugation occurs when microbial processes transform inorganic mercury into dimethyl mercury.

At least 26 oxidative, 7 reductive, and 14 hydrolytic transformations of pesticides had been identified as of 1975 (Goring et al., 1975). Detailed identification and discussion of specific reactions can be found in Alexander (1981) and Scow (1982). Section 3.4 discusses the effects of environmental factors on haz-

ardous waste biodegradation in the deep-well environment.

2.4   Transport Processes

Many factors and processes must be considered when evaluating the movement of deep-well-injected hazardous wastes. Most of these processes are beyond the scope of this reference guide. Four factors, however, are relevant to geochemical characteristics:

■ Hydrodynamic dispersion

■ Osmotic potential

■ Particle migration

■ Density and viscosity

2.4.1   Hydrodynamic Dispersion
Hydrodynamic dispersion refers to the net effect of a variety of microscopic, macroscopic, and regional conditions that affect the spread of a solute front through an aquifer (Mills et al., 1985). Quantifying the dispersion is important to fate assessment because contaminants can

Figure 2-1 Hypothetical Model for Population Changes and Metabolism of a Chemical Modified by Mineralizing and Co-metabolizing Populations (Alexander, 1981).
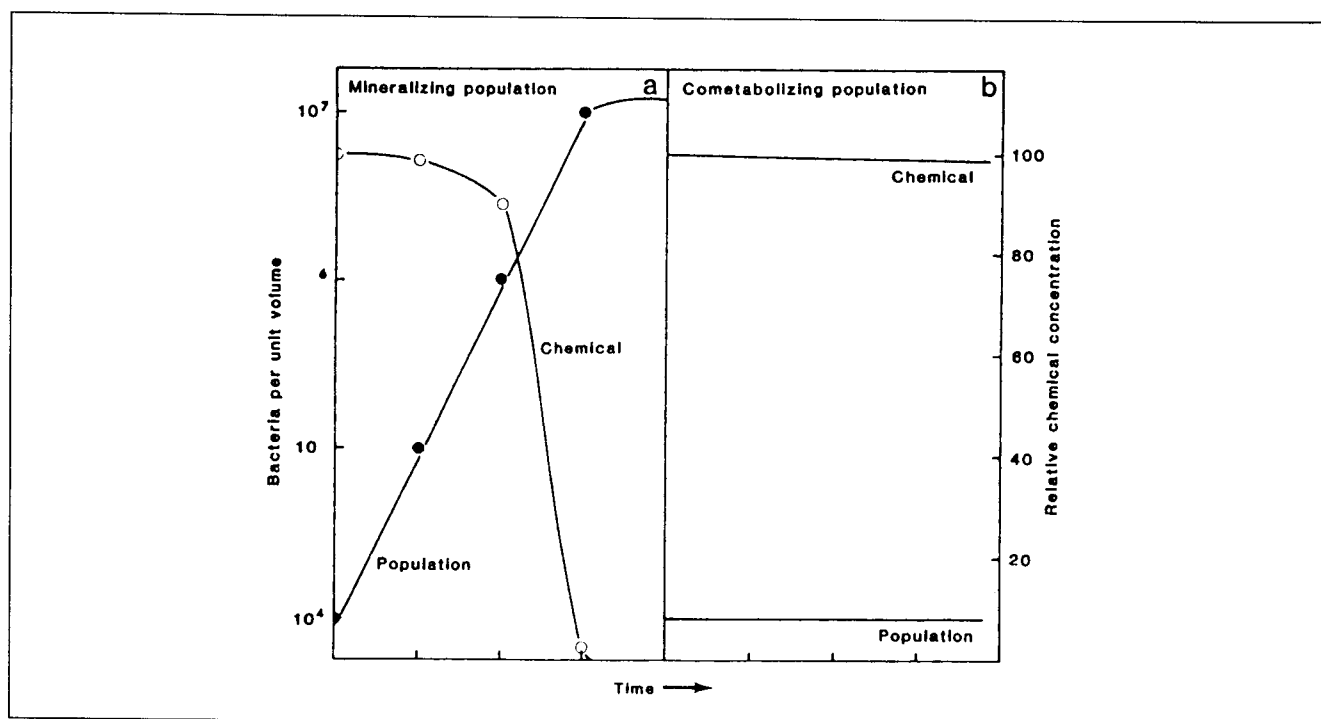
move more rapidly through an aquifer by this process than would be predicted by simple plug flow (i.e., uniform movement of water through an aquifer with a vertical front). In other words, physical conditions (such as more-permeable zones, where water can move more quickly) and chemical processes (e.g., movement of dissolved species at greater velocities than the water moves by molecular diffusion) result in more rapid movement of contaminants than would be predicted by ground-water equations for physical flow, which must assume average values for permeability.

Dispersion on the **microscopic** scale is caused by:

■ Velocity variations resulting from variations in pore geometry and the fact that water velocity is higher in the center of a pore space than that for water moving near the pore wall

■ Molecular diffusion along concentration gradients

■ Variations in fluid properties such as density and viscosity (Section 2.4.4)

Dispersion on the **macroscopic** scale is caused by variations in hydraulic conductivity and porosity, which create irregularities in the seepage velocity with consequent mixing of the solute. Finally, over

large distances, regional variations in hydrogeologic units can affect the amount of dispersion. In hydrogeologic modeling, the hydrodynamic dispersion coefficient (D) is often expressed as the sum of a mechanical dispersion coefficient (D_m) and molecular (Fickian) diffusion (D^*).

In most instances, hydrodynamic dispersion is not great enough to require detailed consideration in hydrogeologic modeling for fate assessment of deep-well-injected wastes. However, regional variations (such as presence of an underground source of drinking water [USDW] in the same aquifer as the injection zone, as is the case in parts of Florida) should be evaluated before a decision is made to exclude it.

2.4.2 Osmotic Potential

Osmotic potential refers to the energy required to pull water away from ions in solution that are attracted to the polar water molecules. In the presence of a semipermeable membrane between two solutions, water molecules will move through the membrane to the side with the higher concentration. This property may be important to fate assessment because in the deep-well environment, shales that serve as confining layers can act as semipermeable membranes if the injected waste significantly changes the solute concentrations (Hanshaw, 1972). In laboratory experiments, Kharaka (1973) found that retardation sequences across geologic

membranes varied with the material, but that monovalent and divalent cations generally followed identical sequences: Li < Na < NH3 < K < Rb < Cs and Mg < Ca < Sr < Ba.

If osmotic effects are possible, several other effects would need to be considered in a geochemical-fate assessment, depending on whether the solute concentration is increased or decreased. If solute concentrations are **increased**, pressures associated with injection would increase beyond those predicted without osmotic effects. Also, the movement of ions to the injection zone from the aquifer with lower salinity (above the clay confining layer) would increase the salinity above those levels predicted by simple mixing of the reservoir fluid and the injected wastes. This action could affect the results of any geochemical modeling.

If solute concentrations are **decreased**, the remote possibility exists that wastes would migrate through the confining layer. For this to occur, solute concentrations above the confining layer would have to be higher than those in the injection zone, and movement, in any event, would be very slow. Since USDWs have salinities less than 10,000 mg/L, compared with typical salinities in injection zones of 20,000 to 70,000 mg/L (see Sections 3.1.3 and 3.2.2), even if this process were to occur it would cause migration only to overlying aquifers that are not USDWs.

2.4.3 Particle Migration
Particle migration can occur when the mixing of incompatible fluids mobilizes clays or very fine particles precipitate out of solution. This process is most likely to occur when solutions with low concentrations of salts are mixed with reservoir fluids containing high concentrations, or when highly alkaline solutions dissolve silica and release fines. This type of reaction is of concern primarily when it occurs near the injection zone, because particle migration can clog pores and drastically reduce permeability. McDowell-Boyer et al. (1986) provide a good review of the literature on subsurface particle migration. Particle migration as it affects well-plugging is discussed further in Section 3.3.1.

It is possible for complex metals ions that are adsorbed onto very small particles of clay to migrate as metal-clay particles. Laboratory experiments found that radioisotope-clay particles at a low salinity were retained in a sand core, but passed through it at a high salinity (Strycker and Collins, 1987). Clay-metal particles would not be expected to travel long distances in deep-well reservoir rocks because the pores would be too small.

Injection of highly acid or alkaline wastes has the potential to dissolve some reservoir rock to create channels that would allow more distant transport of small particles. Table 2-13 summarizes the various physical parameters that affect particle migration in porous-media flow.

2.4.4 Density/Viscosity Differences
Wastes having a different density (weight per unit volume) or viscosity (tendency to resist internal flow) than the injection zone fluids will tend to concentrate in the upper (lower density/viscosity) or lower (higher density/viscosity) portions of the injection zone. Sniegocki (1960) discusses the effects of viscosity and temperature on flow when there is little difference in density between the injected and formation waters. Kaufman and McKenzie (1975) observed that the apparent hydraulic conductivity of the Belle Glade injection zone in Florida increased about 2.5 times because of temperature differences (see Section 7.4).

Frind (1982) examines the basic requirements for the mathematical simulation of density-dependent transport in ground water. Miller et al. (1986) describe a density-driven flow model designed specifically for evaluating the potential for upward migration of deep-well-injected wastes.

2.5 Interaction of Partition, Transformation, and Transport Processes

The actual movement of a specific deep-well-injected hazardous substance depends on the types of processes that act on the waste and on the ways in which different processes interact. Figure 2-2, from McCarty et al. (1981), shows the expected change in concentration over time of a deep-well-injected organic compound in an observation well at an unspecified distance from the original point of injection.

With only dispersion operating, low concentrations are observed before the arrival of a fluid exhibiting ideal plug flow, but dispersion also serves to delay the time it takes for 100% of the initial concentration to be observed. Adsorption combined with dispersion delays the arrival of the compound, and eventually the contaminant will reach full concentration when adsorption capacity is reached. When biodegradation occurs, initial concentrations might well be governed by dispersion alone, until sufficient time has passed for an acclimated bacterial population to establish itself and become large enough to change the

Table 2-13   Physical Parameters Affecting Particle Migration in Porous-Media Flow

Parameter	Significance
Matrix	
Porosity	Indicates voids; space available for retention of clogging material.
Particle size for which 10% of the matrix is smaller than that size	Termed the effective size for filter sands.
Particle size for which 60% of the matrix is smaller than that size	The ratio of the 60% size to the 10% size is an indicator of the uniformity.
Bulk density	For a given material, indicates the closeness of packing and propensity for material movement under stress.
Specific surface area	Relates to surface-active phenomena and adsorption rate.
Grain shapes	Affects shape of pores and thus fluid-flow patterns.
Surface roughness of grains	Affects retention of suspension on the particle surface.
Pore-diameter size and size distribution	Propensity for entrapment or filtration of suspension.
Surface charge of grains	Negatively charged surface grains will attract a suspended particle with a positive charge.
Fluid	
Viscosity	Shear forces and fluid resistance to flow.
Density	Mixing effects when different densities are involved; may affect direction and rate of flow.
Velocity of flow	Hydrodynamic forces on the medium and suspension.
Pressure	Driving force moving the liquid and suspension into and through the medium.
Suspended Particles	
Concentration (inflow, within medium, outflow)	Material available for inflow, retention, and through-flow.
Size	Ability to pass through pore openings.
Shape	Effect on retention or through-flow due to orientation.
Electric charge	Attraction or repulsion to medium or intermediate materials.

Source: Adapted from Signor (1973).

Figure 2-2 Effects of Dispersion, Adsorption, and Biodegradation on the Time Change in Concentration of an Organic Compound in an Aquifer Observation Well. Following the Initiation of water injection into the aquifer at some distance away from the observation well, C represents the observed concentration and C_0 the concentration in the injection water (McCarty, et al., 1981).

Expected responses to a step change in concentration

C/C_0

Ideal plug flow

Dispersion

Sorption and dispersion

Biodegradation and dispersion

Biodegradation, sorption, and dispersion

Time relative to mean residence time of water. t/t_{H_2O}
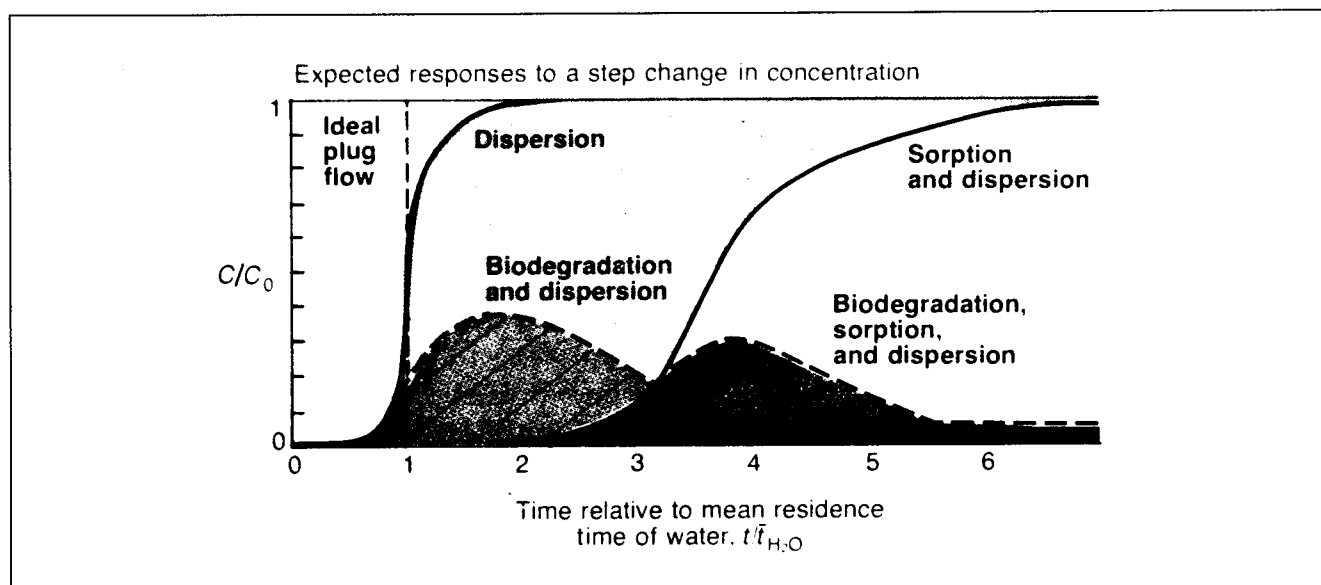
organic concentration significantly. If this occurs, the concentration would decrease and level out at some minimum value. When adsorption acts with biodegradation, the arrival of the contaminant is delayed, as with adsorption alone; then the concentration of the contaminant rises to a maximum level below that of the original concentration and declines as biodegradation becomes active.

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33

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CHAPTER THREE

MAJOR ENVIRONMENTAL FACTORS AFFECTING DEEP-WELL-INJECTION GEOCHEMICAL PROCESSES

Environmental conditions determine in large part the chemical reactions that will occur when waste is injected. For example, precipitation-dissolution reactions are strongly controlled by pH. Thus iron oxides, which may be dissolved in acidic wastes, may precipitate when injection-zone mixing increases the pH of the waste. Similarly, redox potential (Eh) exerts a strong control on the type of microbiological degradation of wastes.

The most variable and site-specific factor is the reservoir rock matrix. Geologic formations vary greatly in chemical and physical properties depending on the conditions under which they formed and the geologic processes to which they have been subjected. Other environmental factors such as pH, Eh, salinity, temperature, and pressure fall within a relatively well-defined range in the deep-well environment, and thus, to a certain extent, restrict the chemical processes that can be expected.

This chapter has four sections:

- Section 3.1 (Major Environmental Factors Influencing Geochemical-Fate Processes) discusses how the environmental factors of pH, Eh, salinity, reservoir matrix, temperature, and pressure affect chemical processes.

- Section 3.2 (Geochemical Characteristics of Deep-Well-Injection Zones) examines the typical range of environmental conditions that occurs in the deep-well environment, including lithology (Section 3.2.1) and the geochemical characteristics of deep-well brines (Section 3.2.2).

- Section 3.3 (Influence of Environment on Waste-Reservoir Compatibility) examines the possible impacts of environmental factors and chemical processes on the operation of injection wells. These impacts include well plugging (Section 3.3.1), well-casing/ confining-formation failure (Section 3.3.2), and well blowout (Section 3.3.3).

- Section 3.4 (Influence of Deep-Well Environmental Factors on Biodegradation) examines in detail the significance of conditions in the deep-well environment as they affect biodegradation of injected wastes.

3.1 Major Environmental Factors Influencing Geochemical-Fate Processes

The previous chapter examined the geochemical processes that can occur in the deep-well environment. The type and outcome of reactions that will actually occur when a waste is injected, however, depend on its chemical characteristics (discussed in Chapter Four) and on injection-zone conditions. This chapter examines six major environmental factors that must be considered. Four (pH, Eh, salinity, and reservoir matrix) are chemical properties or measures of chemical properties of a system. These four provide information on what types of reactions may occur and how they might be expected to proceed. The remaining two factors, temperature and pressure, are physical properties of the system that primarily influence reaction rates. The purpose of this section is to provide a basic understanding of what these environmental factors are, how they are measured or observed, and how they may affect chemical processes.

3.1.1 pH

The symbol *pH* stands for the negative logarithm of the hydronium ion [H_3O^+] activity and is a convenient way of expressing the very low concentrations of H_3O^+ that are present in aqueous solutions. In chemical reactions, the symbol H^+ is often used instead of H_3O^+. Pure water has a pH of 7. Solutions with pH < 7 are acidic, and those with pH > 7 are basic. Acid-base reactions (see Section 2.2.1) determine the pH of a solution at equilibrium.

The pH of a system greatly influences what chemical processes will occur in the deep-well environment.

Directly or indirectly, pH also affects most of the other environmental factors that are discussed in this chapter. Table 3-1 summarizes the significance and some major effects of changes in pH on chemical processes and environmental factors in the deep-well environment.

Very small changes in acidity greatly affect chemical reactions and the form of chemical species in solution. For example, the hydrolysis half-life of hydrogen cyanide is greater than 100,000 years at pH 4 but drops to about 10 years at pH 9 (Scrivner et al., 1986). Figures 4-3, 4-4, and 4-5 in Chapter Four illustrate how pH influences the distribution of molecular and ionic species of cadmium, lead, and mercury.

Buffer capacity is a measure of how much the pH changes when a strong acid or base is added to a solution. A highly buffered solution will show little change; conversely, the pH of a solution with low buffering capacity will change rapidly. Weak acids or bases buffer a solution, and the higher their

Table 3-1   Effects of pH on Deep-Well Geochemical Processes and Other Environmental Factors

Process/Factor	Significance of pH
Partition Processes	
Acid-base	Measures acid-base reactions. Strong acids (bases) will tend to change pH; weak acids (bases) will buffer solutions to minimize pH changes.
Adsorption-desorption	Strongly influences adsorption, because hydrogen ions play an active role in both chemical and physical bonding processes. Mobility of heavy metals is strongly influenced by pH. Adsorption of some organics is also pH-dependent.
Precipitation-dissolution	Strongly influences precipitation-dissolution reactions. Mixing of solutions with different pH often results in precipitation reactions. See also reservoir matrix below.
Transformation Processes	
Complexation	Strongly influences positions of equilibria involving complex ions and metal-chelate formation.
Hydrolysis	Strongly influences rates of hydrolysis. Hydrolysis of aliphatic and alkylic halides optimum at neutral to basic conditions. (Strycker and Collins, 1987). Other hydrolysis reactions tend to be faster at either high or low pH (Kreitler et al., 1988).
Oxidation-reduction	Redox systems generally become more reducing with increasing pH (ZoBell, 1946).
Environmental Factors	
Biodegradation	In combination with Eh, pH strongly influences the types of bacteria that will be present. High- to medium-pH, low-Eh environments will generally restrict bacterial populations to sulfate reducers and heterotrophic anaerobes (Baas-Becking et al., 1960). In reducing conditions, pH strongly affects whether methanogenic or sulfate-reducing bacteria predominate (Strycker and Collins, 1987).
Eh	Increasing pH generally lowers Eh.
Salinity	pH-induced dissolution increases salinity; pH-induced precipitation decreases salinity.
Reservoir matrix	Acidic solutions tend to dissolve carbonates and clays; highly alkaline solutions tend to dissolve silica and clays. Greater pH generally increases cation-exchange capacity of clays.
Temperature	pH-driven exothermic (heat-releasing) reactions will increase fluid temperature; pH-driven endothermic (heat-consuming) reactions will decrease fluid temperature.
Pressure	Will not influence pressure unless pH-induced reactions result in a significant change in the volume of reaction products.

concentration in solution, the greater the buffering capacity. **Alkalinity** (usually expressed in calcium carbonate equivalents required to neutralize acid to a specified pH) is a measure of the buffering capacity of a solution (Hem, 1970).

Acid-base reactions of buffers act either to add or to remove hydrogen ions to or from the solution so as to maintain a nearly constant equilibrium concentration of H^+. For example, carbon dioxide acts as a buffer when it dissolves in water to form carbonic acid, which dissociates to carbonate and bicarbonate ions:

$$CO_2(aq) + H_2O \longrightarrow H_2CO_3^- \longleftrightarrow HCO_3 + H^+ \longleftrightarrow CO_3^{-2} + 2H^+$$
(carbonic acid) (carbonate) (bicarbonate)
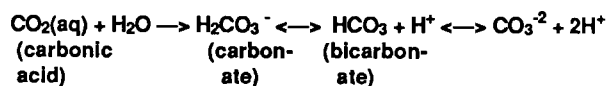
At equilibrium, the concentration of H^+ will remain constant. When a strong acid (represented by H^+ or HA) is introduced into solution, the concentration of H^+ is increased. The buffer compensates by reacting with the excess H^+ ions, moving the direction of the above reaction to the left. By combining with bicarbonate and carbonate ions to form the nonionic carbonic acid, equilibrium is reestablished at a pH nearly the same as that existing before. The buffer capacity in this case is determined by the total concentration of carbonate and bicarbonate ions. When no more carbonate or bicarbonate ions are available to combine with excess H^+ ions, the buffer capacity has been exceeded and pH will change dramatically upon addition of further acid.

3.1.2 Eh and Other Redox Indicators

The term Eh, which is the **oxidation-reduction potential**, (often referred to as **redox** potential), is an expression of the tendency of a reversible redox system to be oxidized or reduced. It is especially significant in its influence on biodegradation processes (see Section 3.4). The energy of oxidation (electron-escaping tendency) present in a reversible oxidation-reduction system (in volts [V] or millivolts [mV]) is measured as the potential difference between a standard hydrogen electrode and the system being measured. Large positive values (up to about +800 mV) indicate an oxidizing tendency, and large negative values (down to about -500 mV) indicate a strong reducing tendency. Eh values of +200 mV and lower indicate reducing conditions in near-surface soils and sediments (Ponnamperuma, 1972).

The Eh of connate waters (water entrapped in the interstices of sediment at the time of deposition) ranges from 0 to -200 mV (Baas-Becking et al., 1960). For example, formation water from two monitoring wells in the lower limestone of the Floridan aquifer near Pensacola ranged from +23 to -32 mV (Goolsby, 1972; see case

study in Section 7.2), and formation fluids from a Devonian limestone in Illinois used for injection at a depth of about 3,200 ft had an Eh of -154 mV (Roy et al., 1989).

Several measures of organic pollutant loading to waters have been developed to indicate the redox status of a system: (1) biochemical oxygen demand (BOD), (2) chemical oxygen demand (COD), (3) total organic carbon (TOC), (4) dissolved organic carbon (DOC), and (4) suspended organic carbon (SOC). When values for any of these parameters are high, oxygen is rapidly depleted in ground waters and reducing conditions will develop. BOD and COD were designed to measure oxygen consumption during the microbial degradation of municipal sewage. They are only semiquantitative indicators of organic loading because measurement procedures for these parameters have no direct geochemical significance (Hem, 1970). Malcolm and Leenheer (1973) recommend the use of DOC and SOC, which are independent of microbial effects, toxic substance, and variability with diverse organic constituents. TOC, when measured as a single parameter (rather than as the sum of DOC and SOC), provides less information for geochemical interpretation (Malcolm and Leenheer, 1973).

Reducing conditions predominate in the deep-well environment for several reasons:

■ No source of oxygen replenishment exists.

■ Higher temperatures in the deep-well environment are associated with decreases in Eh.

■ Neutral to slightly alkaline water in the deep-well environment favors lower Eh values.

Deep-well injection of wastes can change, at least temporarily, the Eh of the injection zone. For example, Ragone et al. (1973) observed a change from reducing to oxidizing conditions when tertiary-treated sewage (reclaimed water) was injected into the Magothy aquifer, Long Island, New York, at a depth of 400 ft. The reclaimed water had 6.6 mg/L dissolved oxygen compared with no dissolved oxygen in the formation water. On the other hand, the Eh of an acidic waste dropped dramatically, from +800 mV to around +100 mV, when mixed with siltstone under conditions of low oxygen and simulated deep-well temperature and pressure (Roy et al., 1989). Similarly, the Eh of an alkaline waste dropped from +600 mv to about +200 mV (Roy et al., 1989). All the case studies in Chapter Seven with sufficient data to evaluate redox potential had reducing conditions (Monsanto, Section 7.2;

American Cyanamid, Section 7.3; Belle Glade, Section 7.4; and Wilmington, Section 7.5). In each case, reducing conditions were indicated by the inorganic byproducts of anaerobic microbial degradation.

3.1.3 Salinity and Specific Conductance

Salinity is defined as the concentration of total dissolved solids (TDS) in a solution, usually expressed in mg/L. The TDS concentration in water is usually determined from the weight of the dry residue remaining after evaporation of the volatile portion of the original solution. Ground water may be classified into four salinity classes (Hem, 1970):

■ Slightly saline (1,000 to 3,000 mg/L)

■ Moderately saline (3,000 to 10,000 mg/L)

■ Very saline (10,000 to 35,000 mg/L)

■ Brine (more than 35,000 mg/L)

Seawater is about 35,000 mg/L.

Water with a salinity of less than 10,000 mg/L is considered to be a potential underground source of drinking water. By regulatory definition, deep-well injection of hazardous waste can occur only in very saline waters or brines. Actual salinities of waters in currently used deep-well injection zones vary greatly (see Section 3.2.2). In this reference guide, the term *brines* is used to refer to the natural waters in deep-well injection zones. As noted above, however, this term is not technically correct if TDS levels are less than 35,000 mg/L.

Solutions of substances that are good conductors of electricity are called **electrolytes**. Sodium chloride, the major constituent of seawater, is a strong electrolyte. Most salts, as well as strong acids and bases, are strong electrolytes because they remain in solution primarily in ionic (charged) forms. Weak acids and bases are weak electrolytes because they tend to remain in nonionic forms. Pure water is a nonconductor of electricity.

The conductivity of solutions is measured as **specific conductance**, which may be expressed as micromhos per centimeter (mhos/cm) or millimhos per centimeter (mmhos/cm) at 25°C. Seawater has a specific conductance of about 50 mmhos/cm. Salinity shows a high correlation with specific conductance at low to moderate TDS levels, but the concentrations of ions in brines are so high that the relationship between concentration and conductance becomes ill-defined (Hem, 1970).

As discussed in detail in Section 3.2.2 (Brine Chemistry), in situ waters in the deep-well environment have high salinities and also act as strong electrolytes. Geochemical systems with these characteristics are much more complex and difficult to model than those with low TDS levels (see discussion of Aqueous and Solution Geochemistry Models, Section 5.2.1).

3.1.4 Reservoir Matrix

With few, if any, exceptions, deep-well injection zones will be sedimentary rock, and the reactions that take place when hazardous wastes are injected are determined largely by the physical and chemical properties of that rock. The most important physical properties of sedimentary rocks in relation to deep-well geochemical interactions are **texture** (the proportions of different sized particles in a sediment) and **specific surface area** (see Section 6.2.2). The most important chemical property is **mineralogy**, defined by the types and proportions of minerals present.

3.1.4.1 Classification of Sedimentary Rocks

Sedimentary rocks can be broadly classified as clastic and nonclastic. **Clastic** sediments include sandstones, siltstones, and shales and are formed by the deposition and cementation of soil and rock material that has eroded from another location. These sediments are classified primarily by particle size. The U.S. Department of Agriculture (USDA) classification system is commonly used to describe the size of grains in a clastic sediment:

■ Clay (<0.002 mm)

■ Silt (0.002 to 0.05 mm)

■ Sand (0.05 to 2.0 mm)

■ Gravel (> 2.0 mm)

Clastic sedimentary rocks are classified according to the predominant particle size: clay (shale), silt (siltstone), or sand (sandstone). Note that the word *clay* used in reference to texture has a distinctly different meaning from its use in mineralogy. Clay particle size is used to describe both clays and other minerals less than 0.002 mm in diameter. Clay minerals are classified according to crystalline structure (see Section 3.1.4.2) and these minerals are typically, but not always, in the clay-particle size range (see Section 3.1.4.4)

Nonclastic rocks, in which precipitation (commonly carbonates) is the main contributor to rock formation, are classified according to mineral composition. The most important nonclastic rocks for deep-well injection are

limestone (made up mostly of calcium carbonate) and dolomite (calcium-magnesium carbonate). Nonclastic rock texture can vary widely depending on the proportions of clastic and precipitated material and the extent to which dissolution and reprecipitation occur after the sediment is deposited.

3.1.4.2 Sedimentary-Rock Minerals
A mineral is defined as a naturally occurring, homogeneous solid with a definite chemical composition and (usually) a well-defined crystalline structure. There are hundreds of different minerals, but relatively few account for most of the volume in sedimentary rocks. In sandstones and siltstones, quartz (silica, SiO_2) is the most common mineral, generally followed by feldspars (potassium-, sodium-, or calcium-aluminum silicates). In shales, a variety of clay minerals dominate. In limestone, calcite (calcium carbonate) is the most common mineral. The mineral dolomite (calcium-magnesium carbonate) gives its name to strata composed of that mineral.

The rest of this section focuses on clay minerals because of their significance in defining adsorption capacity, and also because of their possible contribution to well plugging (see Section 3.3.1). The importance of clays in catalyzing other reactions was discussed in Section 2.3.5. Two broad groups are recognized: **silicate clays** and **hydrous-oxide clays**. Each is discussed below, along with a few additional minerals.

Silicate Clays. Silicate clays have a sheetlike lattice structure with either silicon (Si) in coordination with four oxygen atoms (silica tetrahedra) or aluminum (Al) in coordination with six oxygen (alumina octahedra). The strong adsorptive capacity of clay is derived from the negative charges created at the edges of these crystalline sheets, where oxygen atoms (O^{-2}) have extra electrons that are not bonded to the cations in the crystalline structure. The negative charge can be further increased when ions with a lower valence substitute for ions with a higher valence in the sheet structure (for example, Al^{+3} substitutes for Si^{+4} in tetrahedral sheets and Mg^{+2} for Al^{+3} in octahedral sheets).

Silicate clays are classified according to stacking arrangements of the tetrahedral (silica) and octahedral (alumina) lattice layers and their tendency to expand in water. The stacking type strongly affects certain properties, including (1) surface area, (2) the tendency to swell during hydration, and (3) **cation-exchange capacity (CEC)**, the ability of a mineral surface to adsorb ions. CEC is the sum of exchangeable cations that a material can adsorb at a specific pH. It is commonly reported as milliequivalents per 100 grams (meq), where 1 meq is 1 mg of hydrogen or the amount

of any other ion that will combine with or displace 1 mg hydrogen. The current Standard International unit for reporting CEC is centimoles per kilogram (Soil Science Society of America, 1987).

Table 3-2 summarizes some properties of silicate clay minerals. The montmorillonite group is most sensitive to swelling and has a high CEC, because the 2:1 lattice structure (two octahedral sheets separated by a tetrahedral sheet) forms sheets that are loosely connected by exchangeable cations. The exchange sites between 2:1 lattice layers can be easily hydrated (i.e., adsorb water molecules) under certain conditions. Because the water molecules have a greater diameter than the cations that hold the sheets together, hydration pushes the layers apart. This process is discussed further in Section 3.3.1 (Well Plugging). Vermiculite has stronger negative charges on its inner surfaces than montmorillonite because of the substitution of lower-valence magnesium ions for aluminum. This factor results in an even higher CEC than that found in montmorillonite, but it also has the effect of bonding the 2:1 sheets more strongly. Consequently, vermiculite clays are less susceptible to swelling.

In Table 3-2, the clays are listed from most reactive (montmorillonite and vermiculite) to least reactive (kaolinite). The 1:1 lattice structure in kaolinite creates strong bonds between the paired sheets, resulting in a low surface area and CEC. Illite and chlorite have intermediate surface areas, CEC, and sensitivities to swelling.

Clay minerals in sedimentary formations commonly have characteristics of more than one clay mineral, called **mixed-layer clays**. These minerals have properties and compositions that are intermediate between two well-defined clay types (e.g., chlorite-illite, illite-montmorillonite, etc.).

Hydrous-Oxide Clays. Hydrous-oxide clays are less well understood than silicate clays (Brady, 1974). These clays are oxides of iron, magnesium, and aluminum associated with water molecules, although the mechanism by which the water molecules are held together is somewhat uncertain. Because of the lower overall valence of the cations in hydrous-oxide clays compared with silicate clays, CEC is lower. Jenne (1968) suggests that hydrous oxides of magnesium and iron furnish the principal control on the fixation of cobalt, nickel, copper, and zinc heavy metals in soils and freshwater sediments. Precipitation of hydrous-oxide clays may also be significant in waste-brine interactions, as discussed in Section 3.3.1.

Table 3-2   Important Characteristics of Silicate Clay Minerals

Property	Type of Clay[a]				
	Montmorillonite (Smectite)[b]	Vermiculite	Illite	Chlorite	Kaolinite
Lattice type[c]	2:1	2:1	2:1	2:2	1:1
Expanding?	Yes	Slightly	No	No	No
Specific surface area (m^2/g)	700-800	700-800	65-120	25-40	7-30
External surface area	High	High	Medium	Medium	Low
Internal surface area	Very high	High	Medium	Medium	None
Swelling capacity	High	Med-High	Medium	Low	Low
Cation exchange capacity (meq/100 g)	80-120	100-150+	10-40[e]	10-40[e]	3-15[e]
Other similar clays	Beidellite Nontronite Saponite Bentonite[d]				Halloysite Anauxite Dickite Nacrite

[a]Clays are arranged from most reactive (montmorillonite) to least reactive (kaolinite).
[b]The term smectite is now used to refer to the montmorillonite group of clays (Soil Science Society of America, 1987).
[c](tetrahedral:octahedral layers).
[d]Bentonite is a clay formed from weathering of volcanic ash and is made up mostly of montmorillonite and beidellite.
[e]Upper range occurs with smaller particle size.

Sources: Adapted from Grim (1968), Brady (1974), and Ahlrichs (1972).

Other Minerals. Quartz and feldspar, the dominant silicate minerals in clastic sedimentary formations in terms of volume, also have negative charges on crystal surfaces, which serve as exchange sites in adsorption-desorption processes. The CEC of quartz and feldspars is much lower than that for silicates in clays, primarily because these minerals are found mostly in the sand and silt fractions in sediments. However, when waste is injected into sandstones, quartz and feldspar can provide most of the exchange sites for adsorption of waste constituents because they are a large percentage of the rock by weight unless silicate clays coat sand grains and line pore spaces or fractures (see Section 3.1.4.4).

3.1.4.3 Organic Matter in Sedimentary Rocks
Forms of organic matter called **humic substances** may significantly affect geochemical fate processes in the deep-well environment, although this topic has received little attention in this context. Important chemical properties of humic substances include:

■ High adsorption capacity for metals and organic pollutants (see Section 5.2.2.1).

■ Ready ability to form complexes with heavy metals (Khan, 1980; Raspor et al. 1984; Weber, 1983).

■ Possible incorporation of organic pollutants that have similar structures to the building block of humus (such as chlorinated phenols, naphtholic compounds, and halogenated anilines) into the structure of humus during its formation (Bollag, 1983).

■ Ability to solubilize organic compounds that are otherwise water-insoluble (Khan, 1980).

■ Ability to increase hydrolysis reactions as a catalyst or, conversely, slow the rate of hydrolysis reactions by adsorption (Perdue, 1983).

42

- Potential to store both oxidizing and reducing agents (Valentine, 1986).

- Ability to slow rates of other oxidation-reduction reactions through adsorption (Valentine, 1986)

- Ability to strongly influence the size of microorganism populations indigenous to deep-well formations based on the amount of dissolved organic matter in ground water.

Humic substances comprise a general class of biogenic, refractory, yellow-black organic substances. They are ubiquitous, occurring in all terrestrial and aquatic environments. Although they have been studied by scientists for about 200 years, no fundamental, or even generally accepted, understanding of the nature, origin, and geochemical role of humic substances has been developed (Aiken et al., 1985).

Humic substances are classified into three major groups: (1) humic acids (insoluble at pH 2; soluble at higher pH), (2) fulvic acids (soluble under all pH conditions), and (3) humins (insoluble residue). All humic acids have colloidal properties. Their structure is based primarily on six-membered aromatic and heterocyclic rings, and may include benzene, naphthalene, and anthracene rings in their structure (Manaskaya and Drozdova, 1968).

Humic Substances In Sedimentary Rocks. Sedimentation removes organic materials from biologically active oxidizing environments with moderate temperatures. When buried, organic materials are subjected to reducing environments with high temperatures and pressures that favor abiotic alterations of these materials (Meinschein, 1971).

Organic matter in sedimentary rocks may be grossly classified as bitumen, comprising organic substances that are extracted by neutral organic solvents, and kerogen, consisting of organic materials that are not readily soluble in such solvents (McNabb and Dunlap, 1975). The bitumen fraction usually contains numerous hydrocarbon materials, fatty acids, porphyrins and many other substances, depending to some extent on the organic solvent used for extraction. The kerogen fraction constitutes the bulk of organic matter in subsurface environments, usually comprising 80 to 99 percent of the total organic content of nonpetroleum-bearing sedimentary materials (Tissot and Welte, 1978). The composition of the kerogen fraction is very complex and variable, generally consisting primarily of humus-like materials.

Kerogen and other humic substances have been studied most widely in relation to the formation of petroleum deposits (Abelson, 1978; Tissot and Welte, 1978; Durand, 1980). Kerogen may have a wide variety of nitrogen, oxygen or sulfur (NOS) functional groups attached to its surface, such as -SO3H, -NH2, -COOH, -OH, as well as saturated hydrocarbons and aromatic rings; NOS functional groups in particular may be reactive adsorbents (Apps, 1988). The specific surface area of organic detritus in near-surface sediments can be large and can make a significant contribution to its total adsorption capacity (Sposito, 1984; Karickhoff, 1984). On the other hand, Grim (1968) states that organic matter in ancient sediments is not likely to exhibit as high a CEC as that in near-surface sediments, because of metamorphosis. The effect of humic substances on deep-well injection merits additional research.

Organic Matter In Ground Water. Dissolved humic substances in ground water may be geochemically significant as complexing agents and as a substrate for microorganisms. The low dissolved-organic-carbon content of most ground waters means that complexation of heavy metals by humic substances generally will not be a major process (Thurman, 1985). The amounts of dissolved organic matter in ground waters are sufficient to support small but diverse populations of microorganisms that may be able to adapt and degrade deep-well-injected wastes (see Section 3.4).

Except as noted below, most ground waters contain less than 1 mg dissolved organic carbon/liter. Kuznetsov et al. (1963) report that dissolved organic matter in ground waters typically ranges from tenths to tens of mg/L. Thurman (1985), using data primarily from Leenheer et al. (1974), reports the following median concentration of organic carbon in various types of aquifers: sand and gravel, limestone, and sandstone—0.7 mg/L; igneous—0.5 mg/L; oil shales—3.0 mg/L; organically rich recharge waters—10.0 mg/L; and petroleum-associated waters—100.0 mg/L.

The origin of soluble organic compounds dissolved in ground water is not well-understood, but it is generally thought to consist mostly of humic substances, naphthenic acids, and phenolic compounds derived from the organic matter in sedimentary rocks or lignin degradation products derived from plant residue in surface soil (Davis, 1967; McNabb and Dunlap, 1975; Matthess, 1982). Humic substances in deep aquifers appear to have been derived primarily from kerogen associated with sediments of the aquifer (Thurman, 1985). Means (1982), in a study of the organic geochemistry of ground water from deep aquifers near Hanford, Washington (3,690 to 3,720 ft), and the Finnsjönn (260-582 m), Sternö (320 m), and Stripa (350 m) mine areas of Sweden, found that organic constituents in all

43

the samples consisted predominantly of low-molecular-weight fulvic acid.

Compared to surface waters, humic substances in deep ground waters (greater than 150 m) typically exhibit the following characteristics (Thurman, 1985):

■ They account for less than a third of the dissolved organic carbon, compared to about 50% for surface waters.

■ They are more aliphatic (see Section 4.3), and contain more carbon and less oxygen.

■ They are similar to surface water in carboxyl content (5-6 meq/g), in molecular weights (1000-5000) and in binding constants for copper (logK = 5.6 at pH 6.3).

As with the solid fraction, the dissolved fraction of humic substances has received little study in the context of deep-well injection. Data on dissolved organic carbon (Wilmington, North Carolina, and Pensacola, Florida) and organic carbon (Belle Glade, Florida) reported in Chapter Six, Table 6-6, are consistent with typical values for sedimentary aquifers reported above.

3.1.4.4 Relationship between Mineralogy and Particle-Size Distribution

Table 3-3 shows the relationship between mineralogy and particle size distribution in core samples of the Frio formation, one of the most widely used deep-well injection zones in Texas. Clay minerals, particularly kaolinite, commonly occur as silt-sized particles in this formation. Quartz is present mostly as sand-sized particles, but in individual cores, quartz may be as much as 48% silt-sized and 24% clay-sized. Small percentages of feldspar (2% to 11%) and calcite (2% to 7%) may be in the clay size class.

Particle-size distribution has a critical impact on CEC, as shown in Table 3-4. The CEC of sand is only 3.6 meq/100 g, compared with 32.8 for silt and 80.5 for clay (which includes clay-sized quartz and feldspar particles). Although the silt and clay make up 2.7% of the sediment by weight, they account for 27.1% of the CEC, with silt contributing about half that. Nevertheless, even though sand has a very low CEC, its large percentage by weight ensures that most of the exchangeable sites (72.9%) are in that fraction.

The mineralogical composition of pore surfaces and intergrain voids that come in contact with injected fluids usually is not the same as that of the bulk

Table 3-3   Mineral Composition and Particle-Size Distribution of Core Samples of Upper Frio Formation, Texas

| Mineral | Range of Percentage of Particle Size | | |
	Sand	Silt	Clay
Montmorillonite	0	0-7	1-12
Illite	0	1-5	1-9
Kaolinite	2-6	23-42	39-75
Quartz	69-93	18-48	11-24
Feldspar	2-27	2-8	2-11
Calcite	0.3-6.4	2-11	2-7

Source: Kent (1981).

mass (Roy et al., 1989). Sandstone and siltstone clastics, in particular, often have grain and pore surfaces coated with clays such as chlorite, illite, or kaolinite. Consequently, such clays may be the primary surface reacting with injected fluids even though they may represent a small fraction of the bulk mineralogy of the rock (Wilson and Pittman, 1977).

Particle size also affects the rate of decomposition of organic matter by microorganisms. Messineva (1962), in studies on the geological activity of bacteria in the Soviet Union, found that bacterial mineralization of organic matter occurs most rapidly in sand-silt sediments. In clay and clay-silt sediments the process of mineralization is slowed, despite the fact that the number of bacteria in the clay sediments is considerably greater than that in sand-silt sediments. Sinclair and Ghiorse (1987) find similar relationships between microbiological activity and the saturated zone in near-surface aquifers: gravelly sand is the most biologically active and clayey layers the least.

3.1.5 Temperature and Pressure

Temperature and pressure are primary influences on the rate of chemical reactions. **Temperature** is measured in degrees using three main temperature scales: Fahrenheit ($^\circ F$), Centigrade ($^\circ C$), and Kelvin ($^\circ K$). **Pressure** is measured in a variety of units, the most common being atmospheres (atm), megapascals (MPa), pounds per square inch (psi), and bars (approximately equal to atmospheres). Both temperature and pressure increase with depth below the earth's surface. Consequently, temperatures and pressures in the

Table 3-4   Effect of Particle Size on Cation-Exchange Capacity (CEC) of Natural Streambed Sediments, San Mateo County, California

Material	Diameter (mm)[a]	CEC (meq/100 g)	Percentage by Weight	Percentage by CEC
Gravel	<2.0	0	2.6	0
Sand	0.074-2.0	3.6	94.7	72.9
Silt	0.004-0.074	32.8	1.9	13.3
Clay	<0.004	80.5	0.8	13.8

[a] USDA particle-classification boundaries differ slightly for silt-sand (0.05 mm) and clay-silt (0.002 mm).

Source: Brown (1979).

deep-well environment are significantly higher than those in the near-surface environment.

Geothermal gradients in the subsurface typically range from $1^{\circ}C$ per 50 ft to $1^{\circ}C$ per 150 ft, with most regions having a gradient of around $1^{\circ}C$ per 100 ft (Roedder, 1959). Tables giving data on temperature gradients for 679 wells located in 23 states (Alabama, Arkansas, California, Colorado, Illinois, Iowa, Kansas, Kentucky, Louisiana, Michigan, Mississippi, Montana, Nevada, New Jersey, New Mexico, North Dakota, Oklahoma, Oregon, Pennsylvania, Texas, Washington, West Virginia, and Wyoming) can be found in Van Orstrand (1934). Table 3-5, drawn from a variety of sources, shows temperatures and pressures at various depths. Temperature can vary greatly at the same depth in different locations. For example, temperatures at approximately the same depth in Florida differ by almost $26^{\circ}C$.

The velocity of most acid-base and dissolution reactions increases as temperature increases. Higher temperatures generally increase the rate of redox reactions as well; however, the effect is difficult to predict exactly because the interactions among competing reactions may offset the effect of increased temperature (Valentine, 1986). In contrast, higher temperatures usually decrease the amount and rate of adsorption, because these reactions are generally exothermic (heat-producing) (Strycker and Collins, 1987). An exception has been noted by Choi and Aomine (1974), who found that adsorption rates of pentachlorophenol on soil increase 6% to 12% when samples of three different soils are subjected to an increase in temperature from 4° to $33^{\circ}C$. Adsorption decreased by 9% in a fourth sample. Laboratory adsorption experiments at constant, simulated deep-well pressure with phenol and 1,2-dichloroethane result in decreased adsorption with

increased temperature (Donaldson et al., 1975; Collins and Crocker, 1988).

Greater pressures tend to decrease the growth and survival of bacteria, but for certain species increased temperature counters this effect. For example, growth and reproduction of *E. coli* essentially stops in nutrient cultures at $20^{\circ}C$ and 400 atm (40.5 MPa). When the temperature is increased to $40^{\circ}C$, however, growth and reproduction are about the same as at near-surface conditions (ZoBell and Johnson, 1949).

Roy et al. (1989) conducted one of the most comprehensive evaluations of geochemical interactions between wastes and different rock types at elevated temperatures and pressures. Their studies employed batch-type tests in which two waste streams (acidic and alkaline) were mixed separately with three rock formations (Mt. Simon sandstone, Proviso siltstone, and Potosi dolomite) in short-term (15-day) studies. Long-term (150-230/day) studies have been completed, but the results have not yet been published. The short-term studies were conducted at three temperature/ pressure combinations representing conditions at the surface ($25^{\circ}C$/0.1 MPa), at 1,500 ft ($40^{\circ}C$/6.0 MPa), and at 3,000 ft ($55^{\circ}C$/11.7 MPa). The long-term studies were conducted at $52^{\circ}C$/10.8 MPa. Table 3-6 summarizes the effects observed in the short-term studies of increasing temperature and pressure on pH, Eh, and the concentrations of calcium, magnesium, aluminum, silicon, and sulfate in solution. As temperature and pressure increase, neutralization generally increases, with the greatest effect occurring in waste-sandstone reactions and the least occurring in waste-dolomite reactions. As noted in Section 2.3.1, Roy et al. (1989) observed that increased temperature and pressure are required to reduce the pH of alkaline

waste below the regulatory limit of 12.5. In this study, both the acid and alkaline systems show greater reductions in Eh with increased temperature and pressure, with the alkaline system showing the most

dramatic reductions. Table 3-6 indicates that higher temperature and pressure both increase and lower concentrations of Ca, Mg, Al, Si, and sulfate in solution, depending on the ion and the waste system.

Table 3-5   Temperature and Pressure at Different Depths

Location/Depth		Temperature			Pressure			Sources
Feet	Meters	°C	°F	°K	Atm	MPa	Psi	
Illinois								
5,300[a]	1,615	46	115[a]	319	155	15.7	2,275[a]	Kamath and Salazar, 1986
Florida[b]								
2,800[a]	850	42	108[a]	315	—	—	—	Henry and
2,900[a]	885	16	61[a]	289	—	—	—	Kahout, 1972
New York								
4,050	1,235[a]	40[a]	104	313	122	12.4[a]	1,800	Ragone et al., 1978
Texas/Tennessee								
—	—	60	140[a]	333	100[a]	10.1	1,470	Scrivner et al., 1986
North Carolina								
1,000[a]	305	75[a]	167	348	—	—	—	Peek and Heath, 1973
Texas[c]								
3,499[a]	1,065	49[a]	120	322	—	—	—	Kreitler et. al,
9,950[a]	3,035	107[a]	225	380	—	—	—	1988
3,450	1,050[a]	64[a]	147	337	112[a]	11.3	1,645	Donaldson and Johansen, 1973
Unspecified[d]								
3,280	1,000[a]	50[a]	122	323	132[a]	13.4	1,940	Roedder, 1959
—	—	—	—	—	205	20.7[a]	3,000	Collins and Crocker, 1988

[a]Value(s) reported in citation.
[b]From two locations.
[c]Frio formation (Kreitler et al., 1988) and Miocene sand (Donaldson and Johansen, 1973).
[d]Typical pressure.

Table 3-6   Effects of Increased Temperature and Pressure on Waste-Rock Mixtures[a]

Parameter	Mt. Simon Sandstone	Proviso Siltstone	Potosi Dolomite
pH (Neutralization)			
Acidic waste	Greater	No correlation	No correlation
Alkaline waste	Slightly greater	Somewhat greater	Somewhat greater
Eh (Reduction)			
Acidic waste	Slightly greater	Somewhat greater	Somewhat greater
Alkaline waste	Much greater	Much greater	Little change
Ca Concentration			
Acidic waste	Little change	Slightly higher	Higher
Alkaline waste	Lower[b]	Lower	Lower[c]
Mg Concentration			
Acidic waste	Slightly higher	Higher	Higher
Alkaline waste	—[c]	—[c]	—[c]
Al Concentration			
Acidic waste	Lower	Lower	Lower
Alkaline waste	Higher	Higher	Lower
Si Concentration			
Acidic waste	Higher	No correlation	No correlation
Alkaline waste	Higher	Higher	Lower
SO_4^{-2} Concentration			
Acidic waste	Slightly lower	Lower	Higher
Alkaline waste	Higher	Slightly higher	Higher

[a]Parameter at higher temperature and pressure (55°C/11.7 MPa) compared to near surface conditions (25°C/0.1 MPa).

[b]Precipitated.

[c]Below analytical detection limit (0.07 mg/L).

Source: Adapted from Roy et al. (1989) and Roy (unpublished data).

3.2 Geochemical Characteristics of Deep-Well-Injection Zones

This section provides information on the range of environmental conditions that occur in deep-well-injection zones in different geologic regions of the United States. Section 3.2.1 (Lithology) discusses the types of sedimentary formations that are suitable for deep-well injection and confining layers and provides some information on geologic formations that are currently used, or have been used in the past, for deep-well injection of wastes. Section 3.2.2 (Brine Chemistry) discusses the typical range of chemical characteristics of formation waters found in injection zones.

3.2.1 Lithology

Rock that can be mapped over a large area based on mineralogy, fossil content, or other recognizable characteristic is called a **formation**. The lithology (texture and mineralogy) of a geologic formation influences its suitability for deep-well injection. Sedimentary carbonates and sandstones usually have suitable geologic and engineering characteristics for disposal of hazardous wastes by deep-well injection. These characteristics include sufficient porosity, permeability, thickness, and extent to permit use as a liquid-storage reservoir at safe injection pressures (Warner et al., 1986). In 1981, 62% of the injection wells in the United States were drilled into two types of reservoir rocks, either consolidated sandstone or unconsolidated sands that had not yet been altered by cementation to form a strongly cohesive sandstone (see Table 3-7). The latter were usually of Tertiary age. At that time (1981), 34% of all wells used limestones and dolomites as reservoir rock and 4% used miscellaneous formations. The physical and chemical characteristics of the mineral components of sedimentary formations used for injection are discussed in Section 3.1.4 (Reservoir Matrix).

Sedimentary-rock formations that overlie the injection formation are called **confining layers**. To prevent injected wastes from migrating to higher strata or to potential underground sources of drinking water, a confining layer must have certain geologic and engineering characteristics:

■ Sufficient thickness and area to prevent upward migration of wastes.

■ Low porosity and permeability and the ability to maintain low porosities and permeabilities when interacting with wastes that may dissolve minerals through neutralization.

Table 3-7 Lithology and Age of Geologic Formations Used for Injection of Industrial Wastes

	Percentage of Wells[a]		
	1967	1973	1981
Lithology			
Sand	30	34	—
Sandstone	45	28	—
Subtotal	75	62	62
Limestone and dolomite	22	34	34
Other			
Evaporites	—	—	3
Shale	—	—	1
Schist and gneiss	—	—	<1
Subtotal	3	4	4
Age			
Quaternary	—	2	—
Tertiary	—	27	39
Mesozoic			
Cretaceous	—	—	7
Triassic	—	—	<1
Subtotal	—	12	7
Paleozoic			
Permian-Mississippian	—	15	15
Devonian-Silurian	—	15	15
Ordovician-Cambrian	—	29	23
Subtotal	—	—	59
Precambrian	—	<1	<1
Total Wells	277	277	269

[a]Percentage based on a total of 277 wells in 1967 and 1973, and 269 wells in 1981.

Sources: Adapted from Warner and Orcutt (1973) and Reeder (1981).

■ Lack of natural continuous fracturing or faulting, and resistance to artificial fracturing in response to injection pressures.

■ No abandoned unplugged or improperly plugged wells.

Sedimentary rocks that are most likely to meet the first three criteria are unfractured shale, clay, siltstone, anhydrite, gypsum, and salt formations. Massive limestones and dolomites (i.e., carbonates with no continuous fracturing and solution channels) can also serve as confining layers. Their suitability must be determined case by case (Warner et al., 1986). The fourth criterion has no relationship to lithology.

Formations from all geologic periods have been used for deep-well injection, but Paleozoic rocks are used for most injection zones (53% in 1981), followed by Tertiary-age formations (39%) (see Table 3-7). Older Paleozoic rocks have been more frequently used for injection primarily because they tend to be more deeply buried. However, the more recent Tertiary-age Gulf Coast sediments are also very thick, and most injection in rocks of this age takes places there.

Dozens of specific formations have been used over the years. Some, such as the Cambrian-age Mt. Simon sandstone, have been used since at least the 1960s for injection of hazardous wastes in several states (Illinois, Indiana, Michigan, and Ohio). Other formations (such as at Wilmington, North Carolina— see the case study in Section 7.5) have proved to be unsuitable and have been abandoned. Table 3-8 lists some of the formations that have been used in the last several decades; however, not all are still used. For example, Pennsylvania currently does not have any Class I wells, but at least four formations were used in the past.

Figure 3-1 shows major sedimentary basins and other geologic features in the United States that are significant in deep-waste injection well-site evaluations, and Figure 3-2 provides a general indication of site suitability based on geologic factors. A large number of national, regional, and state waste-injection suitability studies have been published. These are listed in Table 3-9.

3.2.2 Brine Chemistry
Brines are classified according to their chemical constituents. At least nine distinct types are recognized by petroleum geologists (Donaldson, 1972), but most brines encountered in injection operations are either Na-Cl or Na-Ca-Cl brines (Kreitler, 1986). None is similar to seawater, and the geochemical mechanisms by which such brines develop are not well-understood. Three mechanisms have been proposed to explain the high concentrations of dissolved solids and the chemical composition of brines (Hanor, 1983), but at present there is no consensus on their relative importance in explaining brine chemistry (Kreitler, 1986). The dominant mechanism at

work in a deep-well environment has important implications for the hydrodynamic conditions affecting the movement of injected wastes. The mechanisms and their implications are summarized in Table 3-10. The salinity, pH, and chemical composition of the very saline and briny waters into which hazardous wastes are injected can vary greatly, both among geologic basins and within a single formation. Table 3-11 summarizes salinity and pH of some major geologic basins and formations.

Figure 3-1 shows the locations of the basins in Table 3-11. Maximum salinities in the Tertiary section of the Gulf of Mexico basin (the most extensively used strata for deep-well injection) reach almost four times that of seawater. The Michigan basin has the highest salinity, reaching 400,000 mg/L TDS, more than 11 times that of seawater. In Florida, however, where seawater circulates through the Floridan aquifer, maximum salinities tend to be controlled by the salinity of the seawater (Henry and Kahout, 1972).

The Frio formation, in Texas, receives more hazardous waste by volume through deep-well injection than any other geologic formation in the United States. Table 3-11 shows that its average salinity is about twice that of seawater (72,185 mg/L TDS), but individual samples range from a low of 10,528 mg/L TDS (barely above the salinity cutoff for potential USDWs), to a high of more than 118,000 mg/L TDS. Data from sites in Illinois and North Carolina indicate the presence of very saline water (around 20,000 mg/L TDS, but still less saline than seawater).

The importance of pH in influencing geochemical processes was discussed in Section 3.1.1. Table 3-11 shows that the pH of formation waters in the Frio formation varies widely from moderately acidic (5.7) to moderately alkaline (8.2), with nearly neutral averages (6.8). The pH of formation waters from other injection sites tends to be more alkaline, ranging from slightly alkaline (Belle Glade, Florida, pH 7.5) and moderately alkaline (Wilmington, North Carolina, pH 8.6), to very alkaline (Marshall, Illinois, pH 7.1 to 10.7).

3.3 Influence of Environmental Factors on Waste/Reservoir Compatibility

This section focuses on environmental conditions that may result in physical or chemical incompatibilities between wastes and reservoirs. Determining the potential for incompatibility is a part of the geochemical fate assessment that must be undertaken for any injection project because of possible operational problems that

Table 3-8   U.S. Geologic Formations Being Used for Hazardous Waste Disposal[a]

Type of Formation/Name	Age[b]	State	# Wells[c]	Depth (ft)	Sources
Unconsolidated Sand					
Catahoula		TX	—	3,700-5,000	Donaldson, 1972; Kent, 1981
Cockfield		LA	—	3,000	Donaldson, 1972
Frio		TX	—	5,800-7,500	Donaldson, 1972; Kent, 1981
Glorieta		TX	—	1,300	Donaldson, 1972
Miocene		TX	—	3,000-6,000	Kent, 1981
Nactoch		LA	—	1,000	Donaldson, 1972
Wilcox	Eocene	AL	2	3,400-3,800	Hanby et al., 1973; Hanby, 1986
Woodbine		TX	—	2,500-5,000	Kent, 1981
Yegua		TX	—	3,400-4,500	*ibid.*
Sandstone					
Bethel		IN	—	2,800	Donaldson, 1972
Burgoon		PA	—	1,000	*ibid.*
Eau Claire		IN	—	4,000	*ibid.*
Eutaw	Cretaceous	FL	—	3,500	*ibid.*
Glorieta	Permian	KS	2	1,100	Latta, 1973
Granite Wash (chert)		TX	—	5,300-5,500	Donaldson, 1972; Kent, 1981
Greta		TX	—	4,500	Donaldson, 1972
Mount Simon	Cambrian	IL	—	4,000	*ibid.*
		IL	2	2,600-3,100	Brower et al., 1989
		IN	—	5,500	Donaldson, 1972
		OH	6	2,800	Clifford, 1973; Bentley et al., 1986
		PA	1	—	Reeder, 1981
		MI	—	—	Briggs, Jr., 1968
Oriskany		PA	—	5,500	Donaldson, 1972
Potsdam	Cambrian	NY	—	1,000-12,600	McCann et al., 1968
Red Mountain	Silurian	AL	1	4,400	Hanby et al., 1973
Simpson		TX	—	6,000-6,200	Kent, 1981
Sylvania		MI	—	1,000	Donaldson, 1972
Tar Springs		IN	—	2,300	*ibid.*
Theresa	Cambrian	NY	—	—	McCann et al., 1968
Tuscarora	Silurian	PA	—	3,700	Hardaway, 1968
Yeso		NM	—	1,000	Donaldson, 1972

Table 3-8 (continued)

Type of Formation/Name	Age[b]	State	# Wells[c]	Depth (ft)	Sources
Carbonate					
Arbuckle	Cambro-	KS	—	2,000	Donaldson, 1972
dolomite	Ordovician	OK	—	4,000	*ibid.*
		KS	25	3,300-6,300	Latta, 1973
Bass Islands	Cambrian	PA	1	1,600	Donaldson, 1972; Reeder, 1981
Cedar Valley		IL	—	2,500	Donaldson, 1972
Dundee		MI	—	4,000	*ibid.*
Ellenberger dolomite		TX	—	6,000-6,200	Kent, 1981
Eminence-Potosi	Cambrian	IL	4	3,600-5,000	Brower et al., 1989
Hunton limestone		TX	—	5,700-5,800	Kent, 1981
Lake City	Eocene	FL	—	1,800	Donaldson, 1972
Salem Mississippian		IL		1,500-2,100	Brower et al., 1989
St. Peter		KY	—	1,000	Donaldson, 1972
San Andres		TX	—	5,000	*ibid.*
Devonian limestone	Devonian	IL	1	2,400	Brower et al., 1989
Virginian limestone	Pennsylvanian	KS	—	3,200	Donaldson, 1972
?		KS	2	3,900-4,400	Latta, 1973
Other					
Wellington (salt)	Permian	KS	2	220-420	Latta, 1973

[a]Section 3 of U.S. EPA (1985) contains a detailed compilation of injection and confining-zone characteristics (facility name, lithology, thickness, formation name) for Class I hazardous waste injection wells as of 1983.

[b]Age indicated only if specified in reference source.

[c]Dash indicates that reference did not specify number of wells.

Table 3-9   Sources of National, Regional, and State Information on Suitability of Geologic Formations for Deep-Well Injection

Geographic Area	References
National	
United States	Love and Hoover (1960), AAPG (1968), Interstate Oil Compact Commission (1968), Piper (1969), Rima et al. (1971), Reeder et al. (1977), Warner and Lehr (1977)
Regional	
Anadarko Basin (CO, KS, OK, TX)	MacLachlan (1964)
Appalachia	Colton (1961)
Atlantic and Gulf Coastal Plain	LeGrand (1962)
Midwest	ORSANCO (1973, 1976)
Williston Basin (MT, ND, SD)	Sandberg (1962)
State	
Alabama	Alverson (1970), Tucker and Kidd (1973), Hanby et al. (1973), Hanby (1986)
California	Repenning (1960)
Colorado	MacLachlan (1964), Gabarini and Veal (1968), Peterson et al. (1968), Irwin and Morton (1969)
Florida[a]	Garcia-Bengochea and Vernon (1970), Henry and Kahout (1972), Miller (1979), Vecchioli (1981)
Illinois	Bergstrom (1968a,b), Bond (1972), Brower et al. (1989)
Kansas	MacLachlan (1964), Edmund and Gobel (1968), Irwin and Morton (1970), Latta (1973)
Michigan	de Witt (1960), Briggs (1968)
Montana	Beikman (1962), Sandberg (1962)
New Mexico	Repenning (1959), Peterson et al. (1968), Irwin and Morton (1970)
North Dakota	Sandberg (1962)
New York	Kreidler (1968), McCann et al. (1968), Waller et al. (1978)
Ohio	Clifford (1973, 1975), Bentley et al. (1986)
Oklahoma	MacLachlan (1964), Irwin and Morton (1969)
Oregon	Newton (1970)
Pennsylvania	Hardaway (1968), Rudd (1972)
South Dakota	Sandberg (1962)
Texas	MacLachlan (1964), Irwin and Morton (1970), Kent (1981), Bassett and Bentley (1983), Kreitler (1986), Kreitler et al. (1988)
Wyoming	Beikman (1962)

[a]See also references for case studies in Chapter Seven, Sections 7.2, 7.3, and 7.4.

Figure 3-1   Geologic Features Significant in Deep-Waste Injection-Well Site Evaluation, and Locations of Industrial-Waste Injection Systems, 1966 (Warner, 1968).
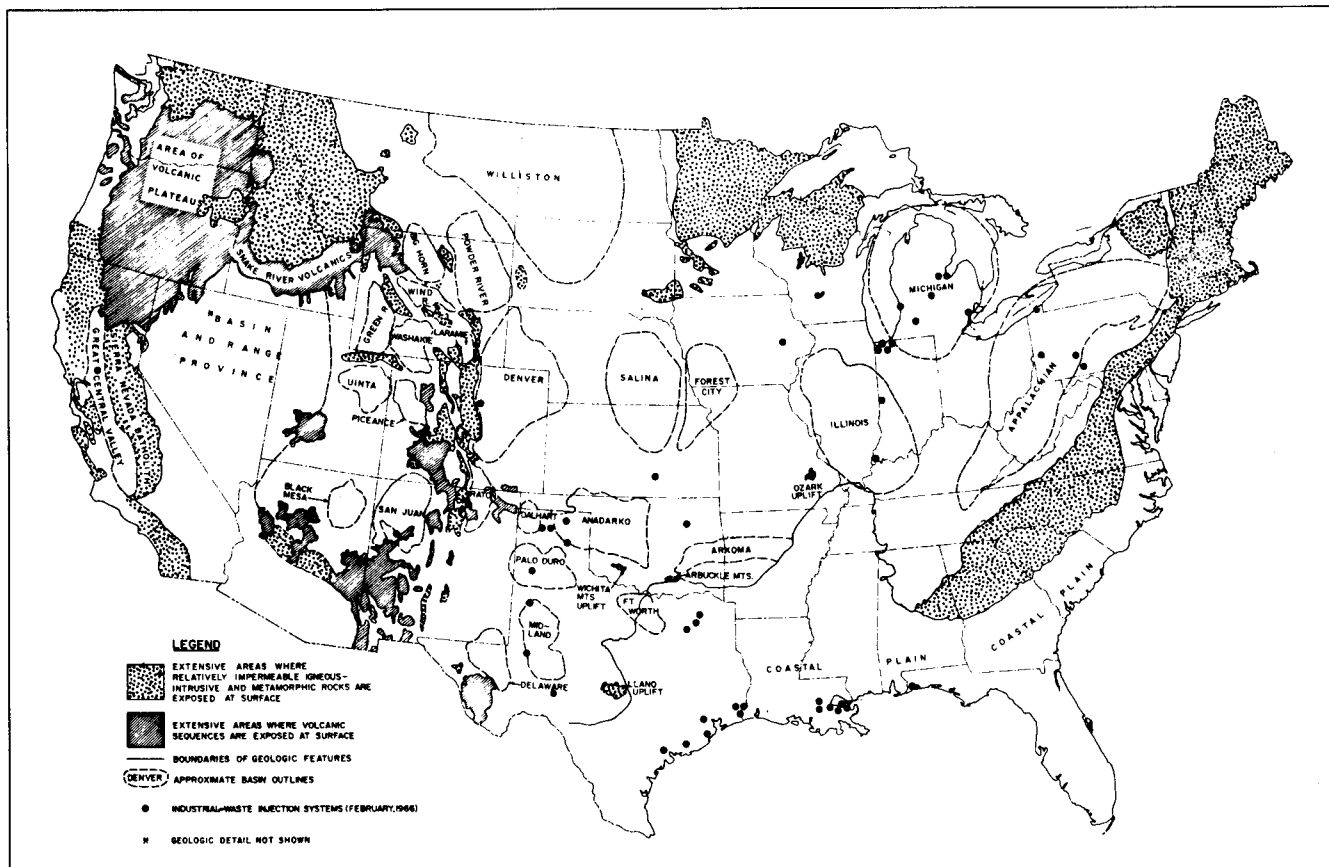
Table 3-10   Implications of Brine-Formation Mechanisms on Movement of Injected Wastes

Mechanism	Brine Type	Implications
Residual left after precipitation of evaporites (salt deposits).	Na-Ca-Cl	Brines are as old as the formation in which they occur; stagnant conditions exist.
Solution of halite present as bedded or domal salt-evaporite deposits.	Na-Cl Na-Ca-Cl	Active hydrologic conditions exist, although neither the mechanism nor the rate of fluid movement is indicated.
Reverse osmosis. Basinal waters forced through low-permeability shales, leaving the high pressure side.	Na-Cl Na-Ca-Cl	Active hydrologic conditions exist because large volumes of water would have to pass brine through a basin to reach observed brine concentrations.

may result from waste/reservoir incompatibility. The major operational problems that can occur are:

■ Well plugging (Section 3.3.1)

■ Casing/confining layer failure (Section 3.3.2)

■ Well blowout (Section 3.3.3)

In extreme situations, incompatibility between injection fluids and reservoir components can be so great that deep-well disposal will not be the most cost-effective approach to waste disposal. In other situations, such remedial measures as pretreatment or controlling fluid concentrations or temperatures can permit injection even when incompatibilities exist. In addition to operational problems, waste-reservoir incompatibility can cause wastes to migrate out of the injection zone (casing/confining-layer failure) and

even cause surface-water contamination (well blowout).

Four major types of chemical interactions are important when evaluating compatibility:

■ Waste interactions with brine

■ Waste interactions with rock

■ Waste-brine mixture interactions with rock

■ Microbiological interactions with the waste/brine/ rock system

Each interaction involves numerous chemical processes. The dominance of a specific interaction depends on the type of waste, the characteristics of the brine and rock in the reservoir, and environmental conditions. Table 3-12 describes some of the more common processes that may result in incompatibility.

Figure 3-2   Site Suitability for Deep-Well Injection of Industrial Waste, and Locations of Industrial Waste Disposal Wells, 1976 (Reeder et al., 1977).

LEGEND

Unfavorable under all conditions

Generally unfavorable but may have limited use under restricted conditions

Favorable under controlled conditions

●   Disposal Wells

✛   Abandoned or plugged Disposal Wells
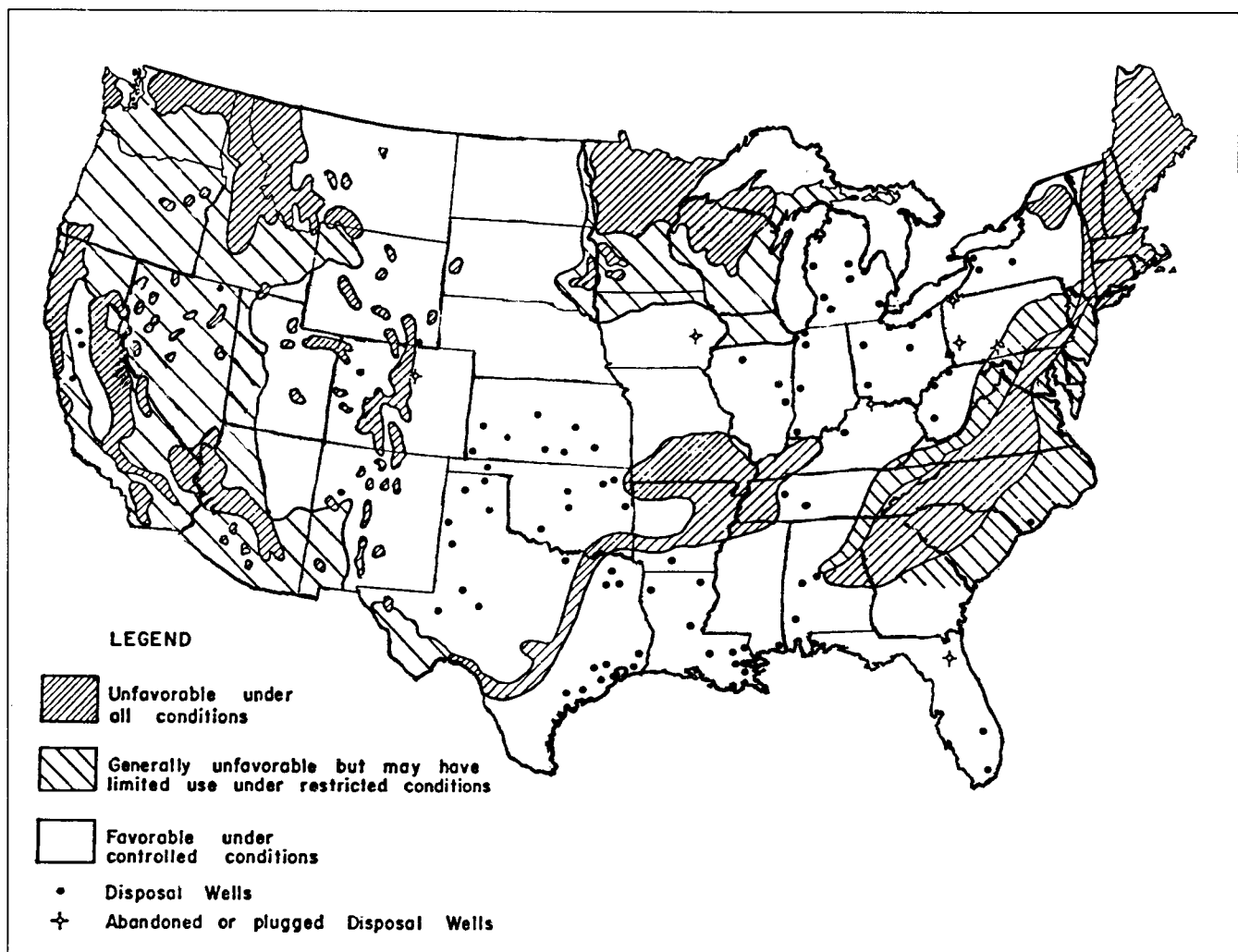
Table 3-11   Selected Parameters of Brines from Formations Used for Deep-Well Injection of Hazardous Wastes

Geologic Formation and/or Location	Salinity (mg/L)	pH	Sources
Major Geologic Basins[a]			
Gulf of Mexico (Tertiary)	130,000	—	Krietler, 1986
East Texas	260,000	—	
Palo Duro (Texas)	250,000	—	
Illinois	200,000	—	
Michigan	400,000	—	
Frio Formation (Texas)			
Average (32 samples)	72,185	6.8	Kreitler et al., 1988
Minimum	10,598	5.7	
Maximum	118,802	8.2	
Floridan Aquifer			
Maximum	35,000	—	Inferred from Henry and Kahout, 1972
Belle Glade, Florida			
Average (6 samples)	—	7.5	Kaufman et al., 1973
Wilmington, North Carolina[b]			
Average (4 samples)	19,150	8.6	Leenheer and Malcolm, 1973
Illinois			
Marshall[c]	22,000	7.1	Roy et al., 1989
HCl injection formation	23,500	to 10.1	Kamath and Salazar, 1986
Indiana			
Steel mill waste-injection formation	113,825	—	Hartman, 1968

[a]All salinity figures for basins are maximums.
[b]Sandstone, gravel, limestone aquifers.
[c]Devonian limestone.

Table 3-12   Processes Significant in Different Types of Waste-Reservoir Interactions

Interaction	Process
Waste with in situ fluids	Precipitation may result from incompatible brine. Hydrolysis may detoxify wastes. Complexation may increase or decrease mobility depending on conditions. Oxidation or reduction of wastes may occur.
Waste with rock	Dissolution by highly acidic or alkaline wastes may threaten well and rock integrity. Gases generated by dissolution of carbonates may cause immiscible phase separation and well blowout. Adsorption on mineral surfaces may immobilize wastes. Clays may be mobilized and clog pores.
Waste/Brine with rock	Waste/brine precipitates may clog pores. Successive adsorption/desorption reactions may occur at a particular location as waste/brine mixtures of varying proportions come in contact with the rock.
Microbiota	May form mats that clog pores near the injection well. May transform waste to nontoxic or other toxic forms.

3.3.1 Well Plugging

The term *well plugging* refers to any of a variety of processes that reduce the permeability of the injection formation or the screens that are placed in the well's injection interval. When permeability is reduced, injection rates must be reduced and/or injection pressures increased. Table 3-13 lists a number of ways in which plugging may occur. One or more of these situations will probably take place in most injection wells; the number and severity of reactions will determine whether serious operational problems arise. If plugging is confined to the immediate vicinity of the injection well, wastes will not migrate into the injection zone until permeability is reestablished by physical or chemical means (see Table 3-13). Partial reductions in permeability may allow wastes to move into the injection zone but at increased pressures. This latter situation may contribute to well-casing or confining-layer failure (Sec-

tion 3.3.2). Clay swelling, mobilization of fine particles by dissolution, and precipitation are the common causes of well plugging.

3.3.1.1 Clay Swelling

Water-sensitive clays are those which tend to swell in the presence of water. Such swelling is most likely to occur when wastes with low salt concentrations replace brines in the injection zone. The reduction in salinity causes adsorbed cations to be released from exchange sites on the clay until concentrations in solution and on adsorption sites are in equilibrium again. The empty exchange sites are then hydrated, resulting in swelling.

When clays swell, pore space is reduced, with consequent reductions in permeability. Permeability reductions will be severe when such water-sensitive clays as montmorillonite are present, but they have

Table 3-13   Causes of Well Plugging and Possible Remedial Actions

Cause	Possible Action
Particulate solids and/or colloids.	Filter before injection.
Bacterial growth on well screen and formation.	Treat with bactericides.
Emulsification of two fluid phases.	Do not exceed solubility limits of organic wastes in water.
Precipitates resulting from mixing of injection and reservoir fluids.	Use pretreatment or buffer of non-reactive water.
Expansion and dispersion of water-sensitive clays (particularly montmorillonite).	Avoid injection of low-salinity solutions in water-sensitive formations. Use clay stabilizers.
Migration of fines (very small particles) released by dissolution.	Neutralize before injection.
Reprecipitation of dissolved material (iron or calcium sulfate).	Use pretreatment.
Change in wettability or reduction in pore dimensions by adsorption (organics with large molecular weight).	Difficult to remedy.
Flow of unconsolidated sands into bore.	Use gravel-pack well screen. Inject a slug of brine after every period of interrupted flow.
Scaling on injection equipment by precipitation from injection fluid.	Use pretreatment; flush with solutions to remove accumulated scale.
Entrapped gases.	Remove gases from waste before injection or treat to prevent gas formation in the injection zone.

Sources: Adapted from Barnes (1972), Donaldson and Johansen (1973), Hower et al. (1972), Davis and Funk (1972), Veley (1969), and Orlob and Radhakrishna (1958).

also been observed in unconsolidated sand reservoirs consisting of less-sensitive clays such as illite and kaolinite (Baptist and Sweeney, 1955).

The sensitivity of clays to changes in salinity can be drastically reduced by adding various metal and alkaline-earth compounds, which form complex metal ions by hydrolysis (Veley, 1969). Apparently, these complexes are adsorbed so strongly to the clay surfaces that they remain adsorbed even when salinities are reduced, thus preventing hydration of exchange sites in the expandable lattice structure. Table 3-14 lists the effectiveness of various compounds in preventing permeability reductions caused by clay swelling, as shown by laboratory tests using Berea sandstone. Some of these compounds are available as commercial preparations to treat formations by reducing water sensitivity. Such treatment, however, will probably drastically reduce adsorption as a means of immobilizing injected wastes, since the compounds are resistant to ion exchange.

Additional discussion of water-sensitive clays and responses to pH and salinity changes can be found in the following references: Jones (1964), Land and Baptist (1965), and Mungan (1965).

3.3.1.2 Fine-Particle Mobilization
Highly alkaline wastes can reduce the permeability of the injection zone by dissolving silica and releasing fines (clay particles) that migrate and plug pores (Hower et al., 1972). Sandstones tend to be most sensitive to this reaction.

3.3.1.3 Precipitation
Many reactions between injected wastes and reservoir fluids can cause precipitation in deep wells (Headlee, 1950; Selm and Hulse, 1960; Warner, 1966; Warner and Doty, 1967). Alkaline earth metals (calcium, barium, strontium, and magnesium) can precipitate as insoluble carbonates, sulfates, orthophosphates, fluorides, and hydroxides. Other metals such as iron, aluminum, cadmium, zinc, manganese, and chromium can precipitate as insoluble carbonates, bicarbonates, hydroxides, orthophosphates, and sulfides. Finally, some oxidation-reduction reaction products such as hydrogen sulfide can precipitate.

Table 3-14   Effectiveness of Various Metal Ions in Controlling Formation-Water Sensitivity[a]

Reduce Sensitivity	No Effect	Increase Sensitivity
Thorium(IV) nitrate	Magnesium[b]	Sodium[b]
Zirconium oxychloride	Barium[b]	Potassium[b]
Aluminum[b]	Strontium[b]	Ammonium[b]
Tin[b]		Cesium[b]
Lead[b]		Lithium[b]
Indium[b]		Rubidium[b]
Iron[b]		
Titanium[b]		
Hafnium[b]		

[a]Sandstone cores were treated with a sequence of fluids: (1) 3% calcium chloride brine, (2) distilled water (k_o), (3) test solution, (4) distilled water, (5) 3% sodium chloride brine, and (6) distilled water (k_d). The ratio of k_d/k_o measured the solution's effectiveness in preventing permeability reduction. Perfect protection would produce $k_d/k_o = 1.0$ when cores were not stabilized with the test solution (step 3). In the base case (no test solution), k_d/k_o averaged 0.003.

Reduced sensitivity: $k_d/k_o > 0.8$

No Effect: Did not cause damage or increased sensitivity to distilled water, but did not prevent damage compared to base case.

Increased Sensitivity: Caused severe permeability damage either during injection of the test solution or during injection of distilled water immediately after the test solution.

[b]Specific compounds used were not identified.

Source: Adapted from Veley (1969).

Ferric hydroxide, which is gelatinous, is more likely to clog pores and reduce permeability than barium sulfate and calcium sulfate, which are finely crystalline (Warner, 1966). Above pH 10, calcium, barium, strontium, magnesium, and iron all form gelatinous hydroxide precipitates. Lower-pH solutions containing bicarbonates will convert to carbonates if the pH is raised, resulting in iron, calcium, and magnesium carbonate precipitates (Strycker and Collins, 1987). Dissolution reactions involving silica in low-pH solutions can sometimes even reduce permeability by reprecipitation elsewhere, thus clogging pores (Grubbs et al., 1972). Table 3-15 summarizes examples of field

Table 3-15   Examples of Waste/Reservoir Incompatibility

Waste	Reservoir	Interaction	Sources
Ferric chloride	Dolomite (fractured)	Ferric-hydroxide precipitate. Neutralization with HCl was not successful; neutralization with acetic and citric acid prevented precipitation but was too expensive. Intermittent initial injection to allow a coating of precipitate on fracture surfaces prevented further precipitation.	Hower et al., 1972
Acidic iron-rich pickling liquor	Dolomitic sandstone	Permeability of sandstone unchanged, but permeability of dolomite reduced by 1 to 3 orders of magnitude by precipitation of iron carbonate and/or hydroxide.	Ragone et al., 1978
Acidic aluminum nitrate radio-active waste	Carbonates Limonite	Precipitation of aluminum and ferric oxide gels.	Roedder, 1959
Phenolic wastes (petrochemical)	Miocene sands	Potential loss of permeability due to clay swelling minimized by adding 1.5% brine to waste stream.	Sadow, 1963
Sulfuric acid pickling liquor	Mt. Simon sandstone	Precipitation of calcium sulfate. Injection of fresh-water buffer zone solved the problem.	Hartman, 1968
Zeolite water softener back-wash wastes	Arbuckle formation (Kansas)	Chromates and phosphates added to the waste water as corrosion inhibitors formed precipitates when they came in contact with $BaSO_4$, H_2S, and soluble iron in the formation waters.	Latta, 1973
Ferric chloride and ammonium hydroxide	Packed sand column	Ferric hydroxide precipitate reduced permeability of the sand by 30%.	Warner, 1966

and laboratory studies of waste/reservoir compatibility reactions, including precipitation.

3.3.2 Well-Casing and Confining-Formation Failure

Interactions between corrosive wastes and casing and packing can threaten the integrity of a well if proper materials have not been used in construction. Of equal concern is the potential for failure of the confining zone due to physical or chemical effects. For example, dissolution of an overlying carbonate confining layer may allow upward migration of wastes. This process was observed when hot acidic wastes were injected in a Florida well (see case study in Section 7.4).

Chemically active injected fluids can also have negative impacts on the mechanical properties of the reservoir rock. For example, adsorption of aluminum and iron hydroxides and ferric chloride on quartz and other silicates can weaken the surface silicon-oxygen bonds by hydrolysis, reducing the surface energy, surface cohesion, and breaking strength of the formation (Swolf, 1972). In addition, stress changes caused by increased injection pressures can fracture rock, forming permeability channels in a confining formation through which injected fluids could escape (Swolf, 1972).

3.3.3 Well Blowout

Gases entrapped in pore spaces resulting from phase separation of gases from liquids (see Section 2.2.4) can reduce the permeability of a formation (Orlob and Radhakrishna, 1958). This process was the major cause of clogging at ground-water recharge wells in the Grand Prairie Region in Arkansas (Sniegocki, 1963). Normally, pressures in deep-well-injection zones are high enough to keep gases in solution, so phase separation is not a problem. However, it is possible for permeability to be reduced by air entrainment at the same time gases are generated by reactions between the injected waste and reservoir formation. The resulting pressure then forces waste and reservoir fluid up the injection well to the surface, causing a well blowout.

The hazard of well blowout is greatest if hydrochloric acid wastes exceeding certain temperature and concentration limits are injected into a carbonate formation. When carbonate dissolves in acid, carbon dioxide is formed. Normally, this gas remains dissolved in the formation waters at deep-well temperatures and pressures, but if temperature exceeds $88°F$ or acid concentration exceeds 6% HCl, carbon dioxide will separate from the formation waters as a gas (see Section 7.6). The resulting gas accumulation can increase pressures to a point where if injec-

tion stops or drops below the subsurface carbon dioxide pressure, a blowout can occur. Section 7.6 describes a well blowout and discusses its circumstances.

3.4 Influence of the Deep-Well Environment on Biodegradation

Biodegradation of hazardous organic compounds in ground waters has been the subject of much research in recent years. McNabb and Dunlap, (1975) and Ghiorse and Wilson (1988) provide good general reviews of the topic. Unpolluted near-surface aquifers typically contain enough oxygen for aerobic processes to prevail. For example, Ghiorse and Wilson (1988) summarize biodegradation data on 38 trace organic contaminants in subsurface materials from pristine sites. At most sites aerobic degradation is observed. In contrast, the deep-well-injection environment typically is anaerobic (see Section 3.1.2). This section discusses:

■ Occurrence of microbes in the deep-well environment (Section 3.4.1)

■ Degradation of organic compounds in anaerobic conditions (Section 3.4.2)

■ Microbial ecology of the deep-well environment (Section 3.4.3)

3.4.1 Occurrence of Microbes

Messiniva (1962) classifies subsurface sediments and rocks into geochemically active and geochemically inactive categories, based on microbial activity. Geochemically active sediments and rocks tend to be heterogeneous, containing organic material, nitrogen, and phosphorus, and support indigenous bacteria populations. Geochemically inactive formations do not maintain in situ microbial populations and lack fermentive properties when microorganisms are added. Such rocks typically are homogeneous, well-sorted clays (Messiniva, 1962). As noted in Section 3.1.4.4, Sinclair and Ghiorse (1987) describe similar relationships between microbiological activity and the saturated zone in near-surface aquifers: gravelly sand was the most biologically active and clayey layers the least.

It is now generally accepted that microorganisms are ubiquitous in the deep subsurface, although, as noted, not all strata are biologically active. Microorganisms have adapted to the complete range of environmental conditions that exist on and below the earth's surface. They have been observed at pressures up to 25,000 psi, temperatures up to $100°C$, and salt

59

concentrations up to 300,000 mg/L (Kuznetsov et al. 1963). Pokrovskii (1962), using the 100°C isotherm as the lower boundary of the biosphere, identifies three geothermal provinces in the European U.S.S.R.: (1) low temperature (the Ukrainian shield), where the isotherm lies at 10,000 to 15,000 m; (2) moderate temperature (Russian platform), where the isotherm lies at depths from 2,900 to 5,500 m; and (3) high temperature (Black Sea Basin), where the isotherm lies at 1,500 to 2,500 m, with some locations where it reaches the surface. The currently accepted upper-temperature limit for life is about 120°C (Ghiorse and Wilson, 1988), which would place the limit even deeper than that estimated by Pokrovskii, although the diversity and activity of microorganisms at extreme temperatures will surely be limited. The temperature values reported for injection zones in the United States (see Table 3-5) generally range between 40° and 75°C, which is about the optimum range for growth of thermophilic bacteria (see Section 3.4.3).

Most pre-1970 research on microorganisms in the deep-surface was done by petroleum microbiologists. Dunlap and McNabb (1973) summarize data from 30 studies reporting isolation of microorganisms from deep-subsurface sediments. Because deep-well injection zones in the Gulf Coast region (where most deep-well injection of hazardous wastes occurs) are commonly associated with petroleum-producing strata, this research probably has some relevance. Sulfate-reducing organisms are ubiquitous (Postgate, 1965). Kuznetsov et al. (1963), in an analysis of 50 samples of oilfield waters in the Soviet Union, found methanogenic organisms in 23 samples. Sazonova (1962), in a study of 18 oil deposits in the Kuibyshev region, U.S.S.R., found sulfate-reducing and methane-forming bacteria to be most common; denitrifying bacteria were also frequently observed. Denitrifying and sulfur-oxidizing bacteria are widespread in deep artesian waters in the Soviet Union, occurring at depths exceeding 1,800 m (Gurevich, 1962).

Ghiorse and Wilson (1988) review 14 studies, published between 1977 and 1987, characterizing subsurface microorganisms in pristine aquifers; only three studies involve samples deeper than 1,000 ft below the surface. Olson et al. (1981) found sulfate-reducing and methanogenic bacteria in stratal waters from wells 1,800 m deep in the Madison Limestone in Montana. White et al. (1983) in a comparison of microbial activity in the Bucatanna clay at 410 m near Pensacola, Florida, with that in the shallow Fort Polk aquifer, in Louisiana, found the biomass to be about half that in the shallow aquifer and found greater evidence of the byproducts of anaerobic bacterial activity. Weirich and

Schweisfurth (1983) found 10^3 viable organisms/g at a coal layer 405 m below the surface but no viable counts in unsaturated sandstone overlying the coal, at 23 to 343 m.

Other relatively recent studies of microbial activity in deep aquifers include DiTommaso and Elkan (1973), Willis et al. (1975), Ehrlich et al. (1979), and Christofi et al. (1985). DiTommaso and Elkan (1973) conducted microbiological studies of a formation in Wilmington, North Carolina, into which industrial waste was injected at a depth of 850-1,000 ft (see Section 7.5). Samples from an unpolluted observation well yielded mostly denitrifying bacteria. No sulfate-reducers or methanogens were identified in the pristine samples, although significant quantities of methane production began after the injected wastes reached the observation well (see Section 3.4.2). The authors speculated that methanogens in the pristine samples were not identified because they were adapted to pressures in the formation (200 psi) and would not grow in the cultures at atmospheric pressure.

Willis et al. (1975) examined samples from (1) an uncontaminated 1,500-ft monitoring well associated with a waste-injection facility at Pensacola, Florida (see Section 7.2), (2) an uncontaminated 1,000-ft monitoring well associated with the facility in North Carolina discussed in the previous paragraph, and (3) a 1,000-ft well near Calabash, North Carolina. The Florida sample contained no detectable sulfate, about 1 mg/L hydrogen sulfide, and a small amount of dissolved nitrogen and methane. Methanogens and denitrifiers were identified in the sample, but no sulfate reducers. The two North Carolina wells contained sulfate-reducers as well as methanogens and denitrifiers. Inorganic constituents were not analyzed for the well that was sampled, but four observation wells in the vicinity of the North Carolina observation well contained sulfate concentrations between 210 and 740 mg/L (Leenheer and Malcolm, 1973).

Ehrlich et al. (1979) examined microbial populations in samples of industrial wastes containing acrylonitrile and inorganic sodium salts (nitrate, sulfate, and thiocyanate) that had been injected to a depth of 375-425 m at second waste-injection facility at Pensacola, Florida (see Section 7.3). Samples were obtained by allowing the injected waste to backflow, with a maximum estimated aquifer residence time of 107 hours. Denitrifying bacteria dominated in the waste/formation-water mixture (10^5 to $>10^6$ organisms/mL), although substantial populations of both aerobes and anaerobes were also present (10^3 to 10^6 organisms/mL).

Christofi et al. (1985, as reported by Strycker and Collins, 1987) sampled underground mines in Europe ranging from 600 to more than 3,000 ft deep for microbiological activity. Salinity ranged from less than 570 mg/L to more than 132,000 mg/L chloride. Microorganisms were found in all samples, although the greatest variety appeared in the least-saline aquifer.

3.4.2 Degradation of Organic Compounds In Anaerobic Conditions

Anaerobic biodegradation of xenobiotic (manmade) organic compounds has received less study than aerobic biodegradation. For example, the most comprehensive study of biodegradation of organic priority-pollutant compounds (Tabak et al. 1981) uses aerobic conditions. Kobayashi and Rittmann (1982) list about 90 examples of hazardous anthropogenic compounds and the microorganisms that can degrade them, but less than a third of the examples involve anaerobic degradation.

The three most significant groups of bacteria that may mineralize hazardous organic compounds are (1) denitrifiers (which reduce nitrate to nitrogen), (2) sulfate reducers (which reduce sulfate to hydrogen sulfide), and (3) methanogens (which reduce carbon dioxide to methane). Environmental conditions favoring or restricting activity of these major groups are discussed in Section 3.4.3. Tables 3-16, 3-17, and 3-18 list published biodegradation studies under denitrifying, sulfate-reducing and methanogenic conditions. Where the studies report the amount of degradation at specified time periods, these data are also included in the tables.

Biodegradation of organic compounds under denitrifying conditions (see Table 3-16) has been the least-studied of the three groups. Ehrlich et al. (1979) inferred that acrylonitrile injected into a carbonate aquifer was completely degraded because the waste was not found in samples taken from a monitoring well where the waste arrived about 260 days after injection began, nor in any subsequent samples (see Section 7.3). Bouwer and McCarty (1983a) observed partial to almost complete degradation of carbon tetrachloride (> 95%), bromodichloromethane (> 55%), dibromochloromethane (> 85%), and bromoform (> 90%) in laboratory batch experiments simulating denitrifying conditions. Compounds studied that did not show significant degradation under these conditions include chlorinated benzenes, ethylbenzene, naphthalene, chloroform, 1,1,1-trichloroethane, and 1,2-dibromomethane. Phthalic acids (Aftring et al., 1981), phenol (Ehrlich et al., 1983), tri-sodium nitrilotriacetate (Ward, 1985), and o- and m-xylene (Kuhn et al., 1985) are other compounds for which degradation has been observed under denitrifying conditions.

Degradation of organic compounds by sulfate-reducing bacteria (see Table 3-17) has been studied mostly in the context of petroleum deposits (Novelli and ZoBell, 1944; Rosenfeld, 1947; Davis, 1967). Zajic (1969) states that these microbes are good scavengers of organic waste products regardless of source of waste. Novelli and ZoBell (1944) reported finding some strains of sulfate-reducing bacteria that use hydrocarbons, beginning with decane and higher forms, paraffin oil and paraffin wax. In this study, the aromatic hydrocarbons—benzene, xylene, anthracene, and naphthalene—are not degraded, nor are aliphatic hydrocarbons, hydrocarbons with molecular weight lower than that of decane, or hydrocarbons of the naphthene series (cyclohexane). Rosenfeld (1947) reported that high-molecular-weight aliphatic hydrocarbons are quickly decomposed by sulfate-reducing bacteria. However, current thinking is that molecular oxygen is required to degrade saturated hydrocarbons and that the experiments in the above-cited papers did not fully simulate anoxic conditions (Schink, 1988).

Only a few recent studies investigate degradation of organic compounds under sulfate-reducing conditions. Gibson and Suflita (1986) found phenol to be almost completely degraded under sulfate-reducing conditions in three months and found that various chlorophenols showed some degradation (not complete) during the same period. Smolenski and Suflita (1987) found that sulfate-reducing bacteria degraded cresols more readily than methanogenic bacteria, with p-cresol degraded most readily, m-cresol less readily, and o-cresol persisting over 90 days.

Degradation of organic compounds by methanogens has been the most extensively studied of the three groups (see Table 3-18). Methanogenic bacteria can readily degrade a number of monocyclic aromatics (phenol and some chlorophenols [Gibson and Suflita, 1986] benzene, ethyl benzene [Wilson et al., 1987] and a number of C_1 and C_2 halogenated aliphatic compounds [Bouwer et al., 1981; Roberts et al. 1982; Bouwer and McCarty, 1983a; Wilson et al., 1986]). However, the amount of degradation depends on the specific compound and conditions favorable for bacteria that can adapt to degrade the compound. For example, Godsy et al. (1983) studied biodegradation of 13 chlorophenols in the field and laboratory, but only two (2-methylphenol and 3-methylphenol) biodegraded significantly.

Table 3-16   Organic Compounds Degraded Under Denitrifying Conditions

Compound	% De-graded[a]	Time Period[a]	Reference
Acrylonitrile	100	< 9 mo	Ehrlich et al., 1979
Benzoate	—	—	Evans, 1977
Carbon tetrachloride	>95	3 wk	Bouwer and McCarty, 1983b
Bromodichloromethane	>55	6 wk	
Dibromochloromethane	>85	6 wk	
Bromoform	>90	6 wk	
Phthalic acids	—	—	Aftring et al. 1981
Phenol	—	—	Ehrlich et al., 1983
Tri-sodium nitrilotriacetate	—	—	Ward, 1985
o-, m-Xylene	—	—	Kuhn et al., 1985
p-Cresol	—	—	Bossert and Young, 1986

[a]Dashes indicate degradation was observed, but not quantified.

Table 3-17   Organic Compounds Degraded Under Sulfate-Reducing Conditions

Compound	% De-graded[a]	Time Period[a]	Reference
Benzoate	100	3 mo	Gibson and Suflita, 1986
Phenol	99	3 mo	
2-Chlorophenol	20	3 mo	
4-Chlorophenol	26	3 mo	
2,4-Dichlorophenol	39	3 mo	
2,5-Dichlorophenol	48	3 mo	
3,4-Dichlorophenol	29	3 mo	
2,4,5-Trichlorophenol	52	3 mo	
o-,m-,p-Cresols	—	—	Smolenski and Suflita, 1987
Grease	—	—	Pipes, 1960
Keratins	—	—	
Organic sludge	—	—	

[a]Dashes indicate degradation was observed, but not quantified.

Table 3-18   Organic Compounds Degraded under Methanogenic Conditions

Compound	% De-graded[a]	Time Period[a]	Reference
Benzoate	—	—	Evans, 1977 Ferry and Wolfe, 1976
m-Cresol	—	—	Smolenski and Suflita, 1987[b]
o-, m-, p-Cresol	—	—	Goerlitz et al., 1985[b]
Benzene	99	120 wk	Wilson et al., 1987[b]
Ethylbenzene	99	120 wk	
o-, m-, p-Xylene	—	—	
Benzoate	100	3 mo	Gibson and Suflita, 1986
3-Chlorobenzoate	100	3 mo	
3,4-Dichlorobenzoate	96	3 mo	
3,5-Dichlorobenzoate	100	3 mo	
Phenol	100	3 mo	
2-Chlorophenol	100	3 mo	
3-Chlorophenol	100	3 mo	
4-Chlorophenol	100	3 mo	
2,4-Dichlorphenol	100	3 mo	
2,5-Dichlorphenol	83	3 mo	
2,4,5-Trichlorophenol	39	3 mo	
Phenol	—	—	Ehrlich et al., 1983
Phenol	—	—	Godsy et al., 1983
2-Methylphenol	—	—	
3-Methylphenol	—	—	
Phenol	—	—	Suflita and Miller, 1985
Chlorophenols			
Halogenated aliphatics	—	—	Wood et al., 1985
C₁ and C₂ Halogenated aliphatics[c]			Bouwer and McCarty, 1984
Chloroform	99	48 hr	Bouwer and McCarty, 1983a
Carbon tetrachloride	>99	48 hr	Bouwer et al., 1981
1,1,1-Trichloroethane	97	48 hr	
1,1,2,2-Tetrachloroethane	97	48 hr	
Tetrachloroethylene	76	48 hr	
Bromoform	>99	48 hr	
Bromodichloromethane	>99	48 hr	
Dibromochloromethane	>99	48 hr	
1,2-Dibromomethane	>99	48 hr	
1,1-Dichloroethylene	—	—	Barrio-Lage et al., 1986[b]
cis-trans-1,2-Dichloroethylene	—	—	

Table 3-18 (continued)

Compound	% De-graded[a]	Time Period[a]	Reference
Bromoform	—	—	Roberts et al, 1982[b]
Chloroform	—	—	
Chlorodibromomethane	—	—	
Dichlorobromomethane	—	—	
Tetrachloroethylene	—	—	
1,2-Dibromomethane	99	16 wk	Wilson et al., 1986[b]
1,1,1-Dichloroethane	99	40 wk	
trans-1,2-Dichloroethane	87	40 wk	
Trichloroethylene	66-99	40 wk	
Styrene	99	16 wk	
1,1,1-Trichloroethane	—	—	Vogel and McCarty, 1987
1,1,1-Trichloroethane	—	—	Barker et al., 1986[a]
o-Xylene	—	—	
Acetic acid	—	—	DiTommaso and Elkan, 1973
Formic acid	—	—	
Methanol	—	—	

[a]Dashes indicate degradation was observed, but not quantified.

[b]Listed by Ghiorse and Wilson (1988) as carbon dioxide being dominant electron acceptor; degradation data, where given, are also taken from this source.

[c]Percentages shown are for acclimated methanogenic biofilm column as reported in Bouwer and McCarty (1984). Bouwer et al. (1981), and Bouwer and McCarty (1983b) report data on different experiments that resulted in different percentages in some instances.

As discussed in the next section, biodegradation in ground-water systems may involve complex interactions among many types of bacteria, including denitrifying, sulfate-reducing, methanogenic, and others. Whether complete mineralization occurs depends on the compound, environmental conditions at the site, and the microorganisms that are best adapted to those conditions. For example, Wood et al. (1985) identify a number of species of facultative anaerobes that degrade certain halogenated aliphatic hydrocarbons (tetrachloroethylene, trichloroethylene, and 1,1,1-trichloroethane) but in the process form intermediate hazardous compounds that are not easily biodegraded (vinyl chloride, 1,1- and 1,2-dichloroethane, and trans- and cis-1,2 dichloroethene-- see Chapter Two, Table 2-6).

Iron- and manganese-reducing and ammonia-producing bacteria may also be significant in biochemical reactions that occur in the subsurface environment, but during the preparation of this refer-

ence guide no studies were identified that reported on the degradation of hazardous organic compounds by these bacteria. Iron and manganese oxides usually are broken down through microbial reduction (Silverman and Ehrlich, 1964). Consequently, the possibility of this process should be considered when evaluating chemical reactions of iron and manganese species in the deep-well environment. Lovley (1987) reviews the literature on biomineralization of organic matter with the reduction of ferric iron, and Ehrlich (1987) reviews the literature on manganese oxide reduction through anaerobic respiration. Neither of these papers cite any studies using xenobiotic compounds.

3.4.3 Microbial Ecology
Shturm (1962) reviewed the interactions among ecological factors on microorganisms in oil deposits and concluded that these interactions are not well enough understood to establish any complete picture

of their total effect on the activity of microorganisms. In a more recent review of the biology of methanogenic bacteria Zeikus (1977) similarly concluded that relatively little is known about the chemical and mechanistic limitations of anaerobic decomposition of organic matter in nature.

As noted in Section 3.1.4.3, the dissolved-organic-carbon content of subsurface waters is sufficient to maintain a small but diverse population of microorganisms. Denitrifiers, sulfate-reducers, and methanogens are likely to be present in low numbers in most ground water unless conditions strongly favoring one group exist. Consequently, when a potential energy source in the form of an organic contaminant enters the water, the group most capable of utilizing the substrate at the environmental conditions existing in the aquifer will adapt and increase in population, while the population of other indigenous microbes will remain small or possibly be eliminated.

Effects of Salinity Typical salinities in deep-well injection zones range from about 20,000 to 70,000 mg/L (see Table 3-11), which is within the optimum range (50,000-60,000 mg/L) for halophilic organisms (Kuznetsov et al. 1963). Many nonhalophilic bacteria can also live within this range. For example, a test of 14 microbe genera representing widely varying groups showed that most grew in salt concentrations of up to 60,000 mg/L (Hof, 1935, as cited by Zajic, 1969). Nitrification readily occurs at high salinities. Rubentschik (1929, as cited by Zajic 1969), observed conversion of ammonia to nitrate at concentrations of 150,000 mg/L NaCl, and isolated a culture of *Nitrosomonas* showing optimal growth at 40,000 mg/L. However, very high concentrations may slow denitrification. Hof (1935) found that it took more than three times as long for the same amount of gas to be generated from denitrification at 300,000 mg/L NaCl as at 30,000 mg/L NaCl (10 vs. 3 days). Sulfate reduction readily occurs in solutions containing up to 200,000 mg/L NaCl, with an upper limit of 300,000 mg/L (Zajic, 1969)

Effects of Pressure In general, growth and reproduction of both aerobic and anaerobic bacteria occurring at near-surface conditions decrease with increasing pressures (ZoBell and Johnson, 1949). However, certain **barophilic** (pressure-loving) bacteria have adapted to the temperature and pressure conditions in the deep-well environment. For example, aliphatic acids (acetate ions) are degraded by methanogenic bacteria in oilfield waters as long as temperatures are lower than 80°C (Carothers and Kharaka, 1978). Additionally, ZoBell and Johnson (1949) found that certain sulfate-reducing

bacteria isolated from oil-well brines located several thousand feet below the surface are metabolically more active when compressed to 400 to 600 atm (40.5 to 60.8 MPa) than at 1 atm. On the other hand, the pressures in deep-well waste injection formations may be sufficiently high to kill or otherwise severely affect the metabolic activity of microbes from surface habitats that may be indigenous to the injected wastes (McNabb and Dunlap, 1975).

Sulfate-Reducing Bacteria Sulfate-reducing bacteria are adapted to survive in a wide range of anaerobic environmental conditions. The literature on sulfate-reducers in the subsurface is extensive, primarily because most early studies looked for only this type of bacteria (McNabb and Dunlap, 1975). Sulfate-reducers tolerate an Eh range from +600 to -400 mV and salinities up to 300,000 mg/L NaCl and can tolerate levels of heavy metals that would be toxic to other organisms (Zajic, 1969). Booth and Mercer (1963) found that concentrations of ionic copper greater than 50 mg/L are toxic to several important sulfur-reducing species.

Postgate (1959) states that an Eh of -200 mV or less is required for initiation of growth. The extreme pH limits for sulfate-reducing bacteria are 4.2 to 10.5, with maximum growth observed at a pH of 7 (ZoBell, 1958). Neutral or slightly alkaline conditions are preferred (Bass-Becking et al., 1960). Shturm (1962) found that the optimum pH for sulfate-reducing bacteria from two different oil fields were 8.2 and 9.6 but that bacteria from the former field would not grow at pH 9.0. Baas-Becking and Kaplan (1956 as reported by Shturm, 1962) found a pH of 6.2 to 7.9 and an Eh ranging from -50 to -150 mV as most favorable for the growth of sulfate-reducing bacteria in estuarine environments.

Sulfate-reducing bacteria grow at temperatures from 0° to 100°C (ZoBell, 1958), although the optimum temperature range for growth of thermophilic bacteria is 45° to 60°C (Shturm, 1962). The temperature for maximum growth of sulfate-reducing bacteria in sea water lies between 40° and 45°C (Shturm, 1962). Sulfate-reducing bacteria from saline formation water found in petroleum-bearing formations at a depth greater than 1,000 to 2,000 m grows better at pressures ranging from 400 to 1,000 atm than at atmospheric pressure (Shturm, 1962). Halophilic sulfate-reducing bacteria with an optimum salinity level above 120,000 mg/L have not been found (Shturm, 1962).

Oxygen inhibits sulfate reduction, and phenols and chlorophenol function as bactericides to sulfate

reducers (Zajic, 1969). Bivalent cations may inhibit sulfate-reducing bacteria, although the reason is not understood (Kuznetsov et al., 1963). Porter (1946) reports the following sequence of relative inhibition of sulfate-reducing bacteria by cations: $Na < K < NH_4 < Mg < Ca < Ba < Mn < Fe^{+2}, Zn < Fe^{+3} < Al < Pb < Cu < Hg < Ag$. Ashirov (1962) considers dissolved hydrogen sulfide gas (H_2S) and CO_2 in formation waters to be indicative of sulfate-reducing activity in the formation.

Methanogenic Bacteria Methanogenic bacteria may survive in a wide range of environmental conditions, although they may not grow optimally. The addition of sulfate and other compounds (nitrate, nitrite, acetylene) to sediments has been shown to inhibit methanogenesis (Zeikus, 1977). Kelly and Chynoweth (1979) note that methane production is a good measure of decomposition of organic matter in sediment, provided there is an absence of oxygen, nitrate, or sulfate, all of which inhibit methanogenesis. Martens and Berner (1974) indicate that methanogenesis in marine sediments is not initiated until sulfate is depleted from interstitial water. Cappenberg (1975) suggests that the inhibition of methanogenesis by the presence of sulfates results from the production of toxic H_2S. Winfrey and Zeikus (1977) show that sulfate inhibits methanogenesis in freshwater sediments by altering normal carbon and electron flow during anaerobic mineralization and propose that sulfate reducers assume the role of methanogens in sulfate-containing sediments by metabolizing methanogenic precursors.

The optimum temperature for methane production by species in sediments of Lake Mendota, Wisconsin, measured in vitro was 35° to 42°C, well above the maximum in situ temperature of 23°C (Zeikus and Winfry, 1976). Temperatures in the deep-well environment commonly fall within this optimal range (see Table 3-5). DiTommaso and Elkan (1973) report that 20-50 micrograms of iron per liter are required for methane fermentation.

Belyaev and Ivanov (1983) found methanogenic bacteria to be widespread in ground waters of the Caspian depression at depths from 30 to 750 m. No methanogens were found in the deepest sample (1600 m), although other environmental conditions (pH, Eh and salinity) fell within the range at which methanogens were active at shallower depths. Active methanogenesis occurred at Ehs ranging from +115 to -30 mV, with maximum production in the +70 to +100 mV range. Surface waters at the site studies were measured at Eh>+300 mV, and, although

methanogens were present, methane production did not occur. Belyaev and Ivanov (1983) also reported data on methane production from Devonian oil-bearing sediments at a depth of 1500-1700 m in the Tartar Republic. The formation waters were highly saline (230,000 mg/L) and slightly acid (5.7-5.9 pH) with a high content of organic carbon (290-315 mg/L), and no methanogens were found. However, when surface waters were flooded into oil-bearing beds to maintain pressure for oil production, the diluted brines (8,000 to 58,000 mg/L, pH 6.8-7.0, and Eh +65 to +100 mV, organic carbon 5.0-16.1 mg/L) supported active methanogenic populations (600-6,000 cells/L).

Interactions Among Microbial Groups. Decomposition of organic matter in anaerobic environments often depends on the interaction of metabolically different bacteria. Degradation in this situation is a multi-step process in which complex organic compounds are degraded to short-chain acids by facultative bacteria and then to methane and carbon dioxide by methanogenic bacteria. In these interactions, methanogens may function as electron sinks during organic decomposition by altering electron flow in the direction of hydrogen production (Zeikus, 1977). The altered flow of interspecies hydrogen transfer that occurs during coupled growth of methanogens and nonmethanogens may result in (1) increased substrate utilization, (2) different proportions of reduced end products, (3) increased growth of both organisms, and (4) displacement of unfavorable reaction equilibria (Zeikus, 1977).

Ferry and Wolfe (1976) demonstrated the importance of intermediate microbial degradation steps in the anaerobic degradation of benzoate. In mixed cultures that ferment aromatic compounds to CO_2 and methane, the benzene nucleus is first reduced and then cleaved to aliphatic acids by facultative Gram-negative organisms, which are then converted to suitable substrates for various methane bacteria to complete the process (Evans, 1977). Wolin and Miller (1987) present a more recent discussion of interspecies relationships in methanogenesis.

Redox conditions favoring denitrification lie somewhere between those for aerobic and methanogenic decomposition (Bouwer and McCarty, 1983b). However, denitrification and methanogenesis are not entirely mutually exclusive. Ehrlich et al. (1983) observed evidence of both denitrifying and methanogenic bacteria in phenol-depleted zones of a creosite-contaminated aquifer and concluded that the denitrifying bacteria contributed to degradation. In this study, denitrifiers and iron reducers were the dominant anaerobes in contaminated wells. Methane

production was highest in the closest wells downgradient from the contaminated site, indicating the development of redox zones with methanogenic conditions strongest where contaminant concentrations were highest, changing to stronger denitrifying conditions where contaminant concentrations were lower.

Facultative-anaerobic heterotrophic bacteria from oil-productive horizons in the Soviet Union degrade oil accompanied by the elimination of gas containing methane (14-35%), carbon dioxide (1.9-5.0%), hydrogen (4.4-6.2%), and nitrogen (61-78.1%) (Shturm, 1962). The generation of methane and nitrogen indicates that both methanogenic and denitrifying bacteria were probably active in the degradation process. Nazina et al. (1985) report on an aerobic-anaerobic microbial succession, including hydrocarbon oxidizing, sulfate-reducing, fermenting, and methanogenic bacteria, in water-flooded petroleum bearing rock of the Apsheron Peninsula in the Soviet Union.

Studies by the U.S. Geological Survey at the Wilmington, North Carolina, deep-well waste-injection facility (see Section 7.5) also provide evidence of simultaneous degradation of organics by denitrifying and methanogenic organisms (Leenheer and Malcolm, 1973). When the dilute waste front, containing organic acids, formaldehyde, and methanol, reached the first observation well, production of gases increased dramatically. For a period of about 6 weeks, about half the gas volume was methane and about a quarter, nitrogen (N_2). Two weeks later nitrogen had increased to 62% and methane dropped to 33%, and after another three weeks nitrogen had increased to 68%, while methane had dropped to 12%. These relationships indicate that the methanogens were more sensitive to the increases in waste concentration as the dilute front passed the observation well and more concentrated waste reached the site.

The inhibiting effects of sulfates on methane production would seem to indicate that sulfate-reduction will take place in preference to methanogenesis as long as sulfates are present. However, the ecological significance of sulfate reducer/methanogen inter-relationships is not well-understood (Zeikus, 1977). Cappenberg (1975) found that lactate metabolism of sulfate-reducing bacteria in the upper sulfate-containing sediment layers at Lake Vechten provided the main energy source to acetate-fermenting methanogens located lower down. Cappenberg (1975) also found that in laboratory experiments, acetate utilization was greatly enhanced by the presence of sulfate-reducing species with a methanogenic species compared with the methanogenic species by itself using the same

substrate, but that the H_2S produced by the sulfate reducers was toxic to the methanogens. Smolenski and Suflita (1987) found that cresols degrade better in sulfate-reducing conditions than in methanogenic conditions and that sulfate additions increase the rate of p-cresol metabolism in methanogenic incubations.

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CHAPTER FOUR

GEOCHEMICAL CHARACTERISTICS OF HAZARDOUS WASTES

This chapter relates the chemical characteristics of inorganic and organic hazardous wastes to the important fate-influencing geochemical processes occurring in the deep-well environment. Section 4.1 discusses the differences between inorganic and organic hazardous wastes; Section 4.2 examines the important properties of inorganic hazardous wastes and provides detailed information on those identified in 40 CFR Part 261 as hazardous; Section 4.3 follows a similar format to present information on organic hazardous wastes; and Section 4.4 suggests resources and ways to obtain detailed information on compounds of interest.

4.1 Inorganic vs. Organic Hazardous Wastes

Hazardous wastes are broadly classified as either organic or inorganic. Carbon is the central building block of **organic** wastes, whereas **inorganic** wastes are compounds formed by elements other than carbon (except for a few carbon-containing compounds such as metal carbonates, metal cyanides, carbon oxides, and metal carbides). Heavy metals may straddle the definition: although usually associated with inorganics, they can also be incorporated into organic compounds. In fact, organic forms of heavy metals, such as dimethyl mercury, are often more toxic than inorganic compounds formed by the same metal.

A major difference between organic and inorganic hazardous wastes is that, with the exception of cyanide, inorganics cannot be destroyed by being broken down into nonhazardous component parts, because at least one element in the compound is toxic. Inorganic hazardous wastes containing toxic elements can be transformed from a more to a less toxic form, but can never be transformed to a nontoxic form (see Section 4.2).

Toxic organic compounds (with the exception of organometallic compounds containing toxic metals), however, may be rendered harmless in some cases by being broken down into their inorganic components: carbon, hydrogen, oxygen, and other nontoxic elements. Most hazardous organic substances must be manufactured under carefully controlled conditions and are highly unlikely to form from the basic elements of hydrogen, oxygen, and others under uncontrolled deep-well environmental conditions. Therefore, once these wastes have completely broken down, their detoxification can be considered permanent (see Section 4.3).

Another major difference between inorganic and organic compounds is the number of compounds. Inorganic elements that exhibit toxic properties at levels of environmental concern number in the dozens, and only ten are regulated as hazardous wastes under the UIC program (arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, thallium, and cyanide). Additionally, the number of inorganic compounds that any individual toxic element may form is limited (probably fewer than 50). On the other hand, the extreme versatility of carbon as a building block for organic compounds means that literally millions are possible, and the number that exhibit toxic properties is probably on the order of thousands or tens of thousands. At this time, however, the number of organic compounds specifically regulated as hazardous is fewer than 200.

Regardless of whether a waste is classified as organic or inorganic, it must have certain physical and chemical properties to be suited for deep-well injection. Because water is the medium for injection, injected wastes, whether organic or inorganic, will typically be liquid and/or water-soluble or miscible, and relatively nonvolatile. Table 1-1 in Chapter One lists the major properties used to characterize hazardous substances in emergency responses to spills and indicates the physical state typically required for deep-well injection.

4.2 Chemical Properties of Inorganic Hazardous Wastes

The only means by which inorganic wastes can be rendered nonhazardous are dilution, isolation (as in deep-well injection), in some cases changes in oxidation state, and neutralization. As noted in Chapter One (Section 1.2), acidic wastes made up one-fifth of the injected waste volume and involved one-third of the injection wells in 1983. Most of the volume was from inorganic acids (hydrochloric, sulfuric, and nitric). Acid-base characteristics and neutralization are discussed in detail in Chapter Two (Sections 2.2.1 and 2.3.1), so the remainder of this section will focus on heavy metals and other hazardous inorganics (selenium and cyanide).

Inorganic elements can be broadly classified as **metals** and **nonmetals**. Most metallic elements become toxic at some concentration. Table 4-1 lists 26 elements and compounds that have been identified as toxic by various sources. Nine elements (arsenic, barium, cadmium, chromium, lead, mercury, nickel, selenium, and thallium) and cyanide are defined as hazardous inorganics for purposes of deep-well injection.

In aqueous geochemistry, the important distinguishing property of metals is that in general they have a positive oxidation state (donate electrons to form cations in solution), while nonmetals have a negative oxidation state (receive electrons to form anions in solution). All elements in Table 4-1 are metals except for arsenic, boron, selenium, and tellurium. Figure 4-1 shows the location of the elements in Table 4-1 within the periodic table. In reality, there is no clear dividing line between metals and nonmetals. For example, arsenic, which is classified as a nonmetal, behaves like a metal in its commonest valence states and is commonly listed as such. Other nonmetals, such as selenium, behave more like nonmetals.

Figure 4-1 also shows that the metals are divided into light (also called alkali-earth metals) and heavy. All the metals in Table 4-1 are heavy metals except for beryllium and barium. Additionally, Figure 4-1 shows other categories of elements that are or may be significant chemically as dissolved species in deep-well-injection zones: (1) alkali-earth metals (sodium, magnesium, potassium, calcium, and strontium), (2) heavy metals (manganese, iron, and aluminum, which may be significant in precipitation reactions), and (3) nonmetals (carbon, nitrogen, oxygen, silicon, phosphorus, sulfur, chlorine, bromine, and iodine).

4.2.1 Major Processes and Environmental Factors Affecting Geochemical Fate of Hazardous Inorganics

The major processes affecting geochemical fate of hazardous inorganics are acid-base adsorption-desorption, precipitation-dissolution, complexation, hydrolysis, oxidation-reduction, and catalytic reactions. Table 4-2 lists the processes that may be significant for hazardous wastes in the deep-well environment and refers to sections in this reference guide where a detailed discussion can be found. Tables elsewhere in the reference guide that contain detailed information on inorganics are also listed in Table 4-2. The significance of these processes to inorganic wastes is discussed only briefly here; additional information on individual elements is given in Table 4-3.

Acid-base equilibrium is very important to inorganic chemical reactions; Section 2.2.1 discusses the effects of acid-base ionization. Adsorption-desorption (see Section 2.2.2) and precipitation-dissolution (see Section 2.2.3) reactions are also of major importance in assessing the geochemical fate of deep-well-injected inorganics. Interactions between and among metals in solution and solids in the deep-well environment can be grouped into four types: (1) adsorption (including both physical adsorption and ion exchange) by clay minerals (Veley, 1969) and silicates (Brown, 1979) (see Section 2.2.2.2), (2) adsorption and coprecipitation by hydrous iron and manganese oxides (Jenne, 1968; Davis and Leckie, 1978a,b), (3) complexation by organic substances such as fulvic and humic acids (see discussion below), and (4) precipitation or co-precipitation by incorporation in crystalline minerals (see Section 2.2.3 and Section 3.3.1.3 for additional information on common precipitation reactions).

Solution complexation is of major importance for the fate of metals in the deep-well environment (see Section 2.3.2). Soluble metal ions in solution can be divided into three major groups: (1) simple hydrated metal ions (Veley, 1969), (2) metals complexed by inorganic anions, and (3) organometallic complexes (Buffle et al., 1984; Cabaniss et al., 1984; Raspor et al., 1984). Figure 4-2 shows types of metal species and the range of diameters of the different species in water. The stability of complexes between metals and organic matter is largely independent of ligand, and follows the following general relationships (Fuller, 1977):

- Monovalent ions: $Ag > Tl > Na > K > Pb > Cs$

- Divalent ions: $Pt > Pd > Hg > UO_2 > Cu > Ni > Co > Pb > Zn > Cd > Fe > Mn > Sr > Ba$

Table 4-1   Inorganic Hazardous Wastes (Excluding Radioactive Elements)

Element/ Compound	Metal	Non- Metal	EPA UIC	EPA Priority	California List	NRCC[a]
Antimony	X			X		S
Arsenic		X	X	X	X	X
Asbestos		X		X		
Barium	X		X			S
Beryllium	X					S
Bismuth	X					S
Boron		X				S
Cadmium	X		X	X	X	X
Cesium	X					S
Chromium	X		X	X	X	X
Copper	X			X		
Cyanide		X	X	X		
Gallium	X					S
Germanium	X					S
Indium	X					S
Lead	X		X	X	X	X
Mercury	X		X	X	X	X
Molybdenum	X					S
Nickel	X		X	X	X	X
Silver	X			X		S
Selenium		X	X	X	X	
Tellurium		X				S
Thallium	X		X	X	X	S
Tin	X					S
Zinc	X			X		
Zirconium	X					S

[a]X = Separate report available, S = summary information in NRCC (1982).

Sources: U.S. EPA (1985); Callahan et al. (1979); 51 Federal Register 44715, December 11, 1986 (California List); National Research Council Canada (1978a) (As); National Research Council Canada (1979b) (Cd); National Research Council Canada (1976) (Cr); National Research Council Canada (1978b) (Pb); National Research Council Canada (1981) (Ni); National Research Council Canada (1979a) (Hg); National Research Council Canada (1982) (all others).

■ Trivalent ions: Fe > Ge > Sc > In > Y > Pl > Ce > La

Hydration reactions between metal ions and water affect mobility and adsorption but not toxicity (see Section 2.3.3). Hydrolysis is particularly important in the chemistry of cyanide.

Oxidation-reduction reactions may affect the mobility of metal ions by changing the oxidation state (Gulens et al., 1979). The environmental factors of pH and Eh (oxidation-reduction potential) strongly affect all the processes discussed above (see Sections 3.1.1 and 3.1.2 for more information). For example, the type and number of molecular and ionic species of metals change with a change in pH (see Figures 4-3, 4-4, and 4-5). A number of metals and nonmentals (As, Be, Cr, Cu, Fe, Ni, Se, V, Zn) are more mobile under anaerobic conditions than aerobic conditions, all other factors being equal (Fuller, 1977). Additionally, the high salinity of deep-well injection zones increases the complexity of the equilibrium chemistry of heavy metals (Van Luik and Jurinak, 1979; Millero, 1984).

Förstner and Wittmann (1979) make the following observations about the general mobility of heavy metals

Table 4-2 Major Processes and Environmental Factors Affecting the Geochemical Fate of Inorganic Hazardous Wastes

Process/Factor	Location of Additional Information in this Reference Guide	
	Section	Tables
Processes		
Acid-base equilibria	2.2.1	
Adsorption-desorption	2.2.2	2-5, 5-3
Precipitation-dissolution	2.2.3, 3.4.1	
Complexation	2.3.2	
Hydrolysis	2.3.3	
Oxidation-reduction	2.3.4	
Catalysis	2.3.5	
Environmental Factors		
pH	3.1.1	
Eh	3.1.2	
Salinity	3.1.3	
Mineralogy	3.1.4	3-2
Waste/Reservoir Characterization	6.2, 6.3	

Table 4-3 Geochemical Properties of Listed Metals and Nonmetals

Property	Forms/Conditions
Mobility	Cr is very mobile in neutral to alkaline conditions.
	As is more mobile under anaerobic than aerobic conditions and in alkaline conditions.
	Pb^{+2} is relatively immobile except in highly acidic environments.
Strong adsorption on Fe and Mn oxides and hydrous oxides	Cd, Cr(IV), Hg, Ni, Se.
Precipitation	Cd + H_2S —> CdS.
	Cr + organic material —> insoluble (aerobic conditions) precipitates.
	Cr(III) hydroxide, carbonate, and sulfide precipitate (pH > 6); Cr(VI) does not precipitate in these conditions.
	Pb typically precipitates as $Pb(OH)_2$, $PbCO_3$, $Pb_5(PO_4)_3OH$. NaCl increases solubility.
	Ni carbonates, hydroxides, and sulfides are relatively insoluble; Ni oxides in acidic solution may precipitate with neutralization.
Oxidation-reduction	Many selenium compounds can be reduced to produce elemental selenium when exposed to organic matter in subsurface environment.
Bioconversion	$As(OH)_3$ to $As(CH_3)_3$ (anaerobic); Hg (inorganic) to methyl mercury (anaerobic).

Source: Adapted from Strycker and Collins (1987).

Figure 4-1 Periodic Chart of the Elements, Showing Position of Toxic Metals and Nonmetals (Adapted from Lange's Handbook of Chemistry, 1967 edition).
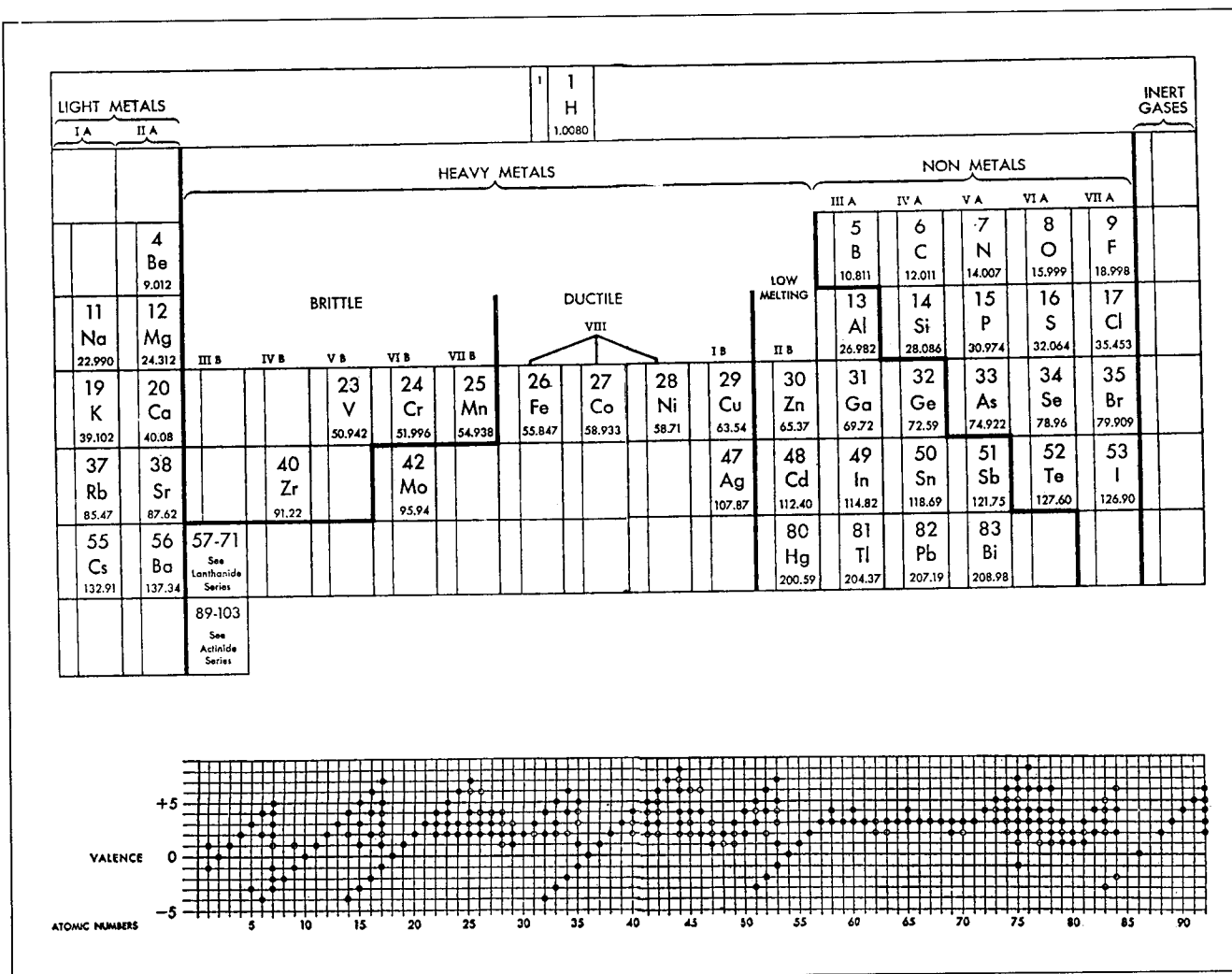
in ground water: (1) mobility tends to increase with increasing salinity because alkali- and alkaline-earth cations compete for adsorption sites on solids, (2) change in redox conditions (lower Eh) can partly or completely dissolve Fe and Mn oxides and liberate other copre-cipitated metals, and (3) when natural or synthetic complexing agents are added soluble metal complexes may form.

4.2.2 Known Properties of Listed Hazardous Inorganics

An extensive body of literature is available on the chemistry of listed inorganic wastes although most of it is oriented toward near-surface environments. For example, Förstner and Wittmann (1979) present a good overview of the aqueous geochemistry of metal contaminants, and the various reports of the National Research Council of Canada provide summaries of the geochemistry of individual metals (see Table 4-1

for citations). Fuller (1977) contains over 200 citations on the movement of metals in soil, and Moore and Ramamoorthy (1984a) devote individual chapters to the chemistry of As, Cd, Cr, Cu, Pb, Hg, Ni, and Zn in natural waters. One source that does discuss the chemistry of listed wastes in the deep-well environment is Strycker and Collins (1987); information on listed inorganic wastes from this source is summarized in Table 4-3. Section 4.4 discusses how to find detailed data on specific compounds.

4.3 Chemical Properties of Organic Hazardous Wastes

Because carbon atoms can form strong bonds with one another while combining with other elements, the number of organic compounds is enormous. More than two million such compounds have been described and characterized, which is more than ten

Figure 4-2   Types of Metal Species in Water (Förstner and Wittman, 1979).

Metal species	Range of diameters (μm)	Examples
Free aquated ions Complex ionic entities Inorganic ion-pairs and complexes		$Fe(H_2O)_6^{3+}$; $Cu(H_2O)_6^{2+}$ AsO_4^{3-}, UO_2^{2+}, VO_3^- $CuOH^+$, $CuCO_3^0$, $Pb(CO_3)_2^{2-}$ $AgSH^0$, $CdCl^+$, $Zn(OH)^-$
Organic complexes, chelates and compounds	0.001	$Me - OOCR^{n+}$, HgR_2

$$CH_2 - C = O$$
$$H_2N \quad\quad O$$
$$Cu$$
$$O \quad\quad NH_2$$
$$O = C - CH_2$$

Metals bound to high molecular weight organic materials Highly-dispersed colloids Metals sorbed on colloids	0.01 0.1	Me-humic/fulvic acid polymers FeOOH, Mn(IV) hydrous oxides $Me.aq^{n+}$, $Me_n(OH)_y$, $MeCO_3$, etc. on clays, FeOOH, organics
Precipitates, mineral particles, organic particles Metals present in live and dead biota		$ZnSiO_3$, $CuCO_3$, CdS in FeS, PbS Metals in algae

Vertical axis labels: In true solution — Dialysable — Membrane filterable — Filterable

(Me = metal; R = alkyl)

Figure 4-3   Distribution of Molecular and Ionic Species of Divalent Cadmium at Different pH Values (Hahne and Kroontje, 1973).
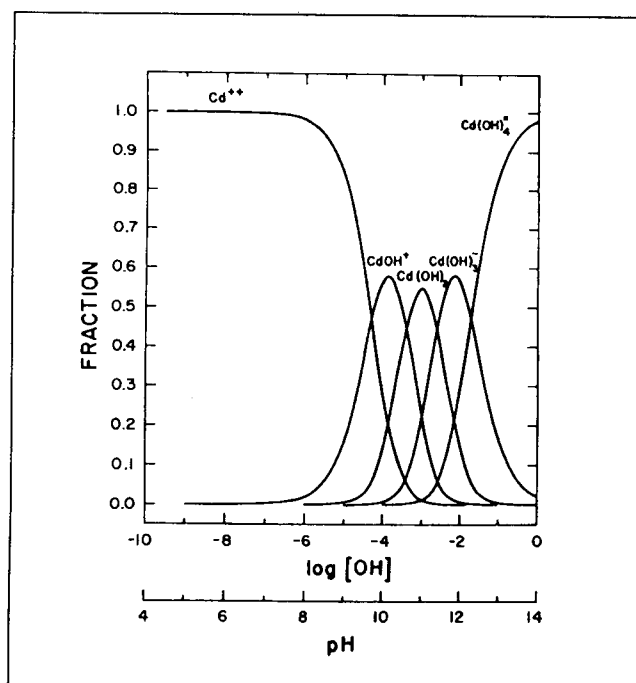
Figure 4-4.   Distribution of Molecular and Ionic Species of Divalent Lead at Different pH Values (Hahne and Kroontje, 1973.)
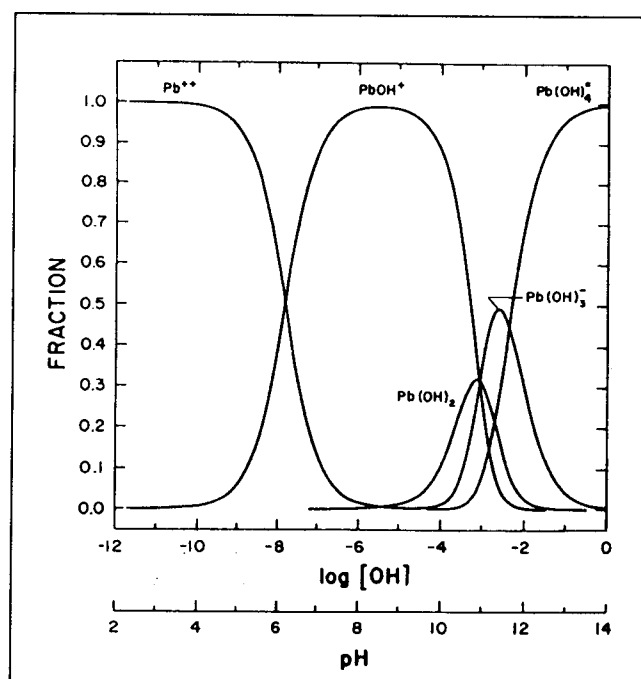
Figure 4-5   Distribution of Molecular and Ionic Species of Divalent Mercury at Different pH Values (Hahne and Kroontje, 1973).
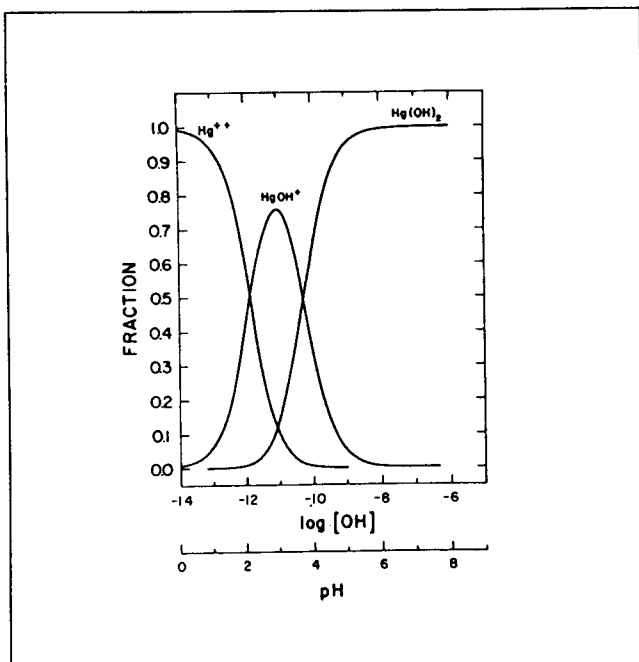
times the total number of known compounds of all other elements except hydrogen. The names and quantity of hazardous organic compounds may be bewildering to those without training in organic chemistry. Further confusion can arise because a single compound may have a popular name and several technical names because of the flexibility in the nomenclature conventions of organic chemistry.

Organic compounds can be broadly grouped into hydrocarbons (compounds formed from only carbon and hydrogen atoms) and their derivatives, in which a hydrogen atom is replaced with another atom or group of atoms, such as a functional group (e.g., an atom or atom group that imparts characteristic chemical properties to the organic molecules containing it). Structurally, organic compounds can also be classified as (1) straight-chain compounds, (2) branched-chain compounds, and (3) cyclic compounds. Another classification of organic compounds divides these compounds between aromatics (those with a six-membered ring structure in which single and double carbon bonds alternate) and aliphatics (those containing chains or nonaromatic rings of carbon atoms).

The large number of organic compounds that have been identified as hazardous makes it im-

possible to discuss individual compounds here. The following sections provide a general overview of the characteristics of seven major groups of hazardous organics: (1) halogenated aliphatic hydrocarbons (Section 4.3.1), (2) halogenated ethers (Section 4.3.2), (3) monocyclic aromatics (Section 4.3.3), (4) phthalate esters (Section 4.3.4), (5) polycyclic aromatic hydrocarbons (Section 4.3.5), (6) nitrogenous compounds (Section 4.3.6), and (7) pesticides (Section 4.3.7). Appendix A lists more than 100 UIC-regulated hazardous organic compounds in alphabetical order and gives their group as defined above, the section in this chapter where the group is discussed, and the table in this chapter that summarizes data on the compound. Appendix B contains an alphabetized list of over 150 organic compounds for which field or laboratory retardation factors/partition coefficients and biodegradation studies have been made, with reference citations for the different types of studies.

Injected organic wastes are subject to a number of geochemical processes in the deep-well environment. Table 4-4 lists the major ones that may be significant and lists the sections in other chapters where these processes are discussed in detail.

Three processes with the potential for the greatest impact on the fate of organic wastes in the deep-well environment are adsorption, hydrolysis, and biodegradation. The summary tables presented for each of the seven groups of organic compounds contain the following information, where available:

- Ratings of the importance of adsorption, hydrolysis, and biodegradation as fate processes, adapted by Mills et al. (1985) from Callahan et al. (1979).

- Additional data on biodegradation from systematic laboratory studies by Tabak et al. (1981) under aerobic conditions (second column), and results of biodegradation studies under anaerobic conditions are summarized in Tables 3-16, 3-17, and 3-18 in Section 3.4 (third column).

- An indication of whether the molecular-topology model of Sabljić (1987) has been used to calculate molecular-connectivity indices and soil adsorption coefficients (k_{oc}—see Section 5.2.2.1) for the compound; this information is useful when the exact physical or chemical properties of the compound are unknown and a structure-activity approach is used to characterize the chemical properties of the compound (see Section 4.4.4).

**Table 4-4   Major Processes and Environmental Factors Affecting the Geochemical Fate of Organic Hazardous Wastes**

Process/Factor	Location of Additional Information in this Reference Guide	
	Section	Tables
Processes		
Acid-base equilibria	2.2.1	2-4
Adsorption-desorption	2.2.2	2-5, 5-3, 5-4
Complexation	2.3.2	2-8
Hydrolysis	2.3.3	2-7, 2-8
Oxidation-reduction	2.3.4	2-9, 2-10, 2-11
Catalysis	2.3.5	
Polymerization	2.3.6	
Thermal degradation	2.3.7	
Biodegradation	2.3.8	2-12, 3-16, 3-17, 3-18
Environmental Factors		
pH	3.1.1	3-1
Eh	3.1.2	
Salinity	3.1.3	3-10, 3-11
Mineralogy	3.1.4	3-2
Lithology	3.1.4	3-3, 3-4, 3-7, 3-8, 3-9
Temperature and Pressure	3.1.5	3-5, 3-6
Waste/Reservoir Characterization	6.2, 6.3	3-15, 6-1, 6-2, 6-3, 6-4, 6-5, 6-6

■ Tables elsewhere in the reference guide where additional information on the compound can be found.

Most of the information in Tables 4-5 through 4-11 is derived from studies oriented toward near-surface fate processes and consequently should be interpreted with caution. Ratings for adsorption and hydrolysis should be generally applicable to the deep-well environment. In some instances a negative rating for hydrolysis has been changed to positive for purposes of deep-well injection because of the longer time frame compared with that for near-surface fate assessment (see Section 2.3.3).

Most studies of the biodegradation of hazardous organic compounds have been performed under aerobic conditions; however, these conditions are most likely to occur only near the injection point. (The first two columns under biodegradation in the summary tables present data drawn from such studies and hence may have limited applicability in the deep-well environment.) A compound will probably have to be susceptible to anaerobic biodegradation for this process to be sig-

nificant in the deep-well environment, and studies on anaerobic degradation of organic compounds are reviewed in Section 3.4. Meikle (1972) describes qualitative relationships in the biodegradation of 21 groups of organic compounds.

4.3.1 Halogenated Aliphatic Hydrocarbons

Hazardous halogenated aliphatic hydrocarbons include mostly straight-chain hydrocarbons (alkanes containing single bonds, such as methane and ethane, and alkenes containing one double bond between carbon atoms, such as ethene and propene) in which one or more hydrogen atoms are replaced by atoms of the halogen group of elements (fluorine, chlorine, and/or bromine). Table 4-5 indicates the importance of various fate processes for 26 hazardous halogenated aliphatic hydrocarbons (note caveats in Section 4.3 about interpreting this information). Moore and Ramamoorthy (1986) review the behavior of aliphatic hydrocarbons in natural waters.

As Table 4-5 shows, the importance of adsorption for many of the compounds in this group is unknown. Adsorption is rated as significant for three compounds

Table 4-5 Geochemical Processes Affecting the Fate of Halogenated Aliphatic Hydrocarbons

Compound[a]	Adsorption	Hydrolysis	Biodegradation	MCI Koc	Tables
Chloromethane (methyl chloride)	-	-	-		2-7
Dichloromethane (methylene chloride)	-	-	?D	y	2-6
Trichloromethane (chloroform)	-	-	?D (An)	y	2-6
Tetrachloromethane (carbon tetrachloride)	?	-	-D (An)	y	1-3, 2-6, 5-5
Chloroethane (ethyl chloride)	-	+	?(An)		2-6, 2-7
1,1-Dichloroethane (ethylidene chloride)	-	-	?A (An)		2-6
1,2-Dichloroethane (ethylene dichloride)	-	-	?B	y	5-4
1,1,1-Trichloroethane (methyl chloroform)	-	-	-B (An)	y	2-6
1,1,2-Trichloroethane	?	-	-C	y	
1,1,2,2-Tetrachloroethane	?	-	-N (An)	y	
Hexachloroethane	?	?	?D		
Chloroethene (vinyl chloride)	+	-	-A (An)		2-6
1,1-Dichloroethene (vinylidene chloride)	?	-	?A		
1,2-trans-Dichloroethene	-	-	?B		
Trichloroethene	-	-	?A	y	
Tetrachloroethene (perchloroethylene)	-	-	+A	y	
1,2-Dichloropropane	?	+	-A	y	2-7
1,2-Dichloropropene	?	+	-A		
Hexachlorobutadiene	+	?	?D		
Hexachlorocyclopentadiene	+	+	-D		2-7
Bromomethane (methyl bromide)	-	+	-		
Bromodichloromethane	?	-(+)	?A (An)		2-7, 5-5
Dibromochloromethane	?	-	?N (An)		5-5
Tribromomethane (bromoform)	?	-	?A (An)		5-5
Dichlorodifluoromethane	?	-	-		
Trichlorofluoromethane	?	-	-N		

Key:

-	Not likely to be an important process.
+	Could be an important fate process.
?	Importance of process uncertain or not known.
(+)	Revised rating in relationship to deep-well injection.
D	Significant degradation, rapid adaptation (aerobic).
A	Significant degradation, gradual adaptation (aerobic).
B	Slow to moderate degradation, concomitant with significant volatilization.
C	Very slow degradation, with long adaptation period required.
N	Not significantly degraded under the conditions of test method (aerobic).
(An)	Subject to anaerobic degradation (see Tables 3-16, 3-17, and 3-18).
y	Soil adsorption coefficient (Koc) calculated by Sabljić (1987) from molecular connectivity index.

[a]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981); Sabljić (1987).

(chloroethane, hexachlorobutadiene, and hexachlorocyclopentadiene). Hydrolysis may be an important process for eight compounds in this group (chloromethane, dichloromethane, chloroethene, 1,2-dichloropropane, 1,2-dichloropropene, hexachlorocyclopentadiene, bromomethane, and bromodichloromethane). Callahan et al. (1979) rates biodegradation as significant for tetrachloroethene only, whereas Tabak et al. (1981) found most compounds in the group are subject to significant degradation under experimental aerobic conditions. At least ten of the compounds are subject to biodegradation under anaerobic conditions. Britton (1984) discusses microbial degradation of aliphatic hydrocarbons in more detail.

4.3.2 Halogenated Ethers

Ethers are either aliphatic (chain-structure) or aromatic (ring-structure) hydrocarbons containing an oxygen atom connected to two carbon atoms by single bonds. In halogenated ethers, one or more halogens (chlorine or bromine) replace hydrogen in the aliphatic or aromatic portion of the molecule. Table 4-6 indicates the importance of various processes for seven hazardous halogenated ethers (note caveats in Section 4.3 about interpreting this information). This group contains mostly aliphatic ethers except for 4-chlorophenyl

phenyl ether and 4-bromophenyl phenyl ether, which are aromatic hydrocarbons.

Adsorption is very likely to be a more significant process for the aromatic halogenated ethers than for the aliphatic halogenated ethers. Hydrolysis is important for two of the aliphatic ethers: bis(chloromethyl) ether and 2-chloroethyl vinyl ether. The group appears generally resistant to biodegradation, although under certain conditions several may be degraded. No examples of anaerobic biodegradation of these compounds were found during the literature review done to prepare this reference guide.

4.3.3 Monocyclic Aromatic Hydrocarbons and Halides

As mentioned, aromatic hydrocarbons have a six-membered ring structure in which single and double carbon bonds alternate. This ring structure tends to be stable, so chemical reactions tend to result in the substitution of hydrogen atoms for another atom or functional group. Table 4-7 indicates the importance of various fate processes for 23 hazardous monocyclic aromatics (note caveats in Section 4.3 about interpreting this information). Five of these compounds are hydrocarbons (benzene, ethylbenzene, toluene,

Table 4-6 Geochemical Processes Affecting the Fate of Halogenated Ethers

Compound[a]	Adsorption	Hydrolysis	Biodegradation	Tables
bis(Chloromethyl) ether	-	++	?	2-7
bis(2-Chloroethyl) ether	-	-	-D	
bis(2-Chloroisopropyl) ether	-	-	-D	
2-Chloroethyl vinyl ether	-	+	?D	2-7
4-Chlorophenyl phenyl ether	+	-	?N	
4-Bromophenyl phenyl ether	+	-	?N	
bis(2-Chloroethoxy) methane	-	?	?N	2-7

Key:
++   Predominant fate-determining process.
-     Not likely to be an important process.
+   Could be an important fate process.
?   Importance of process uncertain or not known.
(+)   Revised rating in relation to deep-well injection.
D   Significant degradation, rapid adaptation (aerobic).
N   Not significantly degraded under the conditions of test method (aerobic).

[a]Additional data on all these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981).

Table 4-7   Geochemical Processes Affecting the Fate of Monocyclic Aromatic Hydrocarbons and Halides

Compound[a]	Adsorption	Hydrolysis	Biodegradation	MCI K_{oc}	Tables
Benzene	+	-	D(An)	y	2-8
Chlorobenzene	+	-	D/A	y	2-6, 5-5
1,2-Dichlorobenzene (o-dichlorobenzene)	+	-	T	y	5-5
1,3-Dichlorobenzene (m-dichlorobenzene)	+	?	?T	y	2-6
1,4-Dichlorobenzene (p-dichlorobenzene)	+	-	-T	y	2-6, 5-5
1,2,4-Trichlorobenzene	+	-	-T	y	2-6, 5-5
Hexachlorobenzene	+	-	-N	y	5-5
Ethylbenzene	?	-	?D/A(An)	y	2-6, 5-5
Nitrobenzene	+	-	-D	y	
Toluene	+	-	?D	y	
2,4-Dinitrotoluene	+	-	-T		
2,6-Dinitrotoluene	+	?	-T		
Phenol	-	-	+D(An)		1-3, 2-4, 2-8, 2-11, 3-7, 5-4
2-Chlorophenol	-	-	?D(An)		2-4
2,4-Dichlorophenol	-		++D	y	2-4
2,4,6-Trichlorophenol	?	-	?D		
Pentachlorophenol	+	-(+)	+A	y	1-3, 2-4
2-Nitrophenol	-	-	-D		2-4
4-Nitrophenol	+	-	-D		2-4
2,4-Dinitrophenol	+	-	-D		2-4
2,4-Dimethyl phenol (2,4-xylenol)	-	-	?D		2-4
p-Chloro-m-cresol	-	-	?D		
4,6-Dinitro-o-cresol	+	?	-N		2-4

Key:

++	Predominant fate-determining process.
-	Not likely to be an important process.
+	Could be an important fate process.
?	Importance of process uncertain or not known.
(+)	Revised rating in relation to deep-well injection.
D	Significant degradation, rapid adaptation (aerobic).
A	Significant degradation, gradual adaptation (aerobic).
T	Significant degradation with gradual adaptation, followed by toxicity.
N	Not significantly degraded under the conditions of test method (aerobic).
(An)	Subject of anaerobic degradation (see Tables 3-16, 3-17, and 3-18).
y	Soil-adsorption coefficient (K_{oc}) calculated by Sabljić (1987) from molecular connectivity index.

[a]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981); Sabljić (1987).

phenol, and 2,4-dimethyl phenol) and the rest are halogenated or nitrogenated derivatives of benzene, toluene, and phenol. Moore and Ramamoorthy (1984b) review the behavior of monocyclic aromatics (Chapter 4) and phenols (Chapter 8) in natural waters.

Adsorption may be important for most of the compounds in this group, whereas hydrolysis may not be a significant process except for pentachlorophenol. Callahan et al. (1979) rated biodegradation as significant only for phenol, 2,4-dichlorophenol, and pentachlorophenol. Tabak et al. (1981) found that significant degradation with rapid or gradual adaptation oc-curred for 15 of the 23 compounds. Anaerobic degradation has been reported for five compounds in this group (benzene, ethylbenzene, phenol, 2-chlorophenol, and 2,4-dichlorophenol). Chapman (1972) discusses in some detail the reaction sequence used for the bacterial degradation of phenolic compounds; Gibson and Subramanian (1984) provide a general review of microbial degradation of aromatic hydrocarbons; and Reineke (1984) reviews microbial degradation of halogenated aromatics.

4.3.4 Phthalate Esters

Esters contain a single oxygen atom attached to a single carbon atom by a single bond, and a second oxygen atom attached to the same carbon atom by a double bond. Phthalate esters form when aliphatic

hydrocarbon groups replace the acidic hydrogen atoms in phthalic acid (benzenedicarboxylic acid). Table 4-8 indicates the importance of various processes to six hazardous phthalate esters (note caveats in Section 4.3 about interpreting this information). All are subject to adsorption and are readily biodegraded under aerobic conditions, but apparently not under anaerobic conditions. Ribbons et al. (1984) review mechanisms for microbial degradation of phthalates. Hydrolysis half-lives of four phthalate esters (dimethyl phthalate, diethyl phthalate, di-n-butyl phthalate, and di-n-octyl phthalate) are on the order of thousands of days, which may be significant in the time frame of deep-well injection. More discussion of the chemical fate of phthalate esters in aquatic environments can be found in Pierce et al. (1980).

4.3.5 Polycyclic Aromatic Hydrocarbons

Polycyclic (also called polynuclear) aromatic hydrocarbons (PAHs) are composed of multiple rings connected by shared carbon atoms (i.e., separate rings are combined by sharing two carbon atoms). Table 4-9 indicates the importance of various processes to the fate of 18 hazardous PAHs (note caveats in Section 4.3 about interpreting this information). All these compounds are pure hydrocarbons except for the two benzo-fluoranthenes, polychlorinated biphenyls (PCBs), and 2-chloronaphthalene. Moore and Ramamoorthy (1984b)

Table 4-8 Geochemical Processes Affecting the Fate of Phthalate Esters

Compound[a]	Adsorption	Hydrolysis	Biodegradation	Tables
Dimethyl phthalate	+	-(+)	+D	2-7
Diethyl phthalate	+	-(+)	+D	2-7
di-n-butyl phthalate	+	-(+)	+D	2-7
Di-n-octyl phthalate	+	-(+)	+A	2-7
bis(2-Ethylhexyl) phthalate	+	-	+A	
Butyl benzyl phthalate	+	-	+D	

Key:
-   Not likely to be an important process.
+   Could be an important fate process.
?   Importance of process uncertain or not known.
(+)   Revised rating in relation to deep-well injection.
D   Significant degradation, rapid adaptation (aerobic).
A   Significant degradation, gradual adaptation (aerobic).

[a]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981).

review the behavior of PAHs (Chapter 5) and PCBs (Chapter 9) in natural waters.

Adsorption and biodegradation under aerobic conditions are significant for the entire group, but PAHs are generally resistent to anaerobic degradation. Safe (1984) reviews the literature on microbial degradation of PCBs. Hydrolysis is not significant for any compounds in the group.

4.3.6 Nitrogenous Compounds

The diverse nitrogenous-compounds group is composed of substances that have in common the substitution of one or more nitrogen-containing functional

Table 4-9   Geochemical Processes Affecting the Fate of Polycyclic Aromatic Hydrocarbons (PAHs)

Compound[d]	Adsorption	Hydrolysis	Biodegra-dation	MCI K_{oc}	Tables
cenaphthene[a]	+	-	+D		
Acenaphthylene[a]	+	-	+D		
Fluorene[a]	+	-	+A		
Naphthalene	+	-	+D	y	5-5
Anthracene	+	-	+A	y	
Fluoranthene[a]	+	-	+A/N		
Phenanthrene[a]	+	-	+D	y	
Benzo(a)anthracene	+	-	+		
Benzo(b)fluoranthene[a]	+	-	+		
Benzo(k)fluoranthene[a]	+	-	+		
Chrysene[a]	+	-	+A/N		
Pyrene[a]	+	-	+D/N	y	
Benzo(ghi)perylene[a]	+	-	+		
Benzo(a)pyrene	+	-	+		
Dibenzo(a,h)anthracene[a]	+	-	+		
Indeno(1,2,3-cd)pyrene[a]	+	-	+		
Polychlorinated biphenyls[b]	+	-	+D/N[a]	y	
2-Chloronaphthalene[c]	-	-	+		

Key:
-    Not likely to be an important process.
+   Could be an important fate process.
?   Importance of process uncertain or not known.
(+)   Revised rating in relation to deep-well injection.
D   Significant degradation, rapid adaptation (aerobic).
A   Significant degradation, gradual adaptation (aerobic).
N   Not significantly degraded under the conditions of test method (aerobic).
y   Soil-adsorption coefficient (K_{oc}) calculated by Sablijić (1987) from molecular connectivity index.

[a]Based on information for PAHs as a group. Little or no information for specific compounds exists.

[b]Biodegradation is the only process known to transform PCBs under environmental conditions, and only the lighter compounds are measurably biodegraded.

[c]PCB-related compound.

[d]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981); Sabljić (1987).

groups for hydrogen in the structure. Amines are derivatives of ammonia and contain a nitrogen atom bonded to at least one carbon atom. Nitrosamines are amines with a nitro (-NO2) functional group; two are aliphatic (dimethylnitrosamine and di-n-propyl nitrosamine) and one is aromatic (diphenylnitrosamine). The two benzidines and 1,2-diphenyl hydrazine are aromatic amines. Acrylonitrile contains the nitrile (-CN) functional group. Table 4-10 indicates the importance of various processes to the fate of seven hazardous nitrogenous compounds (again note caveats in Section 4.3 about interpreting this information). Adsorption is a significant process for all four of the aromatic amines; hydrolysis is not. Compounds in the group are generally not amenable to biodegradation. Acrylonitrile, however, is readily mineralized by anaerobic denitrifying bacteria (see American Cyanamid case study, Section 7.3).

4.3.7 Pesticides

By definition, any pesticide has toxic effects on organisms. Listed pesticides are those which combine high toxicity with resistance to degradation in the environment. Moore and Ramamoorthy (1984b) review the behavior of chlorinated pesticides in natural waters.

Table 4-11 indicates the importance of various fate processes for 15 hazardous pesticides (note caveats in Section 4.3 about interpreting this information). Most of these pesticides are chlorinated hydrocarbons. Adsorption can be an important process for most. All except DDT, endosulfan, and heptachlor resist hydrolysis, and most are also resistant to biodegradation. Kearney and Kaufman (1972) review conditions under which chlorinated pesticides are biodegraded.

4.4 Locating Data on Specific Hazardous Substances

The very large number of hazardous organic and inorganic compounds precludes a detailed presentation of the characteristics of individual hazardous wastes. Data on standard physical and chemical properties of hazardous compounds are, however, available in a number of standard sources. Comprehensive data on the behavior of specific substances in the environment usually are more difficult to obtain. The first three sections below discuss available sources. Section 4.4.1 lists basic references for data on physical and chemical properties, Section 4.4.2

Table 4-10 Geochemical Processes Affecting the Fate of Nitrogenous and Miscellaneous Compounds

Compound[a]	Adsorption	Hydrolysis	Biodegradation	Tables
Dimethylnitrosamine	-	-	-	2-4
Diphenylnitrosamine	+	-	? D/A	2-4
Di-n-propyl nitrosamine	-	-	- N	2-4
Benzidine	+	-	?	2-4
3,3'-Dichlorobenzidine	++	-	-	2-4
1,2-Diphenylhydrazine (hydrazobenzene)	+	-	? T	2-4
Acrylonitrile	-	-	? D (An)	2-4

Key:

++   Predominant fate-determining process.
-   Not likely to be an important process.
+   Could be an important fate process.
?   Importance of process uncertain or not known.
(+)   Revised rating in relation to deep-well injection.
D   Significant degradation, rapid adaptation (aerobic).
A   Significant degradation, gradual adaptation (aerobic).
T   Significant degradation with gradual adaptation, followed by toxicity.
N   Not significantly degraded under the conditions of test method (aerobic).
(An)   Subject to anaerobic degradation (see Table 3-16).

[a]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981).

Table 4-11 Geochemical Processes Affecting the Fate of Pesticides

Compound[a]	Adsorption	Hydrolysis	Biodegradation	Tables
Acrolein	-	-	+ D	
Aldrin	+	-	? N (An)	2-6
Chlordane	+	-	? N	
DDD	+	-	- N	2-6
DDE	+	-	- N	
DDT	+	+	- N (An)	2-6, 2-7
Dieldrin	+	-(+)	- N	2-6, 2-7
Endosulfan and endosulfan sulfate	+	+	+ N	2-7
Endrin and endrin aldehyde	?	-	? N	
Heptachlor	+	++	- N	2-7
Heptachlor epoxide	+	-	? N	
Hexachlorocyclohexane[b]	+	-	+ N	
Isophorone	-	-	? D	
Tetrachlorodibenzodioxin	+	-	-	
Toxaphene	+	-	+	

Key:

++ Predominant fate-determining process.
- Not likely to be an important process.
+ Could be an important fate process.
? Importance of process uncertain or not known.
(+) Revised rating in relation to deep-well injection.
D Significant degradation, rapid adaptation (aerobic).
N Not significantly degraded under the conditions of test method (aerobic).
(An) May be degraded anaerobically (see Table 2-6).

[a]Additional data on all of these compounds can be found in Mabey et al. (1982). See description in Section 4.3 of sources for each column. Note that different sources may give different ratings.
[b]Includes lindane and alpha, beta, and delta isomers.

Sources: Callahan et al. (1979); Mills et al. (1985); Tabak et al. (1981).

identifies sources that may be turned to for up-to-date information on the environmental fate of specific substances, and Section 4.4.3 lists computerized databases that may be useful for either.

In many cases, specific or experimentally measured data are *not* available for the hazardous compound or compounds of interest; Section 4.4.4 therefore discusses using benchmark and structure-activity concepts to evaluate geochemical fate when data are unobtainable.

4.4.1 Basic References
The following is an annotated listing of basic references and computerized databases concerning physical and chemical properties of hazardous compounds.

Dangerous Properties of Industrial Materials, 6th Ed. (1984), edited by N. Irving Sax, Van Nostrand Rienhold, Co., 135 W. 50th St., New York 10020.

This book is a single source of concise data on the hazards of nearly 13,000 common industrial and laboratory materials. The main section, "General Information," gives synonyms, descriptions, chemical formulas, and physical constants.

The Merck Index, 10th Ed. (1983), Merck and Co., Rahway, New Jersey 07065.

This book is a comprehensive encyclopedia of chemicals, drugs, and biological substances with 9,856 listings. An extensive index and cross-index make it easy to use.

NIOSH/OSHA Pocket Guide to Chemical Hazards (1985), U.S. Government Printing Office, Washington, D.C. 20402

This pocket guide summarizes information from the three-volume *NIOSH/OSHA Occupational Health Guidelines for Chemical Hazards*. Data are presented in tables, and the source includes chemical names and synonyms, permissible exposure limits, chemical and physical properties, and other toxicological information.

OHMTADS: Oil and Hazardous Materials Technical Assistance Data System.

This source is a computerized data-retrieval system developed by EPA and accessible through EPA regional offices; it is available as a computer printout, manuals, or microfiches. A total of 126 possible information segments can be used to retrieve data on more than 1,000 oil-based and hazardous substances.

4.4.2 Sources of Information on Geochemical Fate

Callahan et al. (1979) summarize the results of a comprehensive literature search on the water-related fate of 129 priority pollutants as of 1979. Mabey et al. (1982) provide additional information on the same compounds. Additionally, Appendix B presents sources of information on the fate of a number of hazardous organic compounds. More than 50 scientific and trade journals are identified as having one or more articles of interest. Journals that most frequently contain papers relevant to deep-well geochemical fate assessment include *Environmental Science and Technology, Geochimica et Cosmochimica Acta, Ground Water, Water Resources Research,* and *Water Research.*

The following indexes and abstract series may be useful in obtaining additional and more recent references (drawn from Webster, 1987):

Biological Abstracts and Biological Abstracts/RRM. Philadelphia, Pennsylvania. Biweekly; published since 1926.

This source presents abstracts from 9,000 primary journals, monographs, symposia, reviews, reports, and other sources. The data base revision, BIOSIS PREVIEWS, is available through BRS and DIALOG from 1969 on.

Chemical Abstracts. Chemical Abstracts Service, American Chemical Society. Weekly; published since 1907.

The weekly issues include keyword and author indexes. Annual and collective indexes include author, general subject, chemical substance, formula, and ring-system indexes. The *Index Guide,* with its supplements, gives cross-references, synonyms, and other information for using the chemical-substance and general-substance indexes. The computerized counterpart, CA SEARCH, can be searched back to 1967.

Current Contents: Agriculture, Biology, and Environmental Science. Institute for Scientific Information. Weekly; published since 1970.

Each issue reproduces the table of contents of the latest issues of more than 100 journals and the contents of current books. A Title Work Index facilitates locating desired articles or books. The "Current Contents Address Directory, Science and Technology" provides addresses of authors currently publishing in these fields. Also, tear sheets or photocopies of most articles are available through a document-delivery service called "The Genuine Article."

Environment Abstracts. EIC/Intelligence. Monthly (bimonthly May/June, Nov/Dec); published since 1971.

This journal covers published studies such as conference papers, journal articles, and reports on all environmental aspects. Each issue has a review section followed by subject, industry, source, and author indexes. This journal also lists conferences and new books in print. *Environment Abstracts Annual* and *Environment Index* provide cumulative abstracts, and the *Index* also has a useful directory listing government and non-government organizations. The computerized counterpart, ENVIROLINE, is available through DIALOG and System Development Corp. (SDC) and can be searched back to 1971.

Pollution Abstracts. Cambridge Scientific Abstracts. Monthly; published since 1970.

This source presents abstracts and indexes for 2,500 publications worldwide on environmental pollution. The abstracts section is arranged under 10 major headings, each containing full citations and abstracts, followed by subject and author indexes. A cumulative index is prepared annually.

The computerized counterpart is available through BRS and DIALOG, from 1970.

Index to Scientific and Technical Proceedings. Institute for Scientific Information, Inc., published monthly, cumulated annually; published since 1978.

The main entry gives the complete bibliographic description of each proceeding with titles and authors of individual papers. An extensive subject index is also provided. Copies of papers may be available though the Institute's Original Article Text Service; a computer search service is also available.

Government Reports Announcements & Index. National Technical Information Service. Biweekly; published since 1965.

NTIS is a central source for U.S. government-sponsored research, development, and engineering reports and also for foreign technical reports. Documents cited are available in microform and paper. Report number, author, title, and other bibliographic information is followed by a brief abstract. Keyword, author, report number, and contact number indexes are prepared annually. The computerized counterpart can be searched back to 1964 and is available through BRS, DIALOG, and SDC. NTIS also offers 28 weekly abstract newsletters covering specific subject areas, the most pertinent being *Environmental Pollution and Control: An Abstract Newsletter.*

4.4.3 Computerized Databases
A large number of computerized databases can be used to obtain data or references providing data on specific hazardous substances. The review by Callahan et al. (1979) mentioned earlier searched 15 databases: AGRICOLA, APTIC, ASFA, BIOSIS, CHEM ABSTRACTS, COMPENDEX, DISSERTATION ABSTRACTS, ENERGYLINE, ENVIROLINE, EPB, NTIS, OCEANIC ABSTRACTS, POLLUTION ABSTRACTS, SCIESEARCH, and SSIE CURRENT RESEARCH. Many are available through government agencies. The *Directory of Online Data Bases* (Cuandra/Elsevier, New York, published quarterly since 1979) contains a master index and information on individual databases. The major private firms offering access to a variety of databases are SDC (telephone: 1-800-352-6689 in California; 1-800-421-7729 in the continental United States outside California), DIALOG (1-800-334-2564), and BRS (1-800-245-4277). Syracuse Research Corporation (1986) maintains several environmental-fate databases.

4.4.4 Benchmark and Structure-Activity Concepts
Where critical information is completely unavailable, two approaches have been developed to evaluate the fate of toxic chemicals in the environment: (1) the **benchmark** concept and (2) the **structure-activity** concept (Haque et al., 1980).

In the first approach, one or more benchmark chemicals are selected from important classes of toxic chemicals and their key environmental parameters and physicochemical properties are measured. These parameters are water solubility, vapor pressure, hydrolysis, soil degradation, adsorption, volatilization, photodegradation, and partition coefficient (Haque et al., 1980). (Vapor pressure, volatilization, and photodegradation are not significant in the deep-well environment.) The behavior of a new chemical or a known chemical for which data are unavailable can then be predicted based on its structural similarity to the benchmark.

The structure-activity approach assumes that certain properties and behaviors of compounds depend on chemical structure. The search for, and use of, quantitative structure-activity relationships (QSARs) to predict the behavior of organic chemicals is receiving increased attention in recent years, primarily in the fields of pharmacology and ecotoxicology. In an early application to environmental fate assessment, Wolfe et al. (1978) use structure-reactivity relationships to estimate hydrolytic persistence of carbamate pesticides. Nirmalakhandan and Speece (1988a) comprehensively review recent developments in the use of QSARs. In another paper, Nirmalakhandan and Speece (1988b) predict aqueous solubility of 200 environmentally relevant organic chemicals based on molecular structure.

Developments that may be particularly valuable for deep-well injection are topological models for biodegradation based on types of bonds and the modulus of the atomic-charge difference across the bonds (Deardon and Nicholson, 1986; as cited by Nirmalakhandan and Speece, 1988a), and the use of the molecular-connectivity index for predicting partition coefficients (Sabljić, 1984 and 1987) (see Section 5.2.2.1). Karickhoff (1984) provides equations for estimating K_{ow} with the addition of ring fragments for aromatic hydrocarbons and for the addition of functional groups.

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CHAPTER FIVE

METHODS AND MODELS FOR PREDICTING THE GEOCHEMICAL FATE
OF DEEP-WELL-INJECTED WASTES

5.1 Basic Approaches to Geochemical Modeling

The geochemical interactions possible between an injected waste and the reservoir rock and its associated fluids can be quite complex. Thus a combination of computer modeling, laboratory experimentation, and field observation will inevitably be necessary to satisfy current regulatory requirements for a geochemical no-migration petition. This chapter covers the computer methods and models available for predicting geochemical fate and includes the following topics:

■ Basic approaches to geochemical modeling, including:

— Model evaluation (Section 5.1.1)

— Model deficiencies (Section 5.1.2)

■ Specific methods and models, including:

— Computer codes for modeling aqueous and solution geochemistry (Section 5.2.1)

— Methods and models for predicting adsorption (Section 5.2.2)

— Quantitative and qualitative models for predicting biodegradation (Section 5.2.3)

— Equations for predicting hydrolysis (Section 5.2.4)

— Chemical transport modeling (Section 5.2.5)

Laboratory methods for geochemical fate assessment are covered in Chapter Six, and field methods are briefly discussed in Section 7.1 of Chapter Seven.

5.1.1 Model Evaluation
The American Society for Testing and Materials (ASTM, 1984) has developed a standard protocol for evaluating environmental chemical-fate models, along with defini-

tions of basic modeling terms, shown in Table 5-1. Predicting fate requires natural phenomena to be described mathematically. The expression of chemical fate can be computerized using a code (see computer-code definition in Table 5-1) to perform the computations and predict the results when inputs simulating conditions of interest are provided.

Two critical aspects of the use of computer codes for predicting geochemical fate are the verification and validation of the models on which the codes are based. In most cases, verifying geochemical codes (testing for internal consistency) is relatively straightforward. Validation studies, in which the model predictions are compared with empirical results, however, have been restricted mostly to simple or partial systems, and only qualitative validation was achieved. The limited number of validation studies raises serious questions regarding the reliability of thermodynamic data and the current understanding of geochemical processes occurring in the deep-well environment (Apps, 1988).

5.1.2 Model Deficiencies
In addition to the general lack of validation, some serious deficiencies remain (Apps et al., 1988):

■ The data on thermodynamic properties of many relevant water-miscible organic species are either incomplete or unavailable.

■ Many minerals are solid solutions (e.g., clays, amphiboles, and plagioclase feldspars). Solid-solution models either have not yet been developed or appropriate algorithms have not been incorporated into computer codes.

■ Models describing the adsorption of water-miscible organic compounds on natural materials are in the preliminary stages of development and have not been correlated with field observations under typical injection-zone conditions. Few computer codes contain algorithms for calculating the distribution of

Table 5-1	Definitions of Terms Used in Chemical-Fate Modeling
Term	**Definition**
Algorithm	The numerical technique embodied in the computer code.
Calibration	A test of a model with known input and output information that is used to adjust or estimate factors for which data are not available.
Computer code	The assembly of numerical techniques, bookkeeping, and control languages that represents the model from acceptance of input data and instruction to delivery of output.
Model	An assembly of concepts in the form of a mathematical equation that portrays understanding of a natural phenomenon.
Sensitivity	The degree to which the model result is affected by changes in a selected input parameter.
Validation	Comparison of model results with numerical data independently derived from experiment or observation of the environment.
Verification	Examination of the numerical technique in the computer code to ascertain that it truly represents the conceptual model and that there are no inherent numerical problems associated with obtaining a solution.

Source: ASTM (1984).

species between the adsorbed and aqueous states.

■ Calcium-sodium-chloride-type brines (which occur typically in deep-well injection zones) require sophisticated electrolyte models to calculate their thermodynamic properties. Many parameters for characterizing the partial molal properties of the dissolved constituents in such brines have not been determined. (Molality is a measure of the relative number of solute and solvent particles in a solution and is expressed as the number of gram-molecular weights of solute in 1,000 grams of solvent.) Precise modeling is limited to relatively low salinities (where many parameters are unnecessary) or to chemically simple systems operating near 25°C.

■ Current computer codes usually calculate only the thermodynamically most stable configuration of a system. Modifications can simulate nonequilibrium but there are limitations on the extent to which codes can be manipulated to simulate processes that are kinetically (rate) controlled: the slow reaction rates in the deep-well environment compared with ground-water movement (i.e., failure to attain local homogeneous or heterogeneous reversibility within a meter or so of the injection site) creates particular problems.

■ Little is known about the kinetics of dissolution, precipitation, and oxidation-reduction reactions in the

natural environment. Consequently, simulating the kinetics of even more complicated injection-zone chemistry is very difficult.

Bergman and Meyer (1982) point out a particularly relevant problem with mathematical models. The relative reliability of mathematical models (compared with physical [microcosm] models based on empirical field or laboratory studies) decreases rapidly as the number of environmental pollutants being modeled increases (see Figure 5-1). Consequently, mathematical models tend to be less cost effective for complex waste streams than are physical (empirical) models.

5.2 Specific Methods and Models

This section examines methods and models available to predict the processes discussed in Chapter Two. Most of the chemical processes discussed there (acid-base equilibria, precipitation-dissolution, neutralization, complexation, and oxidation-reduction) are interrelated, i.e., reactions of one type may influence other types of reactions, and consequently must be integrated into aqueous- and solution-geochemistry computer codes (see Section 5.2.1). Not all aqueous-geochemistry codes handle adsorption; methods for predicting adsorption are discussed in Section 5.2.2. Quantitative and qualitative methods for predicting biodegradation are discussed in Section 5.2.3. It is possible to predict hydrolysis reactions for hazardous wastes without complex computer codes; the necessary equations are

Figure 5-1   Relative Trade-offs Between Physical (Microcosm) and Mathematical Models as Affected by Effluent Complexity (Bergman and Meyer, 1982).
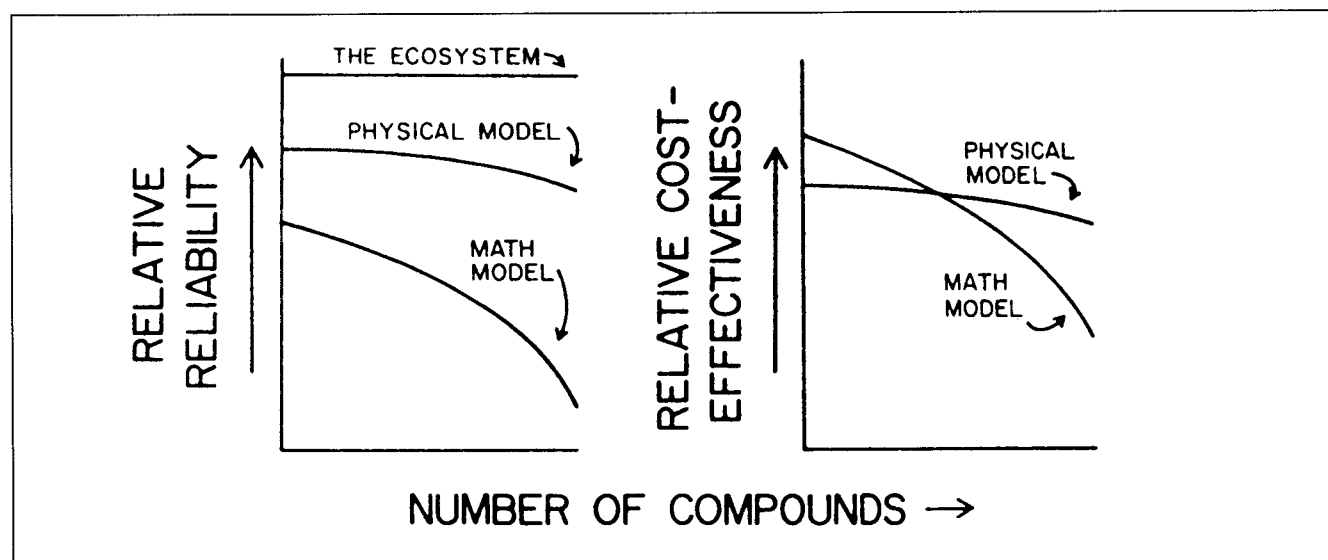
discussed in Section 5.2.4. A detailed examination of models and computer codes for predicting transport of chemicals in the deep-well environment is beyond the scope of this reference guide; nevertheless, they are discussed briefly in Section 5.2.5.

5.2.1 Aqueous- and Solution-Geochemistry Computer Codes

Between 1965 and 1979, more than 25 computer codes that calculate chemical equilibrium in natural waters or similar aqueous systems were described in the literature; between 1979 and 1984 the number more than doubled (Nordstrom and Ball, 1984). Most are not suitable for modeling the deep-well injection of hazardous wastes because they are limited to simulating reactions under one or more of the following conditions: (1) ambient temperatures (25°C), (2) low pressures (1 atmosphere), and (3) relatively low salinities.

When the simulation of deep-well temperatures, pressures, and salinities is imposed as a condition, the number of codes that may be of value is reduced to perhaps half a dozen (see Table 5-2). Other codes, however, may be useful for particular conditions and applications; the following systematic reviews discuss other codes that may be of value: Nordstrom et al. (1979), Anderson (1979), Nordstrom and Ball (1984), Kincaid and Morrey (1984), Sposito (1985), Schechter et al. (1985), Prickett et al. (1986), Carnahan (1987), and Mangold and Tsang (1987).

Nordstrom and Ball (1984) recommend the following six references as covering virtually all the mathematical, thermodynamic, and computational aspects of

chemical-equilibrium formulations: Wigley (1977), Van Zeggeren and Storey (1970), Smith and Missen (1982), Zeleznick and Gordon (1968), Wolery (1979), and Rubin (1983). For a basic understanding of the theory involved in the development of aqueous-electrolyte models, Apps (1988) recommends the following three references: Lewis and Randall (1961), Robinson and Stokes (1959), and Pitzer (1977).

Four types of computer codes are used to model aqueous geochemistry: (1) thermodynamic, (2) distribution-of-species, (3) reaction-progress, and (4) chemical-transport codes. The first three are discussed here. Transport codes that treat both geochemical reactions and transport of species in ground-water flow systems are discussed in Section 5.2.5.

5.2.1.1 Thermodynamic Codes

Thermodynamic codes are used to process empirical data so that thermodynamic data at a standard reference state can be obtained for individual species. They are used to estimate thermodynamic properties of the species of interest at the temperatures, pressures, and ionic concentrations being simulated. **Equations of state**, such as the HKF equation—named after its principal authors Helgeson, Kirkham, and Flowers (Tanger and Helgeson, 1988)—are used to perform these calculations. Assessing the fate of deep-well-injected wastes requires that accurate thermodynamic data be obtained for modeling aqueous electrolytes. The Debye-Hückel (D-H) equation predicts the activity coefficients of species in dilute solutions, but one of the following methods must be used to extend the range of applicability of this equation to higher salinities:

- The B-dot extension of the D-H equation

- The Davies equation

- Pitzer interaction parameter equation (Pitzer and Mayorga 1973).

All three are empirical equations that can be used to predict activity coefficients at high ionic concentrations. The first two equations are applicable up to 0.5 molal ionic concentrations (approximately 29,000 mg/L NaCl), and the third can be used for extremely high salinities (30 molal). Thermodynamic codes may be used separately to generate needed basic thermodynamic data or may be incorporated as subroutines of aqueous geochemistry codes. Table 5-2 lists two thermodynamic codes that may be useful when calculating thermodynamic data for geochemical modeling (several distribution-of-species codes incorporate such codes). Robie et al. (1978) summarize thermodynamic data for 133 oxides and 212 other minerals, including properties at higher temperatures, where available.

5.2.1.2 Distribution-of-Species Codes

Distribution-of-species codes, also called **equilibrium codes**, solve a simultaneous set of equations that describe equilibrium reactions and mass balances of the dissolved elements. The output of these equations is the theoretical distribution of the aqueous species for the dissolved elements. Most codes indicate the saturation state with respect to the solid phase, and many also include equations to describe ion exchange and simple linear adsorption. Two basic approaches are used to model species distribution: equilibrium constants and Gibbs free-energy minimization. The Gibbs free-energy approach has theoretical and computational advantages, but is limited by its lack of accurate and internally consistent thermodynamic data (Nordstrom et al., 1979). Consequently, most codes use the equilibrium-constant approach. One such is SOLMNEQ (see Table 5-2), which has been used by several researchers to simulate deep-well-injection geochemical interactions (Ehrlich et al., 1979; Roy et al., 1989). Van Luik and Jurinak (1979) also have used this approach, along with the cluster integral expansion theory of electrolyte-solution structure, to model the equilibrium chemistry of lead, cadmium, copper, and zinc in brines (2 to 6 molal) at temperatures in the 10° to 35°C range.

5.2.1.3 Reaction-Progress Codes

Reaction-progress codes, also called **mass-transfer codes**, calculate both the equilibrium distribution of aqueous species (as in distribution-of-species codes) and new compositions of the water as selected

minerals and compounds are precipitated or dissolved. The more sophisticated codes incorporate the reaction-path concept, in which incremental steps toward equilibrium are considered along a chosen path of mineral-water reaction. The most versatile and best-documented of this type of code for deep-well conditions is EQ3/6, developed at the Lawrence Livermore National Laboratory. PHREEQE, developed by the U.S. Geological Survey (USGS) has recently been modified to incorporate the Pitzer interaction equations (Crowe and Longstaffe, 1987; Plummer et al., 1988). ECES is a proprietary code with similar capabilities. See Table 5-2 for additional descriptions of these codes.

5.2.2 Adsorption

Mineral surfaces on which adsorption may occur are diverse and complex (see discussion of Reservoir Matrix, Section 3.1.4.2), and the mechanisms by which a hazardous constituent may attach to the solid surface vary substantially (see Section 2.2.2). Therefore, theoretical models that can be used readily to predict adsorption for a variety of compounds over a range of conditions are difficult to develop. Table 5-3 summarizes the applicability of three major methods for predicting adsorption in the deep-well environment. These methods include **adsorption isotherms**, the **clay ion-exchange model**, and the **triple-layer model.**

5.2.2.1 Adsorption Isotherms

The simplest and most widely used method for predicting adsorption is to measure **adsorption isotherms** (the variations in the amount of a substance adsorbed at different concentrations measured at a constant temperature). Empirical constants can be calculated from such measurements. (See Section 6.4.1, for a detailed discussion of methods.) The amount of adsorption at concentrations other than those which were measured can then be predicted using the empirical constants in an appropriate formula. The correct application of this method requires acknowledging such effects as matrix and temperature.

Three types of adsorption isotherms are discussed in this section: (1) the **linear distribution coefficient,** (2) the **Langmuir adsorption isotherm,** and (3) the **Freundlich adsorption isotherm.** The distribution coefficient assumes that adsorption is linear (i.e., the amount of adsorption is directly proportional to the concentration of the compound in solution) and is actually a special case of the Langmuir and Freundlich isotherms, which are nonlinear (Rao and Davidson, 1980).

Table 5-2   Aqueous- and Solution-Geochemistry Models of Potential Value for Modeling Deep-Well Injection

Name/Developer(s)	Description/Comments
Thermodynamic Codes	
SUPCRT Shock and Helgeson (1988,1990) Tanger and Helgeson (1988)	Can be used to calculate dissolution reaction constants at any specified temperature between $0°$ and $800°C$ and 1 to 5,500 bars.
PHAS20 Haas (1974) Haas and Fisher (1976)	Developed by USGS for thermodynamic calculations.
Distribution-of-Species Codes	
SOLMNEQ Kharaka and Barnes (1973)	Handles temperatures of $0°$-$350°C$, pressures from 1-1,000 bars, and salinities up to about 35,000 mg/L. It includes organic complexes and ion-exchange equilibria. The model was used by Ehrlich et al. (1979) and Roy et al. (1989) to simulate injected waste/reservoir interactions.
Reaction-Progress Codes	
EQ3/6 Walters and Wolery (1975) Wolery (1979) Wolery (1983) Jackson and Wolery (1985) Wolery (1986)	Handles temperatures of $0°$-$300°C$, and pressures of 1-500 bars. Earlier version handles salinities up to about 0.5 molal (~29,000 mg/L); latest version contains Pitzer interaction electrolyte model. Has been used to model geochemical evolution of Gulf Coast (Apps et al. 1988) and to simulate evolution of ground waters in basalt (Solomon, 1986). Most thoroughly documented of available models.
PHREEQE Parkhurst et al. (1980) Plummer et al. (1983) Plummer and Parkhurst (1985)	Temperature range is $0°$-$100°C$, at 1 bar up to about 0.5 molal. Has successfully modeled the evolution of ground water with the mineralogy of a limestone and dolomite aquifer in Florida.
PHRQPITZ Plummer et al. (1988)	Incorporates Pitzer interaction electrolyte model in PHREEQE for temperatures up to about $60°C$. Code has been partially validated in laboratory studies at $52°C$ and an ionic strength of 5.8-9.2 molar (personal communication, W. R. Roy, Illinois State Geological Survey, Champaign, Illinois, May 10, 1990).
ECES Scrivner et al. (1986)	Temperature range is $0°$-$200°C$; pressure range is 0-200 atm; ionic strength is 0-30 molal. It incorporates the Pitzer interaction electrolyte model for high salinities. It is a proprietary model licensed by OLI Systems, Morristown, New Jersey.

Sources: Nordstrom et al. (1979); Apps (1988); Plummer et al. (1988).

Table 5-3   Applicability of Methods and Models for Predicting Adsorption in the Deep-Well Environment

Method/Model	Applicability
Methods	
Adsorption isotherms	Relatively easy to measure. The main disadvantage is that the empirical coefficients may change with changing environmental conditions, requiring measurement.
Linear distribution coefficient	Applicable only at very dilute concentrations of organic compounds and where >0.1% organic matter is present. Usefulness is uncertain.
Langmuir	Underlying assumptions for the derivation of the equation typically will not apply.
Freundlich	Limited available data on adsorption under simulated deep-well conditions are best described by the formula; however, the disadvantage of all adsorption isotherms applies.
Models	
Clay ion-exchange model	May be useful for predicting adsorption of heavy metals. Aqueous-phase-activity solid-solution model coefficients can be obtained from distribution-of-species models. Estimating clay-phase activity coefficients is more problematic.
Triple-layer model	Of limited value because of the complexity of adsorption sites, unpredictable interactions among adsorbents, and complications introduced by high salinities.

Linear Distribution Coefficient. The simplest type of isotherm is the linear-distribution coefficient, K_d (Apps, 1988). It is also called the partition coefficient, K_p (Mills et al., 1985). The equation for calculating adsorption at different concentrations is:

$$S = K_d C \qquad [5\text{-}1]$$

where:

S = amount adsorbed (micrograms [μg]/g solid)

C = concentration of adsorbed substance in solution(μg/milliliter [mL])

K_d = distribution coefficient

This equation is widely used to describe adsorption in soil and near-surface aquatic environments. Another widely used linear coefficient is the organic-carbon partition coefficient (K_{oc}), which is equal to the distribution coefficient divided by the percentage of organic carbon present in the system ($K_{oc} = K_d$/% organic carbon), as

proposed by Hamaker and Thompson (1972). Sabljić (1987) presents very accurate equations for predicting the K_{oc} of both polar and nonpolar organic molecules based on molecular topology, provided the organic matter percentage exceeds 0.1%. Karickhoff (1984) discusses in detail adsorption processes of organic pollutants in relation to K_{oc} to adsorption processes of organic pollutants.

Winters and Lee (1987) describe a physically based model for adsorption kinetics for hydrophobic organic chemicals to and from suspended sediment and soil particles. The model requires determination of a single effective diffusivity parameter, which is predictable from (1) compound solution diffusivity, (2) octanol-water partition coefficient, and (3) adsorbent organic content, density, and porosity.

Major problems are associated with using the linear-distribution coefficient for describing adsorption/desorption reactions in ground-water systems. Some of these problems include:

■ The coefficient actually measures multiple processes (reversible and irreversible adsorption,

102

precipitation, and coprecipitation). Consequently, it is a purely empirical number with no theoretical basis on which to predict adsorption under differing environmental conditions or to give information on the types of bonding mechanisms involved.

- The waste-reservoir system undergoes a dynamic chemical evolution in which changing environmental parameters may result in variations of K_d values by several orders of magnitude at different locations and at the same location at different times.

- All methods used to measure the K_d value involve some disturbance of the solid material and consequently do not accurately reflect in situ conditions.

Apps et al. (1977) and Reardon (1981) discuss the problems in using distribution coefficients.

Langmuir Isotherm. The Langmuir equation was originally developed to describe adsorption of gases on homogeneous surfaces and is commonly expressed as follows:

$$C/S = 1/kS_{max} + 1/CS_{max} \qquad [5\text{-}2]$$

where:

S_{max} = maxmum adsorption capacity (μg/g soil)

k = Langmuir coefficient related to adsorption bonding energy (mL/g)

S = amount adsorbed (μg/g solid)

C = concentration of adsorbed substance in solution (μg/mL)

A plot of C/S versus 1/C allows the coefficients k and S_{max} to be calculated. When kC << 1, adsorption will be linear as represented by Equation 5-1.

The Langmuir model has been used to describe adsorption behavior of some organic compounds at near-surface conditions (Alben et al. 1988). However, three important assumptions must be made:

- The energy of adsorption is the same for all sites and is independent of degree of surface coverage

- Adsorption occurs only on localized sites with no interactions among adjoining adsorbed molecules

- The maximum adsorption capacity (S_{max}) represents coverage on only a single layer of molecules

In a study of adsorption of organic herbicides by montmorillonite, Bailey et al. (1968) found that none of the compounds conformed to the Langmuir adsorption equation. Of the 23 compounds tested only a few did not conform well to the Freundlich equation.

Freundlich Isotherm. The assumptions mentioned above for the Langmuir isotherm generally do not hold true in a complex heterogeneous media such as soil (Rao and Davidson, 1980). The deep-well environment is similarly complex and consequently the few studies of adsorption in simulated deep-well conditions (Donaldson and Johansen, 1973; Donaldson et al., 1975; Collins and Crocker, 1988) have followed the form of the Freundlich equation:

$$S = KC^N \qquad [5\text{-}3]$$

where S and C are as defined in Equation 5-1 and K and N are empirical coefficients. Taking the logarithms of both sides of Equation 5-3:

$$\log S = \log K + N \log C \qquad [5\text{-}4]$$

Thus, log-log plots of S versus C provide an easy way to obtain the values for K (the intercept) and N (the slope of the line). The log-log plot can be used for graphic interpolation of adsorption at other concentrations, or, when values for K and N have been obtained, the amount of adsorption can be calculated from Equation 5-3. Figure 5-2 shows an example of adsorption isotherms for phenol adsorbed on Frio sandstone at two different temperatures. (Note that when N = 1, Equation 5-3 simplifies to Equation 5-1 [i.e., adsorption is linear]). This simplified form is used by Lindstrom et al. (1971) to model transport of chemicals in saturated soils. However, Lindstrom et al. (1971) state that it is the most specialized and least generally applicable of the three mathematical models they developed.

Figure 5-2   Freundlich Isotherm for Phenol Adsorbed on Frio Core (Collins and Crocker, 1988).
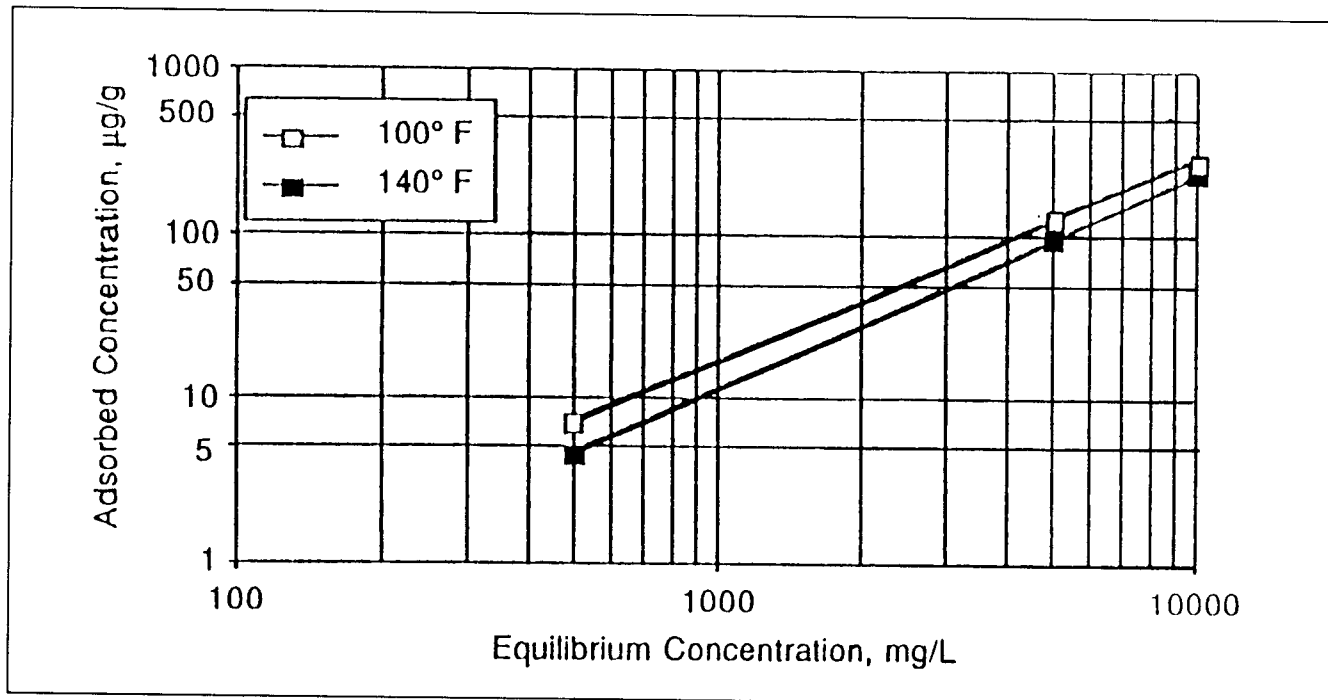
Weaknesses In Nonlinear Adsorption Isotherms.
The Langmuir equation has a strong theoretical basis, whereas the Freundlich equation is an almost purely empirical formulation because the coefficient N has embedded in it a number of thermodynamic parameters that cannot easily be measured independently (Apps, 1988). These two nonlinear isotherm equations have most of the same problems discussed earlier in relation to the distribution-coefficient equation. All parameters except adsorbent concentration (C) must be held constant when measuring Freundlich isotherms, and significant changes in environmental parameters, which would be expected at different times and locations in the deep-well environment, are very likely to result in large changes in the empirical constants. Alben et al. (1988) discuss sources of uncertainty and bias in experimental Langmuir and Freundlich isotherms.

Table 5-4 shows maximum measured values reported in three studies for adsorption of a variety of organic compounds tested at simulated deep-well temperature and pressure conditions. It illustrates variations that can occur among compounds adsorbed on the same geologic materials and variations that can occur for the same compound adsorbed on different geologic materials. Table 5-4 shows that the amount of adsorption at a given concentration for different organic compounds varies by a factor of 24 (50 milligrams per kilogram [mg/kg] for phenol to 1,200 mg/kg for n-hexylamine at 10,000 mg/L in the Cottage Grove Sandstone). Adsorption can also vary greatly for the same compound depending on the lithology of the

sample. For example, the amount of phenol adsorbed on the Cottage Grove and Frio formations differs by a factor of five at the same concentration level (10,000 mg/L) and the amount of 1,2-dichloroethane differs by a factor of two. Furthermore, adsorption of one compound, 1-butanol, differed by a factor of 10 (30 versus 300 mg/kg) on two separate experiments with the same rock formation.

An assumption implicit in most adsorption studies is that adsorption is fully reversible. In other words, once the empirical coefficients are measured for a particular substance, Equations 5-1 to 5-4 describe both adsorption and desorption isotherms. This assumption is not always true. The problem of irreversible adsorption is discussed in detail in Section 2.2.2.3. Collins and Crocker (1988) observed apparently irreversible adsorption of phenol in flowthrough adsorption experiments involving phenol interacting on a Frio sandstone core under simulated deep-well temperatures and pressures. If adsorption-desorption is not fully reversible, it may be necessary to use separate Freundlich adsorption- and desorption-isotherm equations to model these processes in the deep-well environment (Apps, 1988).

The most extensively studied adsorption-desorption phenomena have been related to the adsorption of pesticides on soils. A number of kinetic, equilibrium, and nonequilibrium models have been developed for pesticide-soil interactions (Van Genuchten et al.,

| Table 5-4 | Results of Adsorption Experiments with Organic Compounds at Simulated Deep-Well Conditions |

Lithology/ Compound	Temp. °C	Pressure (psi)	Concen- tration (mg/L)	Amount Adsorbed (mg/kg)	Source
Cottage Grove Sandstone[a]					
Phenol	66	2,940	10,000	55	Donaldson and Johansen, 1973
1-Butanol	66	2,940	5,000	300	*ibid.*
n-Hexylamine	66	2,940	10,000	1,200 [a]	*ibid.*
Butanal	66	2,940	10,000	175	*ibid.*
Cottage Grove Sandstone					
Phenol	60	3,000	10,000	50	Donaldson et al., 1975
1-Butanol	66	3,000	5,000	30	ibid.
n-Hexylamine	66	3,000	10,000	1,200 [a]	*ibid.*
1,2-Dichloroethane	60	3,000	5,000	300	*ibid.*
2-Butanone	60	3,000	5,000	60	*ibid.*
Crotonaldehyde	60	3,000	10,000	330	*ibid.*
1-Nitropropane	60	3,000	10,000	210	*ibid.*
Propylproponoate	60	3,000	1,500	55	*ibid.*
Pyridine	60	3,000	10,000	290	*ibid.*
Frio Sandstone					
Phenol	60	3,400	10,000	276	Collins and Crocker, 1988
1,2-Dichloroethane	38	3,400	5,000	150	*ibid.*

[a]Adsorption rate curves and Freundlich isotherm plots do not agree in either reference; value taken from the adsorption rate curve.

1974; Rao et al., 1979; Rao and Davidson, 1980). Unfortunately, little work has been done to evaluate their applicability to the deep-well environment.

5.2.2.2 Clay Ion-Exchange Model

As noted above, adsorption isotherms largely are derived empirically and give no information on the types of adsorption that may be involved. Scrivner et al. (1986) have developed an adsorption model for montmorillonite clay that can predict the exchange of binary and ternary ions in solution (two and three ions in the chemical system). This model would be more relevant for modeling the behavior of heavy metals that actively participate in ion-exchange reactions than for organics in which physical adsorption is more important (see Section 2.2.2)

The clay ion-exchange model assumes that the interactions of the various cations in any one clay type can be generalized and that the amount of exchange will be determined by the empirically determined cation-exchange capacity (CEC) of the clays in the injection zone (see Chapter Three, Table 3.2, for data on the CEC of various clay types). The aqueous-phase activity coefficients of the cations can be determined from a distribution-of-species code (see Section 5.2.1). The clay-phase activity coefficients are derived by assuming that the clay phase behaves as a regular solution (Garrels and Christ, 1965; Hildebrand et al., 1970) and by applying conventional solution theory to the experimental equilibrium data in the literature.

Scrivner et al. (1986) compared the ion-exchange model predictions with several sets of empirical data. The model predictions are very accurate for binary-

exchange reactions involving the exchange of nickel ions for sodium and potassium ions on illite and less accurate for ternary reactions involving hydrogen, sodium, and ammonia ions. The deep-well environment, however, is very likely to have multiple exchangeable species (such as Na^+, K^+, Ca^{+2}, and Mg^{+2}), and injected wastes commonly have elevated concentrations of more than one heavy metal (see Chapter One, Table 1-3). These concentrations result in complex ion-exchange interactions that probably exceed the capabilities of the model.

5.2.2.3 Triple-Layer Model

One of the more sophisticated models for describing adsorption phenomena in aqueous solutions is the **triple-layer model** (TLM), also called the Stanford General Model for Adsorption (SGMA) because it has been developed, refined, and tested over a number of years by faculty and researchers at Stanford University (Davis and Leckie, 1978, 1980; Kent et al., 1988). The TLM separates the interface between the aqueous phase and the adsorbent surface into three layers: surface layer, inner diffuse layer, and outer diffuse layer. Each has an electrical potential, charge density, capacitance, and dielectric constant. Hydrogen ions are assumed to bind at the surface plane; electrolyte ions (such as Na^+) bind at the inner diffuse plane. The surface is assumed to be coated with hydroxyl groups (OH^-) with each surface site associated with a single hydroxyl group. The hydroxyl-occupied surface sites may either react with other ions in solution or dissociate according to a series of reactions, with each having an associated equilibrium constant. Experimental terms relate the concentrations of the ions at their respective surface planes to those in the bulk solution. The sum of the charges of the three layers is assumed to be zero (i.e., the triple layer is electrically neutral). For all its sophistication, TLM currently is of limited value for predicting adsorption in deep-well environments (Apps, 1988):

■ Site-binding constants have been determined for only a limited range of simple oxides with only one type of surface site. Multiple-surface site minerals occurring in the deep-well environment such as silicates, aluminosilicates (e.g., feldspars), and complex oxides (such as manganese oxide) will require much more complex TLMs. Data adequate to characterize their behaviors do not exist.

■ Fixed-charge minerals such as clay are even more complex than the multiple-surface site minerals, and both ion exchange and other types of adsorption must be measured to characterize absorption reactions fully. Again, data are not available to predict adsorption by class over a

wide range of clay compositions and environmental conditions, and the outcome of studies to develop these data is uncertain.

■ Minerals with different adsorptive properties in the injection zone may interact to produce results different from those which would be obtained if each mineral were tested separately. No satisfactory model has been developed that predicts adsorption properties of mixtures based on the properties of individual adsorbents.

■ The TLM is based on laboratory measurements of adsorption on materials that are suspended in solution. No satisfactory methods for measuring and interpreting the adsorptive properties of intact host rock have been developed for TLM application.

■ The TLM has been developed using studies based on solutions of relatively low concentrations of dissolved compounds. The very saline and briny conditions found in the deep-well environment may require an entirely different model.

5.2.3 Biodegradation

This section examines two quantitative models for predicting biodegradation: the **kinetic rate expressions** (Section 5.2.3.1) and the **biofilm model** (Section 5.2.3.2). It also examines several qualitative models for describing biodegradation in the deep-well environment (Section 5.2.3.3).

5.2.3.1. Kinetic Rate Expressions

When microorganisms use an organic compound as a sole carbon source, their specific growth rate is a function of chemical concentration and can be described by the **Monod kinetic equation**. This equation includes a number of empirical constants that depend on the characteristics of the microbes, pH, temperature, and nutrients (Callahan et al., 1979). Depending on the relationship between substrate concentration and rate of bacterial growth, the Monod equation can be reduced to forms in which the rate of degradation is zero order with substrate concentration and first order with cell concentration, or second order with concentration and cell concentration (Paris et al., 1981).

The Monod equation assumes a single carbon source. The difficulty in handling multiple carbon sources, which are typical in nature, has led to the use of an empirical biodegradation rate constant k_B:

$$S = k_B C \qquad [5\text{-}5]$$

This equation is of the same form as Equation 5-1 for linear adsorption. Predicting biodegradation using such a rate constant is complicated when multiple biodegradable compounds are present. For example, phenol and naphthalene are both rapidly biodegraded in single-compound laboratory shake-flask experiments when seeded with bacteria from an oil-refinery settling pond, but when the two compounds are combined, naphthalene is not degraded until the phenol is gone (Bergman and Meyer, 1982).

When a compound is co-metabolized (degraded but not used as a nutrient), a second-order biodegradation coefficient can be used to estimate k_B:

$$k_B = k_{B2} B \qquad [5\text{-}6]$$

where k_{B2} is an empirical coefficient and B is the bacterial concentration. Mills et al. (1985) describe the use of these formulations to predict aerobic biodegradation in surface waters and present methods of adjusting for temperature and nutrient limitations. This approach to predicting biodegradation is problematic because it is difficult to obtain empirical coefficients in the deep-well setting.

Baughman et al. (1980) derive a second-order kinetic rate expression as a special case of the Monod kinetic equation. It appears to describe biodegradation of organics in natural surface waters reasonably well:

$$-d[C]/dt = k[B][C] \qquad [5\text{-}7]$$

Paris et al. (1981) found that degradation of several pesticides (2,4-DBE, Malthion, and CIPC) in samples from over forty lakes and rivers fits this second-order model of microbial degradation.

General degradation rate models of organics in soils have been described by Hamaker (1972), Goring et al. (1975), Hattori and Hattori (1976), Larson (1980), and Rao and Jessup (1982). In most instances, biodegradation is the major, but not necessarily the only, process affecting the rate of degradation.

5.2.3.2. Biofilm Model

The most sophisticated model available for predicting biodegradation of organic contaminants in subsurface systems is the **biofilm model**, presented by Williamson and McCarty (1976a,b) and refined over several years by researchers at Stanford University and the University of Illinois/Urbana (Rittmann et al., 1980; Rittmann and McCarty, 1980a,b; McCarty et al., 1981; Bouwer and McCarty, 1984; Chang and Rittmann, 1987a,b).

The biofilm model is based on two important features of the ground-water environment: (1) nutrient concentrations tend to be low, and (2) the solid matrix has a high specific surface area. These characteristics favor the attachment of bacteria to solid surfaces in the form of biofilms so that nutrients flowing in the ground water can be used (ZoBell, 1937; 1943). The presence of low nutrient levels in the ground water also implies that bacteria regularly must use many different compounds as energy sources and, consequently, may select organic contaminants more readily as nutrients (Bouwer and McCarty, 1984).

The basic biofilm model (Williamson and McCarty, 1976a,b) idealizes a biofilm as a homogeneous matrix of bacteria and the extracellular polymers that bind the bacteria together and to the surface. A Monod equation describes substrate use; molecular diffusion within the biofilm is described by Fick's second law; and mass transfer from the solution to the biofilm surface is modeled with a solute-diffusion layer. Six kinetic parameters (several of which can be estimated from theoretical considerations and others of which must be derived empirically) and the biofilm thickness must be known to calculate the movement of substrate into the biofilm.

Rittmann and McCarty (1980a,b) have developed equations for incorporating bacterial growth into the model, allowing the steady-state utilization of substrate materials to be predicted. They also show theoretically and verify experimentally that there is a substrate concentration threshold (S_{min}) below which no significant activity occurs (Rittman and McCarty 1981). McCarty et al. (1981) introduce the idea of secondary substrate utilization by a biofilm, in which microbes can metabolize trace compounds ($S < S_{min}$) in the presence of another substrate that is in sufficient concentrations to support biofilm growth. Bouwer and McCarty (1984) incorporate steady-state utilization of secondary substrates into the model by coupling the biofilm mass (controlled by degradation of the primary substrate) with concentration and individually determined rate parameters for each secondary substrate. Laboratory tests of degradation on a variety of chlorinated

benzenes, nonchlorinated aromatics, and halogenated aliphatics as secondary substrates agreed reasonably well with predicted values (Bouwer and McCarty, 1984). The most recent refinement of the model incorporates the effects of adsorption of material substrate to the surface on which the biofilm is attached, but is restricted to biofilms on activated carbon (Chang and Rittmann, 1987a,b).

When water containing substrate concentrations greater than S_{min} is injected into the subsurface, the model predicts that biofilm development will occur only in the first meter or so of the injection zone (Rittmann et al., 1980). Low concentrations of hazardous compounds will be significantly degraded as secondary substrates only if they are readily biodegraded in the biofilm zone. Any amount not biodegraded in the biofilm zone will tend to persist once it leaves the zone of concentrated biological activity. When substrate concentrations are not sufficient to sustain biofilm development, Bouwer and McCarty (1984) suggest that a simple biodegradation coefficient such as that discussed earlier (Equation 5-5) is probably adequate.

The biofilm model has not been applied to fate assessments of deep-well-injected hazardous wastes. Its greatest potential use for modeling degradation in the deep-well environment may be to predict the conditions under which excessive biofilm development might occur, with associated pore clogging. As noted elsewhere (Table 3-13), chemical treatment of injected fluids with biocides to reduce bacterial activity is a common practice. At the other extreme, highly acid or alkaline wastes can prevent bacterial growth entirely, or concentrations of a specific compound can inhibit bacterial growth through toxic effects. For example, Elkan and Horvath (1977) found that formaldehyde concentrations in a simulated injected waste significantly reduced biodegradation of acetate.

5.2.3.3. Qualitative Models

Several qualitative models for biodegradation in the deep-well environment have been suggested. They do not allow quantitative predictions to be made, but they do provide insight into the types of biodegradation processes that may occur. These models have not been expressed quantitatively to simulate degradation, although relatively simple codes using first-order biodegradation constants (k_B) could probably be developed without much difficulty. In the absence of quantitative models for predicting biodegradation, laboratory simulations must be used to assess biodegradation potential (see Section 6.4.3).

The conceptual geochemical model of acidic waste after injection into the subsurface, proposed by Leenheer and Malcolm (1973), involves a moving front of microbial activity (see Wilmington, North Carolina, case study, Section 7.5) with five zones as shown in Figure 5-3: (1) a dilute zone, controlled by diffusion, (2) a zone where substrate concentrations are sufficiently high to allow significant microbial activity, (3) a transition zone, where increasing waste concentrations create unfavorable conditions for microbial growth, (4) a neutralization zone, where abiotic chemical reactions predominate, and (5) a waste-storage zone where undiluted waste no longer reacts with the host rock. This model implies that the rate of injection far exceeds the zone's capacity for biodegradation.

Figure 5-3   **Proposed Geochemical Model of Waste after Injection into the Subsurface (Leenheer and Malcolm, 1973).**
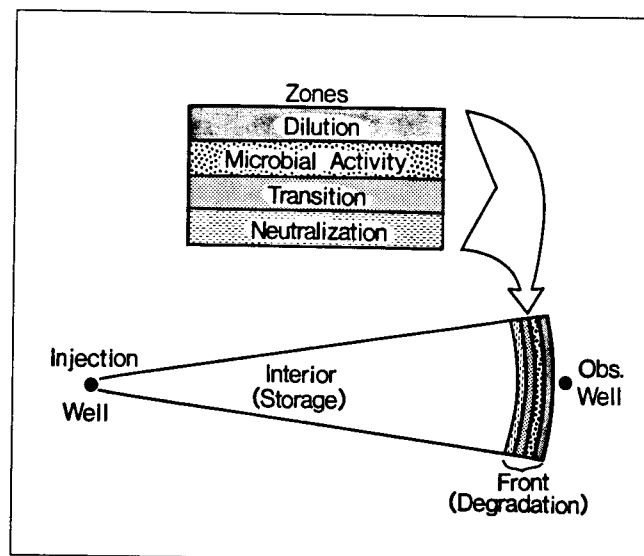
Bouwer and McCarty (1984) suggest a qualitative model that represents nonbiofilm microbial biodegradation over increasing distances from the injection point. This model follows the redox reaction sequence discussed in Section 2.3.4. Table 5-5 shows the progression that would occur as Eh declines with distance from the injection point and lists hazardous organic compounds that would be degraded most readily in each zone. This model implies that most compounds not degraded in their appropriate zone will move through the ground-water system without significant additional degradation. The model also implies, however, that those compounds which are biodegraded by methanogenesis will continue to move through the ground water until degradation is complete.

108

Table 5-5   Redox Zones for Biodegradation of Organic Micropollutants

Increasing Distance from Injection Point ⟶

Biological Conditions			
Aerobic heterotrophic respiration	Denitrification	Sulfate Respiration	Methanogenesis

Organic Pollutants Transformed			
Chlorinated benzenes Ethylbenzene Styrene Naphthalene	Carbon tetrachloride Bromodichloromethane Dibromochloromethane Bromoform (see also Table 3-16)	None specified (see Table 3-17)	C_1 and C_2 Halogenated aliphatics (see also Table 3-18)

Source: Adapted from Bouwer and McCarty (1984).

5.2.4 Hydrolysis

Hydrolysis (see Section 2.3.3) is easily predicted, provided that the rate constants for a compound are known. The rate of abiotic hydrolysis is given by:

$$R = -k_H C_T \qquad [5\text{-}8]$$

where:

R = the rate of hydrolysis, mole liter^{-1} sec^{-1} or µg liter^{-1} sec^{-1}

k_H = specific hydrolysis rate constant, sec^{-1}

C_T = the dissolved plus adsorbed phase concentration of compound C, mole liter^{-1} or µg liter^{-1}

The hydrolysis rate constant, k_H, is actually the sum of three rate constants:

$$k_H = k_n + k_a[H^+] + k_b[OH^-] \qquad [5\text{-}9]$$

where:

k_n = the neutral hydrolysis rate constant for the pH-independent reactions of a chemical with water, sec^{-1}

k_a = the acid-catalyzed hydrolysis rate constant, liter mole^{-1} sec^{-1}

$[H^+]$ = the concentration of hydrogen ion, mole liter^{-1} ($[H^+] \simeq 10^{-pH}$)

k_b = the base-catalyzed hydrolysis rate constant, liter mole^{-1} sec^{-1}

$[OH^-]$ = the concentration of hydroxide ion, mole liter^{-1} ($[OH^-] \simeq 10^{[pH-14]}$)

Note that in an acid solution, $k_b = 0$, and in an alkaline solution, $k_a = 0$. K_H can be adjusted to include the effects of adsorption by multiplying ($k_a[H^+] + k_b[OH^-]$) times the decimal fraction of the total amount of a dissolved compound, C (Mills et al., 1985). At any fixed pH, the half-life of a substance is independent of concentration and can be calculated with the equation:

$$t_{1/2} = 0.693/k_H \qquad [5\text{-}10]$$

Hydrolysis is strongly pH-dependent, with k_a dominant at low pH and k_b dominant at high pH; at pH 7, k_n can often be most important. However, the detailed relationship of pH and rate depends on the specific values of k_n, k_a, and k_b. If these rate constants are known, then the hydrolysis rate at any pH can be readily calculated. Mabey and Mill (1978) provide these data

for a large number of organic compounds, and El-lington et al. (1986, 1987, 1988) provide data on about 70 regulated hazardous pollutants.

Wolfe et al. (1978) use structure-reactivity relationships to estimate hydrolytic persistence of carbamate pesticides. Perdue and Wolfe (1983) develop a mathematical model based on application of the Brönsted equations for general acid-base catalysis, used to forecast the maximum contribution of buffer catalysis in pollutant hydrolysis reactions. They conclude that at the low concentrations of Brönsted acids and bases in most aquatic environments, buffer catalysis is probably insignificant.

Mills et al. (1985) describe step-by-step procedures for calculating k_H, and Scrivner et al. (1986) describe in detail the modeling of cyanide and nitrite hydrolysis in the deep-well environment.

5.2.5 Chemical Transport
It is beyond the scope of this reference guide to discuss chemical-transport models in detail, but basic approaches and important models will be addressed briefly. Currently three major approaches can be used to modeling chemical transport:

■ **Retardation-factor models**, which incorporate a simple retardation factor derived from a linear- or linearized-distribution coefficient.

■ **Integrated models**, in which all mass, momentum, and energy-transfer equations, including those in which chemical reactions participate, are solved simultaneously for each time step in the evolution of the system.

■ **Two-step models**, which first solve mass momentum and energy balances for each time step and then reequilibrate the chemistry using a distribution-of-species code.

Empirically determined retardation factors (either partition coefficients as discussed in Section 5.2.2.1 or breakthrough curve measurements, which are the change in solute concentration measured over time in laboratory or field experiments) have been widely used because of their inherent simplicity (Javandal et al. 1984). Modeling of specific geochemical partition and transformation processes is not necessary if the retardation factor can be determined empirically.

The problems with linear-distribution coefficients discussed in Section 5.2.2.1 apply equally to any retardation factor derived from them. Field measurements can be made but are expensive to obtain and highly site specific. Nevertheless, retardation factors provide some

insight into organic chemical transport. Winters and Lee (1987), in a study of mobility of chlorobenzene, naphthalene, and 4-chlorobiphenyl in ground-water discharge to a sandy stream bed, found that the measured retardation of these compounds generally agreed with that predicted using K_{ow}s and the organic carbon content of the sediment material. However, the large amount of tailing observed in the organic-tracer breakthrough curve resulted in center-of-mass retardation factors up to about two times greater than peak-to-peak retardation factors. This discrepancy underscores the importance of understanding the tailing phenomena in the field before retardation factors are used for modeling (Winters and Lee 1987).

Integrated and two-step chemical-transport models incorporate distribution-of-species or reaction-progress codes into hydrologic transport codes. The few studies in which the two approaches have been tested using the same set of field data have agreed reasonably well; thus one approach does not have an obvious advantage over the other. The two-step approach tends to be computationally less intensive than the integrated approach but may have difficulty maintaining mass balance when rapid precipitation and dissolution occur (Apps, 1988).

Tables 5-6 and 5-7 present a number of models of both types that have been described in the literature. Of the models listed in these tables, DYNAMIX would appear to have the greatest potential for use in simulating chemical transport in the deep-well environment because it incorporates the reaction-progress code PHREEQE, which can handle deep-well temperatures (see Table 5-2). PHREEQE, however, does not incorporate pressure equilibria.

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*References with more than six authors are cited with "et al."

Table 5-6   Integrated Ground-Water Chemical-Transport Models

Developers	Description/Comments
Rubin and James, 1973	Simulates heterovalent ion exchange and changing concentrations of pore-fluid ions in one-dimensional flow.
Vallochi et al., 1981 Vallochi, Roberts, and Street, 1981	Simulates multispecies heterovalent ion exchange under conditions of varying total solution concentrations.
Jennings et al., 1982 Miller and Benson, 1983	Multicomponent equilibrium chemistry in ground water.
Noorishad and Carnahan, 1985 Carnahan, 1986 Noorishad et al., 1987 Carnahan, 1987	CHMTRN includes dispersion/diffusion, advection,adsorption of ions and complexes, aqueous complex formation, and dissociation of water. THCC is a variant that simulates uranium transport with variable temperature and oxidation potential. Latest version is called CHMTRNS and can simulate in one dimension both homogeneous aqueous-phase and heterogeneous temperature-dependent reaction kinetics. Has been applied to a number of simple problems involving both reversible and irreversible dissolution and oxidation-reduction reactions. Has not been tested with complex multicomponent systems.

Source: Apps (1988).

Table 5-7   Two-Step Ground-Water Chemical-Transport Models

Developers	Description/Comments
Grove and Wood, 1979 Reardon, 1981	Solved the nonreacting advective-dispersive transport equation.
Walsh et al., 1982	Uses distribution-of-species code by Morel and Morgan (1972).
Cederberg et al., 1985	TRANQL incorporates distribution-of-species code MICROQL (Westall et al., 1976). Modeling of ion-exchange reactions in artificial recharge in Palo Alto Baylands project yielded the same results as the one-step analysis by Valocchi et al. (1981).
Kirkner et al., 1984, 1985	Models multicomponent solute transport with adsorption and aqueous complexation.
Huyakorn et al., 1983	SATURN incorporates distribution-of-species code MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985).
Narasimhan et al., 1986 Liu and Narasimhan, 1989a,b	DYNAMIX combines the transport code TRUMP (Edwards, 1972) with distribution-of-species code PHREEQE (Parkhurst et al., 1980). Most recent version handles thermodynamics of hydrolysis, aqueous complexation, redox reactions, and precipitation-dissolution. Field-tested by White et al. (1984). Comparison of predicted and laboratory-column uranium transport with one-step code THCC yielded similar results.

Source: Apps (1988).

111

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CHAPTER SIX

FIELD SAMPLING AND LABORATORY PROCEDURES AND PROTOCOLS

6.1 Overview

Laboratory procedures for geochemical-fate assessments of deep-well-injected wastes can be classified into two categories: (1) routine chemical and physical analyses that characterize the waste and reservoir rock (quantities and types of different constituents), and (2) laboratory studies that simulate the geochemical processes in the injection zone. The first type of procedures can be used to identify the types of processes that are likely to be important. They also provide data on basic parameters of the deep-well injection system for hydrologic and geochemical modeling. The second type may help predict how one or more processes will operate in the deep-well environment and may be necessary for verifying the results of geochemical modeling. In the absence of geochemical models, laboratory studies can provide empirical data on specific geochemical processes and their interactions. This chapter provides an overview of these procedures with references for additional information.

6.1.1 Chapter Organization

Section 6.2 (Waste-Reservoir Characterization) lists the physical and chemical properties that may require measurement before the wastes, reservoir rock, and reservoir fluids can be characterized.

Section 6.3 (Waste-Reservoir Interaction Tests) examines the various methods for testing the compatibility of wastes and injection-zone materials and for testing the geochemical interactions among wastes, reservoir rock, and fluids. The types of tests reported in the published literature are also summarized in this section.

Section 6.4 (Geochemical Processes) briefly discusses methods for measuring adsorption and rate constants for chemical transformations, such as hydrolysis and the biodegradability of organic wastes.

Section 6.5 (Quality Assurance/Control Procedures) presents procedures used in sampling and laboratory tests that ensure data reliability.

Section 6.6 (Annotated Bibliography) summarizes references that contain detailed guidance in sampling methods, analytic protocols, and interpretation of results, and tells how to obtain these documents. The listings in this section are also indexed by topic (see Table 6-9).

The references included in this chapter are likely to be useful in a wide variety of situations because (1) they have been cited most frequently in the literature on deep-well injection, and (2) many describe methods designed specifically for use with hazardous wastes and/or deep-well injection.

6.1.2 Selecting Sampling Methods and Laboratory Procedures

Because of the variety of hazardous wastestream compositions and the number of possible variations in the lithology and brine chemistry of the injection zone, no single set of sampling methods and laboratory protocols can cover all situations. For certain parameters, more than one analytic method and more than one standard procedure may be available. For example, procedures recommended by the American Public Health Association (APHA), the American Society for Testing and Materials (ASTM), and the U.S. Geological Survey (USGS) for measuring total dissolved solids all differ slightly (Hem, 1970). Moreover, some state regulatory agencies have their own protocols.

Given the multiplicity of laboratory procedures and protocols, the following steps are suggested for selecting the appropriate methods. The tables referred to are presented in later sections and discussed in detail.

1.   **Select Parameters.** Identify the physical and chemical parameters of the waste and reservoir solids and fluids to be measured. Table 6-1 lists basic parameters for characterizing wastewater. Important physical properties of reservoirs are listed in Table 6-2, methods for

analyzing reservoir rock in Table 6-3, and chemical properties of reservoir rock and fluids in Table 6-4. The greatest judgment will be required in selecting chemical parameters representing reservoir fluids because of the large number of species that may be present in these fluids. Table 6-5 provides guidance in classifying dissolved species, and Table 6-6 indicates species that might be important in different geologic settings. Pay particular attention to dissolved species of possible significance in assessing the reactivity of barium, calcium, iron, magnesium, aluminum, and manganese with injected wastes (see Table 6-5).

2. **Select Laboratory Methods for Measuring Parameters.** Procedures for measuring basic physical and chemical parameters are well-established, although, as noted, different sources may specify slightly different procedures. Consult the U.S. EPA and/or the state regulatory agency to identify preferred analytic procedures for the specific parameters. If specific procedures are not indicated, consult the regulatory agency to determine whether established procedures with which you are familiar are acceptable. Tables 6-2 (reservoir physical properties), 6-3 (methods for chemical analyses), 6-4 (reservoir-fluid chemical properties), and 6-7 (subsurface microbial characterization) list available analytic methods and references with detailed descriptions of laboratory procedures. Additional references may be located using Table 6-9 (annotated bibliography index).

3. **Select Laboratory Methods for Testing Waste-Reservoir Compatibility.** Evaluate waste-reservoir compatibility before undertaking any other geochemical studies. In the worst case, incompatibility may make deep-well injection unfeasible (see the Wilmington, North Carolina, case study, Section 7.5). In other instances, incompatibility can be handled by injecting incompatible waste streams separately or by pretreating the waste stream to improve compatibility (see Texas Petrochemical case study, Section 7.7). Section 6.3 discusses water-reservoir interaction tests in some detail, and Table 6-8 summarizes 14 such studies. The Annotated Bibliography in Section 6.6 indicates which references provide descriptions of laboratory methods.

4. **Select Laboratory Methods for Other Geochemical Fate Studies.** Laboratory waste-reservoir

interaction tests discussed in Section 6.3 may be useful for other aspects of assessing the geochemical fate of injected wastes. Also, Section 6.4 discusses a number of laboratory procedures for studying chemical transformation processes.

6.2 Waste/Reservoir Characterization

Characterizing the wastes and the reservoir into which they are injected requires measuring numerous parameters. The following sections summarize key parameters that may need to be measured in each of the following areas:

■ Waste stream (Section 6.2.1)

■ Reservoir lithology (Section 6.2.2)

■ Formation water (Section 6.2.3)

■ Microbiology (Section 6.2.4)

6.2.1 The Waste Stream
A large number of parameters need to be measured to characterize a waste stream. Table 6-1 lists more than 30 parameters in five categories: (1) waste volume, (2) physical properties, (3) chemical composition, (4) chemical reactivity, and (5) biological characteristics.

■ **Waste volume** is an important measure because of limitations on the physical capacity of the reservoir rock to accept wastes without unacceptable increases in pressure.

■ **Physical properties** affect the flow of injected wastes in the subsurface. For example, temperature, density, and viscosity influence mixing processes in the reservoir fluid. In the Belle Glade case study (Section 7.4), the higher temperature and lower relative density of the waste compared with those of the reservoir fluid accelerated the upward migration of the waste to a shallower aquifer after the confining layer was breached. Also, the type and form of solids and gases dictate the types of pretreatment that can be used to reduce plugging potential.

■ **Chemical composition** influences reactivity (see below) and the kinds of geochemical processes that may occur. Whether the waste is classified as hazardous or nonhazardous will determine which sets of injection regulations apply.

■ **Chemical reactivity** influences the design of the injection well in several ways. Corrosivity and

120

Table 6-1 Basic Parameters for Characterizing Wastewater

I. Volume
Average daily flow rate
Duration and level of maximum flow rate
Maximum rate of change of flow rate

II. Physical Properties
Temperature range
Insoluble components: colloidal, settleable, floatable
Color and odor
Viscosity, density, compressibility
Radioactivity
Foamability
Dissolved oxygen

III. Chemical Composition
Known organic and inorganic components
Chemical oxygen demand, total carbon, extractables
pH, Eh, acidity, alkalinity
Oxidizing or reducing agents (sulfides)
Chloride ion
Hardness (calcium and magnesium)
Nitrogen and phosphorus
Surfactants
Chlorine demand
Total dissolved solids
Specific ions (see Tables 6-5 and 6-6)
Phenol
Grease and hydrocarbons

IV. Chemical Reactivity
Corrosiveness
Chemical stability
Reaction with injection-system components
Reaction with formation waters
Reaction with formation minerals

V. Biological Characteristics
Biochemical oxygen demand
Pathogenic bacteria
Chemical toxicity (aquatic life, bacteria, plants, humans)

Source: Adapted from Tables 5-1 and 5-5 in Warner and Lehr (1977).

chemical stability (see Section 1.1.3) influence the choice of materials. Incompatibility between the waste and the injection system's components, formation waters, and formation minerals (which can cause precipitation, gas bubbles, etc.) must be identified and corrected to ensure proper functioning (see Section 3.3 and Section 6.3). Watkins (1954) describes procedures for corrosion testing.

■ **Biological characteristics** will determine the extent to which microbial action may cause clogging and whether biodegradation may be significant as injected wastes move through the injection zone (see Sections 6.2.4 and 6.4.3).

Several EPA documents describe sampling methods for wastes (deVera, 1980; Ford et al., 1984). A number of tests and methods are required to measure specific waste-stream parameters. Comprehensive compilations have been developed by Longbottom and Lichtenberg (1982), Kopp and McKee (1983), APHA (1985), and ASTM (1966; annual).

6.2.2 Reservoir Lithology
Both physical and chemical properties of the injection formation and confining layer must be measured to characterize the lithology of the reservoir. Warner and Lehr (1977) discuss field sampling methods for rock from coreholes. Hewitt (1963) discusses methods to evaluating water sensitivity of reservoir rocks.

6.2.2.1 Physical Properties
Table 6-2 summarizes the physical properties of the formation rock that must be identified before the fate of wastes can be evaluated. Two types of parameters are listed in this table—those which affect the chemical reactivity of the host rock and those which affect the physical flow of injected wastes. Warner and Lehr (1977) discuss the significance of and methods for measuring or estimating values for those physical properties that primarily affect the physical flow of injected wastes: porosity, bulk density, permeability, compressibility, temperature, and stress. Chemical reactivity of the host rock is influenced in part by the physical parameters of texture (particle-size distribution) and specific surface area. Specific surface area influences the amount of mineral surface available for rock-fluid chemical interactions. Specific surface area increases, from sand to silt to clay particle-size fractions. Porosity and permeability influence chemical reactivity by determining the extent to which fluids can reach available surfaces. Geochemically, **effective porosity**, the amount of interconnnected pore space available for fluid transmission, is more important that total porosity, because it is the effective porosity that determines the amount of matrix surface available for rock-fluid chemical reactions. Thus shale has a very high surface area because it is composed of clay particles, but its low permeability means that little fluid can flow into the rock to allow chemical reactions to

Table 6-2   Physical Properties of Reservoirs Important in Deep-Well Geochemical Fate Assessment

Property	References on Analytic Procedures
Rock	
Texture (particle-size distribution)	Klute, 1986
Porosity	Warner and Lehr, 1977 Collins and Crocker, 1988
Bulk density	Klute, 1986
Specific surface area	Klute, 1986
Permeability	Warner and Lehr, 1977
Compressibility	Warner and Lehr, 1977
Temperature	Warner and Lehr, 1977
Stress	Warner and Lehr, 1977
Reservoir Fluid	
Viscosity	Warner and Lehr, 1977
Density (specific gravity)	Warner and Lehr, 1977 Hem, 1970
Fluid pressure	Warner and Lehr, 1977 Kreitler et al., 1988
Compressibility	Warner and Lehr, 1977

take place. Section 3.1.4 discusses the importance of particle-size distribution.

6.2.2.2 Chemical Properties

The mineralogy of the reservoir rock determines the important chemical properties and strongly influences the ion-exchange and adsorption capacity of the injection zone. Clay mineralogy is especially important because of the possible significance of clays in well plugging (see Section 3.3.1) and the major role of clays in adsorption. Section 3.1.4 (Reservoir Matrix) discusses the geochemical significance of clays and other minerals. Table 6-3 summarizes major laboratory methods used to investigate reservoir rocks, including mineral identification and measurement of adsorption

properties. Section 6.3 discusses laboratory methods for determining waste-rock adsorption interactions.

6.2.3 Formation Water

Scalf et al. (1981), Berg (1982), and Barcelona et al. (1985) describe methods for collecting ground-water samples. In deep-well formations, samples must be collected carefully to minimize the chemical changes that can occur when the sample is brought to the surface. For example, ferrous ion (Fe^{+2}) in solution is unstable in the presence of oxygen, and carbonates and bicarbonates are particularly susceptible to equilibrium shifts if samples are stored in plastic bottles because of carbon-dioxide diffusion (Scalf et al., 1981). Gases dissolved at deep-well pressures will be lost when brought to the surface unless samples are isolated from the atmosphere. Rose and Long (1988) review ground-water sampling methods as they apply to collecting dissolved oxygen. Sampling for other gases would require similar measures.

6.2.3.1 Physical Properties

Warner and Lehr (1977) discuss the significance of physical properties as they relate to reservoir fluids in the injection zone and methods for measuring and estimating these properties (see Table 6-2). As noted in Section 6.2.1, these properties are primarily significant in the mixing process between formation water and injected waste. Fluid pressure, combined with the physical parameters discussed in Section 6.2.2 will determine pumping pressures. Kreitler et al. (1988) describe methods for evaluating formation pressures (see also Section 3.1.5).

6.2.3.2 Chemical Properties

Table 6-4 lists chemical properties required to characterize fully the range of formation fluids that may be found in injection zones. Such properties as pH, Eh, and total dissolved solids strongly influence the geochemical processes that may occur in the deep-well environment. Ostroff (1965) and Collins (1975) discuss sampling of deep formation waters and which constituents to analyze. Table 6-4 also lists the section in this reference guide where a detailed discussion of specific parameters can be found and presents references on analytic procedures for each. Note that not all the parameters listed in Table 6-4 must be determined for all formation fluids; for example, oxygen and hydrogen radioisotope analysis would be required only if the approximate age of the water is desired (Kreitler et al., 1988).

The dissolved species that should be analyzed may also vary depending on geologic conditions. The species present and their concentrations will influence distribution-of-species and precipitation-dissolution reactions with

122

Table 6-3	Chemical Analysis Methods for Reservoir Rock	
Property	**Method**	**Sources on Methods**
Mineralogy	X-ray diffraction Chemical component analysis Microscopic identification (thin sections, heavy minerals) Scanning electron microscopy	Kerr, 1959 Bentley et al., 1986
Clay mineralogy		Carroll, 1970; Grim, 1968
Ion exchange	Cation-exchange capacity	Page et al., 1986
Adsorption	Adsorption isotherms	Collins and Crocker, 1988 Roy et al., 1987
	Calorimetry	Collins and Crocker, 1988
	X-ray diffraction	Carroll, 1970; Grim, 1968
	Spectroscopy UV-visible Electron Spin Resonance (ESR) Infrared (IR)	Skoog, 1985 Mortland, 1970; Theng, 1974

Table 6-4	Chemical Properties of Reservoir Fluids Important in Deep-Well Geochemical Fate Assessment	
Property	**Sources for Analytic Procedures**	**Reference Guide Section No.**
General Chemical Properties		
pH	Barnes, 1964; Kreitler et al., 1988	3.1.1
Eh	Wood, 1976; ZoBell, 1946	3.1.2
Conductivity	Hem, 1970	3.1.3
Alkalinity	Barnes, 1964	3.1.1
Total dissolved solids	ASTM, annual; APHA, 1985; Rainwater and Thatcher, 1960	3.1.3
Inorganic Parameters		
Dissolved inorganic species[a]	ASTM, annual; APHA, 1985; Rainwater and Thatcher, 1960	6.2.3.2
Radioisotopes (oxygen, hydrogen)	Kreitler et al., 1988	6.2.3.2
Organic Parameters		
Dissolved organic carbon (DOC)	Malcolm and Leenheer,1973	3.1.4.3
Total organic acids	APHA, 1985; Kreitler et al., 1988	6.2.3.2
Titrated organic alkalinity	*ibid.*	
Microbiota	American Petroleum Institute, 1965	6.2.4

[a]See Table 6-5.

injected wastes. Dissolved species in formation water can be organized into four categories: (1) cations, (2) anions, (3) gases, and (4) organic acids. Table 6-5 identifies the species that may be present. Within each category, species are ranked according to abundance (major, intermediate, and minor). The table also indicates species of importance in evaluating the reactivity of the reservoir fluids with injected wastes (i.e., when precipitation reactions are a concern).

The presence of dissolved species in reservoir fluids is site-specific. Available hydrogeochemical data for the region and the formations of interest should be evaluated before selecting the species to be analyzed in samples from a potential injection zone. Table 6-6 shows chemical analyses, species analyzed, and concentrations measured in five published studies on reservoir fluids in the injection zones; these studies may provide some guidance in selecting species. The data from Wilmington, North Carolina, are from coastal-plain sediments where injection is no longer practiced (see Section 7.5). The data from Pensacola and Belle Glade, Florida, are from coastal-plain carbonate deposits (see Sections 7.2 and 7.4). The Marshall sample was taken from a Devonian limestone in the Illinois Basin (see Figure 3-1 in Chapter Three). The Frio formation in Texas is an unconsolidated sand that receives more injected wastes than any other formation in the United States.

Deep-well-injection-zone formation fluids are under pressure, leading to difficulties measuring some of their chemical parameters. For example, pH measurements of deep basinal brines have always been considered unreliable because CO_2 degasses when the sample depressurizes as it rises in the well bore or comes in contact with the atmosphere (Kreitler et al. 1988). Kreitler et al. (1988) discuss how titrated inorganic alkalinity can be used to estimate pH in this situation. Sampling techniques that capture any gases passing out of

Table 6-5   Classification of Dissolved Species in Deep-Well Formation Water

Abundance[a]	Cations	Anions	Gases	Organic Acids
Major	Sodium Calcium[b] Magnesium[b]	Chloride Bicarbonate[b] Sulfate[b]	Carbon dioxide	Acetate Propionate
Intermediate	Silica[b] Barium[b] Potassium Strontium Boron Iron[b]	Nitrate Nitrite Orthophosphate Bromide Iodide	Nitrogen Hydrogen Sulfide[b] Methane	Butyrate
Minor	Aluminum[b] Manganese[b] Arsenic Beryllium Cadmium Chromium Cobalt Copper Lead Lithium Molybdenum Nickel Selenium Zinc	Fluoride		

[a]Abundance classification criteria (mg/L): Major: 10^3-10^5; Intermediate: 10^1-10^3; Minor: $<10^1$.
[b]Of possible special significance in assessing reactivity with injected wastes.

| Table 6-6 | Chemical Constituents of Formation Waters Analyzed in Studies Related to Deep-Well Injection |

Constituent[a]	Wilmington, North Carolina	Pensacola, Florida	Belle Glade, Florida	Marshall, Illinois	Frio Formation, Texas
Depth (ft)	900	1,430	1,200	2,395	7,000
Temperature (°C)	22.7	35.2	26.0	—	107
Specific gravity	1.009	—	.008	—	—
pH	7.4	7.4	8.1	9.1	8.2
Eh(mV)	—	-32	—	-154	—
Conductance (%mho/cm^3)	31,800	22,320	—	22,000	—
TDS	20,800	13,700	—	22,000	118,802
Alkalinity	—	—	136	380	2,448
Pheno. alkalinity	—	—	—	66	—
Hardness	2,110	1,060	—	—	—
COD	—	—	36	—	—
Silica	9	18	19	8	30
Calcium	333	181	140	147	9,460
Magnesium	309	142	140	117	2,980
Sodium	6,750	4,920	—	8,370	43,300
Potassium	186	65	—	73	356
Bicarbonate	230	302	—	—	948
Sulfate	273	0	540	182	120
Chloride	12,100	8,150	1,680	12,700	71,400
Fluoride	<1	3	1	20	—
Bromide	—	28	—	—	247
Iodide	—	2	—	—	33
Nitrite/Nitrate	<0.1	0	—	25	—
Ammonium (N)	—	8	<1	—	—
Organic N	—	2	<1	—	—
Orthophosphate	<0.1	0	<0.1	<0.1	—
Hydrogen sulfide	tr.	1	4	—	—
DOC	<1	2	—	—	—
Organic carbon	—	—	2	—	—
Acetate	—	—	—	—	1,270
Propionate	—	—	—	—	207
Butyrate	—	—	—	—	24
Total org. acids	—	—	—	—	1,500
Titrated org. alk.	—	—	—	—	1,457

Table 6-6 (Continued)

Constituent	Wilmington, North Carolina	Pensacola, Florida	Belle Glade, Florida	Marshall, Illinois	Frio Formation, Texas
Aluminum	<1	—	—	0.09	—
Arsenic	<0.01	<0.1	—	<0.05	—
Barium	<1	—	—	1	89
Boron	—	5	—	—	474
Beryllium	—	—	—	<0.01	—
Cadmium	<0.1	—	—	<0.03	—
Chromium	<0.1	—	—	0.26	—
Cobalt	<0.01	—	—	<0.03	—
Copper	<0.1	<0.1	—	<0.03	—
Iron (total)	2	—	—	0.12	999
Ferrous iron	—	2	—	—	—
Lead	<0.01	<0.1	—	<0.03	—
Lithium	<1	<1	—	—	—
Manganese	<1	<0.1	—	0.14	—
Mercury	0.01	—	—	—	—
Molybdenum	<0.01	—	—	0.07	—
Nickel	<0.01	—	—	<0.05	—
Selenium	<0.01	—	—	—	—
Strontium	19	22	—	—	405
Zinc	<0.1	<0.1	—	<0.03	—

[a]Unless otherwise noted, all values are in mg/L.

Sources: Wilmington, NC., Leenheer et al. (1976); Pensacola, FL., Goolsby (1972); Belle Glade, FL., Kaufman et al. (1973); Marshall, IL., Roy et al. (1989); Frio Formation, TX., Kreitler et al. (1988).

solution during depressurization should be used, and the gaseous phase of the sample should be analyzed quantitatively. The types of gases present in brines are also important indicators of microbiological activity, discussed in detail below.

6.2.4 Microbiology

Dunlap et al. (1977), Bitton and Gerba (1984), and Ghiorse and Wilson (1988) describe subsurface sampling methods for microbiological characterization, which requires information on (1) types of microorganisms (species, morphologic groups, etc.), (2) biomass, and (3) viability (how much of the biomass is alive or engaged in metabolic activities). Table 6-7 summarizes the major techniques for characterizing the subsurface and indicates which properties they may be able to identify. Note that most techniques must be used in combination with others. For example, cultures must be examined microscopically as well, and epifluorescence light micros-

copy is most frequently combined with chemical, radioisotope, and dye reduction techniques. Rosswall (1973) and Costerton and Colwell (1979) contain detailed discussions of various study techniques, and Webster et al. (1985) provide a more recent discussion of several methods specifically applicable to subsurface samples. Section 6.4.2 discusses some laboratory methods for evaluating the biodegradability of hazardous wastes and simulating biodegradation in the deep-well environment.

6.3 Waste-Reservoir Interaction Tests

After measuring or estimating the values for the relevant waste, rock, and fluid parameters, the researcher can perform waste-reservoir interaction tests to: (1) identify possible incompatibilities between reservoir components and wastes to be injected, (2) identify chemical interactions, and (3) provide data for predicting the fate of injected wastes. Specific procedures for performing

Table 6-7   Methods for Subsurface Microbial Characterization

Technique	Properties Measured		
	Species/Morph.	Mass	Viability
Microscopic Analyses			
Scanning electron microscope (SEM)[a]	X		
Transmission electron microscope (TEM)	X		
Epifluorescence light microscopy	X	X	X
Cultures			
Aufwuchs methods	X	X	
Nutrient cultures	X	X	
Chemical Analyses			
Muramic acid		X	
Lipid phosphates		X	
Adenosine triphosphate (ATP)		X	
Guanosine triphosphate (GTP)/ATP ratio			X
Inorganic metabolic substrates/products	X		
Radioisotope Analyses			
^{3}H-thymidine in DNA		X	
^{3}H-glucose		X	
Dye-reduction Analysis			
Dye reduction			X

[a]Of limited value because of generally low population densities.

Source: Adapted from Ghiorse and Balkwill (1985).

interaction tests described in the literature vary considerably but can be grouped into two major types: **batch tests** and **flowthrough tests**.

Batch tests are performed by mixing wastes and reservoir materials. The materials are mixed in a series of reactors, which may be subjected to temperatures and pressures that simulate the deep-well environment. At regular intervals, the reactors are opened in sequence and the fluids analyzed. When waste and reservoir fluids are mixed, the presence and type of precipitates may be the main concern; when injection fluid is mixed with reservoir rock, adsorption or dissolution reactions may be of primary interest, and changes in the concentration of species being adsorbed or dissolved species may be measured. (Sections 5.2.2 and 6.4.1 describe the process for developing adsorption isotherms). When neutralization reactions are of interest, measurements continue until the mixture shows no further change in pH. Either disaggregated (crushed) or undisturbed cores may be used in batch tests. When undisturbed cores are used, special procedures should be used to ensure complete saturation of the core material by the fluid being tested. Probably the single best source of information on batch-test procedures for estimating adsorption is Roy et al. (1987).

Flowthrough tests also are used to study interactions between fluids and solids. The solid may be an undisturbed core or packed columns intended to simulate subsurface conditions. In either case the same core is used throughout, and the injected fluid is monitored at the outflow end at specified time

intervals to observe changes in chemistry. In adsorption experiments, equilibrium is obtained when the outflow concentration equals the inflow concentration. If precipitation-dissolution reactions occur, pressure changes caused by clogging or increased permeability may be monitored in addition to chemical changes.

Table 6-8 summarizes information on 14 waste-reservoir interaction tests reported in the literature. It lists the type of test, type of waste, geologic-formation lithology, and, where indicated, the duration and the temperature and pressure conditions. Most of the references in this table describe equipment and procedures for performing the tests. Roy et al. (1989) (batch-test) and Collins and Crocker (1988) (flowthrough tests) are useful, recent sources.

The following issues should be considered when selecting a laboratory method for evaluating interactions between wastes and reservoir materials:

■ The results of any method will contain uncertainties created by the sample chosen (which may not be representative of the injection zone), and possible alteration of in situ properties caused by shaping. Furthermore, because such experiments are usually performed for hours or days, only those reactions which reach equilibrium quickly will be measured. Reactions taking years to reach equilibrium will not be measured.

■ Tests must simulate temperatures and pressures in the injection zone, unless preliminary tests show that these parameters do not significantly affect the processes of interest. For example, Elkan and Horvath (1977) performed preliminary tests of microbiological activity at pressures similar to those in the injection zone being simulated and found no significant difference between activity at the elevated pressure and that at atmospheric pressure. Subsequent experiments were conducted at atmospheric pressure.

■ Results from tests using simulated sand cores or simulated waste solutions have lower confidence levels than those using actual cores and waste streams.

■ Batch experiments using disaggregated material are very likely to overestimate adsorption rates because of the larger surface area created by disaggregation. Batch experiments using undisturbed cores are very likely to yield better results, but they still will not simulate subsurface conditions

as effectively as flowthrough experiments in undisturbed cores.

■ Flowthrough experiments on subsurface cores at simulated temperatures and pressures will probably yield the best results, although the uncertainties listed above still apply (i.e., whether the sample is representative of the injection zone and whether the experiment's duration allows full equilibrium to be reached).

6.4 Geochemical Processes

This section describes laboratory procedures related to the study of (1) adsorption, (2) hydrolysis, and (3) biodegradation. The study of other processes such as acid-base equilibria, dissolution-precipitation, neutralizaton, and complexation all involve batch or flowthrough tests as described in the previous section.

6.4.1 Adsorption Isotherms

Adsorption isotherms (see Section 5.2.2.1) can be measured using either batch (Donaldson and Johansen, 1973; Donaldson et al., 1975) or flowthrough experiments (Collins and Crocker, 1988). Either procedure requires a series of measurements determining over time (at constant temperature) the changes in concentration of a solution with a known starting concentration. Equilibrium adsorption is reached when there is no significant change in concentration of the substance between measurements. Roy et al. (1987) recommend using a rate of change in solute concentration of less than 5 percent per 24-hour time interval. The amount adsorbed at equilibrium (usually expressed as micrograms/gram [$\mu g/g$] solid) can be calculated by dividing the amount adsorbed (beginning concentration minus the final concentration) by the weight of the adsorbing solid. Plotting the equilibrium adsorption value at different concentrations and fitting the data into the appropriate equation form (see Section 5.2.2.1) allow adsorption to be calculated at other concentrations. Measuring adsorption isotherms at two or more temperatures allows the heat-of-adsorption to be estimated, which may be valuable when interpreting thermodynamic mechanisms. Collins and Crocker (1988) describe procedures to estimate heat of adsorption from such data. The previous section (6.3.1) discusses the factors that should be considered in selecting procedures for measuring adsorption.

6.4.2 Hydrolysis

The formulas for calculating rates of hydrolysis (K_H) are discussed in Section 5.2.4. If rate constants for a particular substance cannot be found in the literature, they

Table 6-8   Summary of Waste-Reservoir Compatibility/Interaction Studies

Waste Type	Formation	Time (days)	Temp (°C)	Pressure (MPa)	Source
Batch—Fluids					
Acidic, organic (diluted)	Subsurface bacteria culture	3	20	0.1-27.6	Elkan and Horvath, 1977
49 Organic compounds	Various bacterial cultures	2-8	37-56	0.1	Grula and Grula, 1976
Batch—Disaggregated					
Acidic, inorganic Alkaline, organic	St. Peter sandstone Potosi dolomite Proviso siltstone Brine (Devonian)	15 155-230[a]	25-55 52[a]	0.1-11.7 10.8[a]	Roy et al., 1989
Acidic, organic	Floridan limestone	—	—	5.07	Goolsby, 1972
Acidic, ferric chloride	Dolomite	0.25	43	6.89	Hower et al, 1972
Cresol, sodium borate	Bentonite	—	250	0.1	Apps et al., 1988
Batch—Undisturbed					
Various organics	Cottage Grove sandstone	—	60	20.3	Donaldson and Johansen, 1973
Various organics	Cottage Grove sandstone	—	38-93	20.7	Donaldson
Flowthrough—Column					
Unspecified	Miocene sand	—	—	—	Hower et al., 1972
Acidic, organic	Cretaceous sand (simulated)	80	20	0.1	Elkan and Horvath, 1977

Table 6-8 (Continued)

Waste Type	Formation	Time (days)	Temp (°C)	Pressure (MPa)	Source
Flowthrough—Undisturbed					
Acidic (steel)	Mt. Simon sandstone	—	?	0.1	Bayazeed and Donaldson, 1973
Organic acids, formaldehyde	Poorly consolidated sands	6-18	20	3.4	Leenheer et al., 1976
Acidic pickling liquor	Dolomitic sandstone, dolomite, quartzite	—	40	13.8	Ragone et al., 1978
Phenol (in simulated brine)	Frio sand	—	38-60	24.1	Collins and Crocker, 1988

[a]Unpublished data provided by W. R. Roy, Illinois State Geological Survey.

must be determined by laboratory tests. As noted in Section 2.3.3, the effects of high ionic strength on hydrolysis rates are difficult to predict, so tests should simulate deep-well salinity conditions. Hydrolysis rate constants should probably be measured in simulated deep-well conditions to determine how significantly other environmental factors affect hydrolysis rates. Mill et al. (1982) describe procedures for measuring hydrolysis rate constants. Suffet et al. (1981) contain some additional suggestions for procedures not included in Mill et al. (1982).

6.4.3 Biodegradation

As with adsorption, biodegradation may be tested in the laboratory using either batch (Grula and Grula, 1976) or flowthrough (Elkan and Horvath, 1977) experiments. Pritchard and Bourquin (1984) review the use of microcosms when studying interactions between pollutants and microorganisms. Table 6-8 summarizes temperatures and pressures that have been used to simulate biodegradation under deep-well conditions. The batch experiments performed by Grula and Grula (1976) used enrichment cultures containing single organic compounds. After suitable incubation (typically 24 hours), four or five serial transfers to media of the same composition were made to enhance the selection of microbes with degradative capacity for the specific compound.

Elkan and Horvath (1977) have conducted the most sophisticated laboratory simulations of microbial degradation of injected wastes. Flowthrough experiments using sand-packed columns inoculated with bacterial populations from the injection zone were used to simulate conditions at the Wilmington, North Carolina, case study (Section 7.5). Fluids that simulated the composition and concentration of the actual waste were injected through the columns for 40 to 80 days under a range of experimental conditions. Although the study provided many useful insights into microbial degradation processes, it was not able to simulate their full range of activity. Specifically, all the model experiments had at least one factor that inhibited methanogenesis, which was known to occur in the injection zone.

Where a well is already operating, backflow tests can be used to evaluate biodegradation (see Section 7.1 and case studies in Sections 7.2 and 7.3). The types of biodegradation occurring can be inferred by testing samples for inorganic degradation byproducts (i.e., methane, hydrogen sulfide, and nitrogen).

6.5 Quality-Assurance/Control Procedures

EPA regulations require a quality-assurance and quality-control (QA/QC) plan that covers all aspects of a no-migration demonstration. Minimal requirements for a QA/QC program are described in U.S. EPA (1976) and detailed procedures for laboratory analyses

are presented by Booth et al. (1979); other regulatory agencies may require additional or different procedures. In addition to using standard and approved methods, the researcher must also define the principles and objectives of the QA/QC plan and identify the personnel responsible for implementing it.

Deep-well geochemical-fate modeling will present special challenges for QA/QC planning. The researcher must document original derivations of thermodynamic and kinetic data and obtain all experimental data using analytical methods acceptable to EPA and/or the appropriate regulatory agency. All procedures should be calibrated and referenced to those of the National Bureau of Standards (NBS), the U.S. EPA, or other acceptable body. Deviations from acceptable procedure must be fully documented, with demonstrations that alternatives yield the same- or better-quality results than those currently accepted by the U.S. EPA.

6.6 Annotated Bibliography

6.6.1 How To Use this Bibliography
Table 6-9 lists the references in this bibliography by topic. The annotations briefly describe each document and may identify chapters or sections most likely to be of interest. The references cited may be obtained from (1) the publisher, (2) libraries, (3) the originating trade association, (4) the originating government agency, (5) the Department of Commerce's National Technical Information Service (NTIS), or (6) the author.

6.6.2 Annotations
American Petroleum Institute (API). 1965. *Recommended Practices for Biological Analysis of Subsurface Injection Waters.* RP 38. API, 1220 L St. NW, Washington, D.C. 20005.

Describes methods for (1) identifying microorganisms in a water sample by microscopic examination, general bacterial counts, and sulfate-reducing bacteria counts, and (2) determining effectiveness of chemicals for treating injection water to prevent the growth of sulfate-reducing bacteria.

American Public Health Association (APHA). 1985. *Standard Methods for the Examination of Water and Wastewater, 16th edition.* 1,268 pp. AHPA, 1015 Fifteenth Street NW, Washington, D.C. 20005.

Most pertinent sections include: Part 100, General Introduction (laboratory apparatus, precision, accuracy, quality control; Part 200, Physical Examination (color, conductivity, solids); Part 300,

Determination of Metals; Part 400, Determination of Inorganic Nonmetallic Constituents; Part 500, Determination of Organic Constituents (organic carbon, BOD, COD); and Part 900, Microbiological Examination of Water.

American Society for Testing and Materials (ASTM). Annual Books of ASTM Standards. *Water and Environmental Technology, Volumes 11.01 and 11.02 (Water).* ASTM, 1916 Race St., Philadelphia, Pennsylvania 19103.

American Society for Testing and Materials (ASTM). 1966. *Manual on Industrial Water and Industrial Wastewater, 2nd edition.* ASTM, 1916 Race St., Philadelphia, Pennsylvania 19103.

Part I covers general use of industrial water and problems of sampling and analysis and Part II sets forth ASTM standards. Of particular interest is D1256-61 (Scheme for Analysis of Industrial Wastes and Industrial Waste Water). Analytical methods for a range of inorganic and organic chemical parameters are presented.

Apps, J. 1988. *Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of Deep Disposal Wells.* Draft Report LBL-26007. Lawrence Berkeley Laboratory, Berkeley, CA 94720.

Comprehensive report on the state of the art in geochemical modeling of interactions between hazardous wastes and the injection reservoir. Contains eight major sections: (1) an introduction to the EPA regulations covering no-migration petitions for deep-well injection of hazardous wastes and how the petitions relate to geochemical modeling; (2) discussion of the reactions that must be modeled given the chemical conditions expected in the injection zone; (3) the equations of state that must be used; (4) the availability of thermodynamic data; (5) the availability of geochemical modeling computer codes; (7) criteria affecting the satisfactory chemical modeling of waste injection; and (8) conclusions and recommendations. U.S. EPA (1989) contains a summary of this report.

Apps, J., L. Tsao, and O. Weres. 1988. The Chemistry of Waste Fluid Disposal in Deep Injection Wells. In *Second Berkeley Symposium on Topics in Petroleum Engineering, March 9-10, 1988.* LBL-24337. Lawrence Berkeley Laboratory, Berkeley, CA 94720, pp. 79-82.

Focuses on chemical aspects of deep-well injection of hazardous wastes, including: (1) an overview of types of models for predicting fate and deficiencies in available models; (2) a comparison

Table 6-9   Topical Index to Annotated Bibliography

Topic	Sources
Waste Stream	
Hazardous waste characterization	API, 1965; APHA, 1985; ASTM, annual; ASTM, 1966; Bayzeed and Donaldson, 1973; Berg, 1982; deVera, 1980; Ford et al., 1984; Kopp and McKee, 1983; Longbottom and Lichtenberg, 1982; Malcolm and Leenheer, 1973; Mill et al., 1982; Warner and Lehr, 1977; Watkins, 1954
Resevoir Rock	
Physical characteristics	ASTM, annual; Bentley et al., 1986; Collins and Crocker, 1988; Klute, 1986; Kreitler et al., 1988; USGS, var. dates; Warner and Lehr, 1977
Chemical characteristics	ASTM, annual; Page et al., 1986; Mortland, 1970; USGS, var. dates; Warner and Lehr, 1977; ZoBell, 1946
Mineralogy	Bentley et al., 1986; Carroll, 1970; Grim, 1968; Hewitt, 1963; Kerr, 1959; Klute, 1986; Mortland, 1970; Theng, 1984
Resevoir Fluids	
Physical characteristics	ASTM, annual; Collins, 1975; Ostroff, 1965; USGS, var. dates; Warner and Lehr, 1977
Chemical characteristics	APHA, 1985; ASTM, annual; Apps et al., 1988; Barnes, 1964; Berg, 1982; Collins, 1975; Dunlap et al., 1977; Hem, 1970; Kopp and McKee, 1983; Kreitler, 1988; Malcolm and Leenheer, 1973; Ostroff, 1965; Rainwater and Thatcher, 1960; Scalf et al., 1981; USGS, var. dates; Warner and Lehr, 1977; Watkins, 1954; Wood, 1976; ZoBell, 1946
Other	
Waste-reservoir interactions	Apps, 1988; Collins and Crocker, 1988; Donaldson and Johnasen, 1973; Elkan and Horvath, 1977; Goolsby, 1972; Hewitt, 1963; Hower et al., 1972; Kaufman et al., 1982; Ostroff, 1965; Pritchard and Bourquin, 1984; Ragone et al., 1978; Roy et al., 1987; U.S. EPA, 1989; Warner and Lehr, 1977
Biological characterization	API, 1965; APHA, 1985; Barnes, 1972; Bayzeed and Donaldson, 1973; Bitton and Gerba, 1984; Costerton and Colwell, 1979; Dunlap et al., 1977; Elkan and Horvath, 1977; Ghiorse and Balkwill, 1985; Ghiorse and Wilson, 1988; Pritchard and Bourquin, 1984; Rosswall, 1973; Webster, 1985
Biodegradation	Bitton and Gerba, 1984; Elkan and Horvath, 1977; Ghiorse and Wilson, 1982; Grula and Grula, 1976; Lyman et al., 1982, Pritchard and Bourquin, 1989
Hydrolysis	Lyman et al., 1982; Mill et al., 1982; Suffet et al., 1981
Sampling	Barcelona et al., 1985; Berg, 1982; Bitton and Gerba, 1984; DeVera, 1980; Dunlap et al., 1977; Ford et al., 1984; Ghiorse and Wilson, 1988; Rainwater and Thatcher, 1960; Scalf et al., 1981; USGS, var. dates; Warner and Lehr, 1977
Quality assurance/control	APHA, 1985; Berg, 1982; Booth et al., 1979; U.S. EPA, 1976

of the laboratory simulation of the evolution of Gulf Coast brines using EQ3/6 with actual brines; and (3) the results of laboratory experiments studying the interactions between bentonite clay and a simulated waste of sodium borate and cresol. U.S. EPA (1989) contains a summary of this report.

Barcelona, M. J., J. P. Gibb, J. A. Helfrich, and E. E. Garske. 1985. *Practical Guide for Ground-Water Sampling.* EPA/600/2-85-104, NTIS PB86-137304.

Covers all aspects of ground-water sampling (parameter selection, well placement and construction, monitoring-well design, well development, and recommended sampling protocols.

Barnes, I. 1964. *Field Measurement of Alkalinity and pH.* U.S. Geological Survey Water Supply Paper 1525-H. 17 pp.

Describes detailed procedures for accurate measurement of alkalinity and pH in the field. pH meter readings in the field may be in error as much as 0.5 pH units when the pH of a sample differs greatly from the reference (buffer solutions).

Barnes, I. 1972. Water-Mineral Reactions Related to Potential Fluid-Injection Problems. In *Symposium on Underground Waste Management and Environmental Implications, Houston, Texas,* T. D. Cook, ed. Am. Assn. Petr. Geol. Mem. 18, pp. 294-297.

Discusses thermodynamic aspects of precipitation-dissolution reactions in natural ground waters. No specific data are reported on waste-reservoir interactions.

Bayazeed, A. F., and E. C. Donaldson. 1973. *Subsurface Disposal of Pickle Liquor.* U.S. Bureau of Mines Report of Investigations 7804. 30 pp.

Surveys underground injection of steel-processing waste pickle liquor. Includes (1) data on analyses of waste from several steel companies; (2) a detailed case history of injection into the Mt. Simon sandstone near Gary, Indiana; (3) the results of laboratory experiments on water sensitivity (permeability changes due to changes in salinity) of Mt. Simon and Cottage Grove sandstones; and (4) results of laboratory flow-through experiments using simulated hydrochloric acid pickling liquor.

Bentley, M. E., R. T. Kent, and G. R. Myers. 1986. Site Suitability for Waste Injection, Vickery, Ohio. In *Proc. of the Int. Symp. on Subsurface Injection of Liquid Wastes,*

New Orleans. National Water Well Association, Dublin, Ohio 43017. pp. 330-354.

Site evaluation of a waste injection site in the Mt. Simon Sandstone. Describes results of laboratory tests to characterize core materials (x-ray diffraction, microscopic examination of thin sections of cores to identify minerals and characterize porosity, permeability and porosity), and field tests (drill-stem and pressure-fall-off analysis).

Berg, E. L. 1982. *Handbook for Sampling and Sample Preservation of Water and Wastewater.* EPA 600/4-82-029. NTIS PB83-124503.

Particularly relevant chapters are: (1) General Considerations for a Sampling Program; (4) Statistical Approach to Sampling; (6) Sampling Industrial Wastewaters; (9) Sampling of Ground and Drinking Water; (12) Sampling, Preservation and Storage Considerations for Trace Organic Materials; (15) Sample Control Procedures and Chain of Custody; (16) Quality Assurance; and (17) Sample Preservation. Note that this report supercedes a report by the same title by Moser et al. (1976), EPA/600/4-80-029.

Booth, R. L., et al. 1979. *Handbook of Analytical Quality Control in Water and Wastewater Laboratories.* EPA/600/4-79-019, NTIS PB 297 451.

Details quality control procedures for laboratories that analyze water and wastewater samples.

Bitton, G., and C. P. Gerba (eds.). 1984. *Groundwater Pollution Microbiology.* Wiley-Interscience, New York.

Paper by McNabb and Mallard presents methods for obtaining uncontaminated subsurface samples for microbiological analysis.

Carroll, D. 1970. *Clay Minerals: A Guide to their X-Ray Identification.* GSA Special Paper No. 126. Geological Society of America, Box 9140, Boulder, Colorado 80301.

Not obtained for review.

Collins, A. G. 1975. *Geochemistry of Oilfield Waters.* Elsevier, New York, 496 pp.

Particularly relevant chapters include: (2) Sampling of Oilfield Waters (dissolved gases, unstable constituents, pH/Eh flow sampling chamber), (3) Analysis of Oilfield Water for Physical Properties and Inorganic

Chemical Constituents, (4) Interpretation of Chemical Analyses of Oilfield Waters, (5) Significance of Some Inorganic Constituents and Physical Properties of Oil Field Waters, (6) Organic Constituents in Oilfield Waters, (12) Compatibility of Oil Field Waters.

Collins, A. G., and M. E. Crocker. 1988. *Laboratory Protocol for Determining Fate of Waste Disposed in Deep Wells.* EPA-600/8-88-008, NTIS PB88-166061.

Describes laboratory procedures for: (1) core analysis, (2) brine analysis, (3) dynamic flow-through system that simulates the interactions of hazardous organic wastes with injection zone rock, and (4) static waste/rock interaction tests that simulate longer-term degradation processes. Protocol testing resulted in some data on the adsorption of phenol and 1,2,-dichloroethane in simulated subsurface conditions for the Frio sandstone, and data from earlier adsorption experiments using the Cottage Grove sandstone are presented (see Table 5-4). U.S. EPA (1989) contains a summary of this report.

Costerton, J. W. and R. R. Colwell (eds.). 1979. *Native Aquatic Bacteria: Enumeration, Activity, and Ecology.* ASTM/Special Tech. Pub. 695. (See ASTM [1965] for address).

Papers presented at a symposium sponsored by ASTM in June, 1977. Contains five papers of methods for direct enumeration of aquatic bacteria, five papers on chemical indices of aquatic bacterial populations, and six papers on metabolic potentials of aquatic bacterial populations as indicated by activity measurements.

deVera, E. R. 1980. *Samplers and Sampling Procedures for Hazardous Waste Streams.* EPA 600/2-80-018. NTIS PB80-135353.

Describes procedures for collecting, handling, storing, and recording samples of hazardous wastes. Various sampling devices are discussed, with emphasis on developing a composite liquid-waste sampler (the coliwasa).

Donaldson, E. C., and R. T. Johansen. 1973. History of a Two-Well Industrial Waste Disposal System. In *Symposium on Underground Waste Management and Artificial Recharge,* J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences, pp. 603-621.

Case history of a facility injecting separate acidic and alkaline organic waste streams in Texas (see case study in Section 7.7 and Table 5-4).

Donaldson, E. C., M. E. Crocker, and F. S. Manning. 1975. *Adsorption of Organic Compounds on Cottage Grove Sandstone.* BERC/RI-75/4, Bartlesville Energy Research Center, Bartlesville, Oklahoma.

Presents data on the results of adsorption of nine organic compounds on the Cottage Grove sandstone at 3,000 psi and two temperatures (100° and 150°F). See Table 5-4 for summary of data results.

Dunlap, W. J., J. F. McNabb, M. R. Scalf, and R. L. Cosby. 1977. *Sampling for Organic Chemicals and Microorganisms in the Subsurface.* EPA 600/2-77-176. NTIS PB272679.

Describes methods for obtaining samples of ground-water and earth solids that are not contaminated by near-surface microbes. Procedures described are limited to a depth of about 25 feet below the surface in compact alluvial formations.

Elkan, G., and E. Horvath. 1977. *The Role of Microorganisms in the Decomposition of Deep-Well-Injected Liquid Industrial Wastes.* NSF/RA-770102, NTIS PB 268 646.

Presents results of (1) studies to characterize pre-injection and post-injection microbial populations in injection zones at the Monsanto plant, Florida (see Section 7.2) and Wilmington, North Carolina (see Section 7.5), and (2) laboratory apparatus and procedures for simulating microbial degradation of injected wastes.

Ford, P. J., P. J. Turina, and D. E. Seely. 1984. *Characterization of Hazardous Waste Sites—A Methods Manual: Vol II: Available Sampling Methods, 2nd edition.* EPA 600/4-84-07. Vol III. Available Laboratory Analytical Methods. Available from EPA Cincinnati.

Section 3.4 of Vol. II describes procedures for purging and sampling monitoring wells. Vol. III outlines detailed methodology suitable for hazardous waste analysis and is organized by media and compound.

Ghiorse, W. C., and D. L. Balkwill. 1985. Microbiological Characterization of Subsurface Environments. In *Ground Water Quality,* C. H. Ward, W. Giger, and P. L. McCarty, eds. Wiley Interscience, New York, pp. 386-401.

Reviews available methods for characterizing subsurface microorganisms.

Ghiorse, W. C., and J. T. Wilson. 1988. Microbial Ecology of the Terrestrial Subsurface. *Adv. Appl. Microbiol.* 33:107-172.

Section III (Characterization of Microorganisms and Their Activities in Subsurface Environments) includes subsections on sampling and methods for detection, enumeration, and metabolic activity.

Goolsby, D. A. 1972. Geochemical Effects and Movement of Injected Industrial Waste in a Limestone Aquifer. In *Symposium on Underground Waste Management and Environmental Implications, Houston, Texas,* T. D. Cook, ed. Am. Assn. Petr. Geol. Mem. 18, pp. 355-368.

Reports studies of geochemical interactions between an acidic organic waste and a carbonate injection zone (see Monsanto case study, Section 7.2).

Grim, R. E. 1968. *Clay Mineralogy, 2nd edition.* McGraw-Hill, New York.

Chapters of particular interest include: (5) X-Ray Diffraction Data, (7) Ion Exchange, (8) Clay Water System, (9) Clay Mineral-Organic Reactions, and (11) Optical Properties.

Grula, M. M., and E. A. Grula. 1976. *Feasibility of Microbial Decomposition of Organic Wastes under Conditions Existing in Deep Wells.* BERC/RI-76/6. Bartlesville Energy Research Center, Bartlesville, Oklahoma.

Presents results of aerobic biodegradation experiments on 50 compounds in ten organic groups (mono- and di-carboxylic acids, aldehydes and ketones, amino acids, alcohols, mono- and di-amines, aliphatic nitro compounds, nitriles, aromatic compounds, and miscellaneous) under simulated deep-well temperatures (50° to 70°C) and pressures (100 atm).

Hem, J. D. 1970. *Study and Interpretation of the Chemical Characteristics of Natural Water, 2nd edition.* U.S. Geological Survey Water Supply Paper 1473.

Provides data and discussion for more than 60 constituents and their properties that are included in water analyses for which sufficient data exist to consider sources from which each is generally derived, most probable form of elements and ions in solution, solubility controls, expected concentration ranges, and other chemical factors. Also discusses statistical techniques for analyzing water quality data.

Hewitt, C. H. 1963. Analytical Techniques for Recognizing Water Sensitive Rocks. *J. of Petroleum Technology* 15:813-818.

Describes the following techniques for identifying water-sensitive rocks: (1) flowthrough permeability tests, (2) x-ray diffraction, (3) physical swelling tests, and (4) microscopic examination of thin sections. Presents typical analyses of reservoir rocks that are not sensitive, that are water-sensitive due to swelling clays, and that are water-sensitive due to particle plugging.

Hower, W. F., R. M. Lasater, and R. G. Mihram. 1972. Compatibility of Injection Fluids with Reservoir Components. In *Symposium on Underground Waste Management and Environmental Implications, Houston, Texas,* T. D. Cook, ed. Am. Assn. Petr. Geol. Mem. 18, pp. 287-293.

Discusses clay-mineral sensitivity, presents results of laboratory flow tests in water-sensitive sand, and presents ferric-chloride-dolomite interaction tests.

Kaufman, M. I., D. A. Goolsby, and G. L. Faulkner. 1973. Injection of Acidic Industrial Waste into a Saline Carbonate Aquifer: Geochemical Aspects. In *Symposium on Underground Waste Management and Artificial Recharge,* J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences, pp. 526-551.

Reports results of studies of geochemical interactions between acidic organic wastes and a carbonate injection formation in Belle Glade, Florida (see Case Study, Section 7.4).

Kerr, P. F. 1959. *Optical Mineralogy, 3rd edition.* McGraw Hill, New York. 442 pp.

Provides comprehensive coverage of optical methods for the microscopic identification of minerals.

Klute, A. (ed.). 1986. *Methods of Soil Analysis, Part 1—Physical and Mineralogical Methods, 2nd edition.* ASA Monograph 9. American Society of Agronomy, 677 S. Segoe Rd., Madison, Wisconsin 53711, 1,188 pp.

Contains 50 chapters covering a range of physical and mineralogical methods. Many of the methods for physical characterization can be used to characterize geologic materials.

Kopp, J. F., and G. D. McKee. 1983. *Methods for Chemical Analysis of Water and Wastes.* EPA 600/4-79-020, revised March 1983, NTIS PB84-128677.

This third edition contains the chemical analytical procedures used in U.S. EPA laboratories for examining ground and surface waters, domestic and industrial waste effluents, and treatment process samples. Provides test procedures for measuring physical inorganic and selected organic constituents and parameters. Supercedes report by the same title dated 1979 (NTIS PB 297 686).

Kreitler, C. W., M. S. Akhter, and A. C. A. Donnelly. 1988. *Hydrologic-Hydrochemical Characterization of Texas Gulf Coast Formations Used for Deep-Well Injection of Chemical Wastes.* University of Texas at Austin, Bureau of Economic Geology.

Section 8.3 describes methods for analyzing anions (chloride, bromide, sulfate, ammonia, and iodide), and isotopically analyzing oxygen and hydrogen, and organic acids and organic alkalinity. Section 8 also contains water quality analyses of about 850 samples from the Frio formation in Texas, the most widely used injection zone for hazardous wastes.

Leenheer, J. A., R. L. Malcolm, and W. R. White. 1976. *Physical, Chemical and Biological Aspects of Subsurface Organic Waste Injection near Wilmington, North Carolina.* U.S. Geological Survey Professional Paper 987.

Comprehensively reports on results of field and laboratory waste-aquifer reactivity studies at the Wilmington, North Carolina, injection facility (see case study, Section 7.5).

Longbottom, J. E., and J. J. Lichtenberg. 1982. *Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater.* EPA/600/4-82-057, NTIS PB83-201798.

Describes test procedures for 15 groups of organic chemicals, and includes an appendix defining procedures for determining the detection limit of an analytic method. The test procedures in this manual are cited in Tables 1C (organic chemical parameters) and 1D (pesticide parameters) in 40 CFR 136.3(a).

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt, eds. 1982. *Handbook of Chemical Property Estima-tion Methods: Environmental Behavior of Organic Compounds.* McGraw-Hill, New York.

The most relevant chapters for deep-well injection are Chapter 6 (Rate of Hydrolysis) by Harris, and Chapter 9 (Rate of Biodegradation) by Scow.

Malcolm, R. L., and J. A. Leenheer. 1973. The Usefulness of Organic Carbon Parameters in Water Quality Investigations. In *Proc. of the Inst. of Env. Sciences 1973 Annual Meeting, Anaheim, CA, April 1-6,* pp. 336-340. Available from J. A. Leenheer, USGS MS 408, Box 25046, Federal Center, Denver, Colorado, 80225.

Describes methods for sampling and analysis for dissolved organic carbon (DOC) and suspended organic compounds (SOC). Also discusses the relationship of DOC and SOC to other organic indices (BOD, COD, and TOC).

Mill, T., W. R. Mabey, D. C. Bomberger, T. -W. Chou, D. G. Hendry and J. H. Smith. 1982. *Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water.* EPA-600/3-82-022, NTIS PB83-150888.

Particularly relevant protocols for deep-well injection are described in Chapter 4 (Hydrolysis in Water) and Chapter 8 (Sorption of Organic on Sediments). Each chapter contains procedures for preliminary screening and detailed tests.

Mortland, M. M. 1970. Clay-Organic Complexes and Interactions. *Adv. Agron.* 22:75-117.

Discusses methods for studying clay-organic bonding mechanisms, different types of bonding mechanisms, and the nature of some clay-organic complexes and reactions.

Ostroff, A. G. 1965. *Introduction to Oilfield Water Technology.* Prentice Hall, Englewood Cliffs, New Jersey, 412 pp.

Particularly relevant chapters for industrial-waste injection include: (2) Analysis of Water (sampling methods, determination of components), (3) Scales and Sludges Deposited from Water, (4) Water and Corrosion, (6) Water Treatment Microbiology, and (13) Water for Injection (compatibility tests, water-sensitive formations).

Page, A. L., R. H. Miller, and D. R. Keeney, eds. 1986. *Methods of Soil Analysis, Part 2—Chemical*

and Microbiological Properties, 2nd edition. ASA Monograph 9, American Society of Agronomy, 677 S. Rd., Madison, Wisconsin 53711. 1,159 pp.

Contains 54 chapters covering methods for analyzing chemical and microbiological properties of soils.

Pritchard, P. H., and A. W. Bourquin. 1984. The Use of Microcosms for Evaluation of Interactions Between Pollutants and Microorganisms. *Adv. Microbial Ecol.* 7:133-215.

Comprehensively reviews the use of microcosms (establishment of a physical model or simulation of part of an ecosystem) for studying biodegradation. Topics covered include: role of microcosms in environmental risk assessment, typical microcosm design features, qualitative and quantitative approaches to using microcosms, and field calibration.

Ragone, S. E., R. S. Riley, and R. J. Dingman. 1978. Hydrochemistry and Hydrodynamics of Injecting an Iron-Rich Pickling Liquor into a Dolomitic Sandstone— A Laboratory Study. *J. Res. U.S. Geol. Survey* 6(1):1-9.

Describes development of a high-pressure permeability-testing apparatus for dynamic flow-through waste/reservoir interaction experiments and presents results of experiments in which acidic waste pickling liquor containing high concentrations of iron salts was injected into cores of quartzite, sandstone, and dolomite.

Rainwater, F. H. and L. L. Thatcher. 1960. *Methods for Collection and Analysis of Water Samples.* U.S. Geological Survey Water Supply Paper 1454, 301 pp.

Pertinent sections are: (A) Collection of Samples (site selection, frequency, equipment and sampling instructions); (B) Handling of Water Samples before Analysis; (C) Analysis of Water Samples (types of methods, choice of analytical method); and (D) Analytical Procedures (specific procedures for over 40 inorganic water parameters).

Rose, S., and A. Long. 1988. Monitoring Dissolved Oxygen in Ground Water: Some Basic Considerations. *Ground Water Monitoring Review* 8(1):93-97.

Paper reviewing the geochemical significance of dissolved oxygen in ground water and sampling methods for dissolved gases.

Rosswall, T., ed. 1973. *Modern Methods in the Study of Microbial Ecology.* Bulletins from the Ecological Research Committee, Swedish Natural Science Research Council, Stockholm, 17.

Includes about 80 papers and short communications presented at a symposium held in Uppsala, Sweden, in 1972. Pertinent sessions include: (2) Techniques for the Observation of Microcosms in Soil and Water; (3) Isolation and Characterization of Microorganisms; (4) Techniques for the Determination of Microbial Activity in Relation to Ecological Investigations; (5) Estimation of Microbial Growth Rates Under Natural Conditions; (6) Model Systems; (7) Mathematical Models and Systems Analysis in Microbial Ecology. Also includes summary of a panel discussion on problems of assessing the effect of pollutants on microorganisms.

Roy, W. R., S. C. Mravik, I.G . Krapac, D. R. Dickerson, and R. A. Griffin. 1989. *Geochemical Interactions of Hazardous Wastes with Geological Formations in Deep-Well Systems.* Environmental Geology Notes 130. Illinois State Geological Survey, Champaign, Illinois. [An earlier version of this report by the same title was published in 1988 by the Hazardous Waste Research and Information Center, Savoy, Illinois].

Includes: (1) a description of laboratory procedures for batch-type waste-rock-brine interaction tests at simulated subsurface temperature and pressure conditions; (2) data on geochemical interactions at different temperatures and pressures between two types of hazardous waste (acidic and alkaline) with material from two injection-zone formations and one confining formation that occur in the Midwest (Mt. Simon sandstone, Potosi dolomite, and Proviso siltstone; and (3) a comparison of the empirical data with predictions using two aqueous geochemical codes (WATEQ2 and SOLMNEQF). U.S. EPA (1989) contains a detailed summary of this report.

Roy, W. R., I. G. Krapac, S. F. J. Chou, and R. A. Griffin. 1987. *Batch-Type Adsorption Procedures for Estimating Soil Attenuation of Chemicals.* Draft Technical Resource Document (TRD), EPA/530-SW-87-006-F. NTIS PB87-146155. [The final TRD, titled *Batch-Type Procedures for Estimating Soil Adsorption of Chemicals,* is scheduled for publication in 1990]

Provides a comprehensive report on batch-test procedures for estimating soil adsorption. Includes chapters on selection of soil:solution ratios for ionic and nonionic solutes, determination of equilibration time, construction of adsorption isotherms,

selection of adsorption equations, application of batch-adsorption data and laboratory procedures for generating adsorption data. Literature on the effects of temperature, pH, ionic strength, phase separation, method of mixing, and soil:solution ratios on adsorption were also reviewed.

Scalf, M. R., J. F. McNabb, W. J. Dunlap, and R. L. Cosby. 1981. *Manual of Ground-Water Quality Sampling Procedures*. EPA 600/2-81-160. NTIS PB82-103045.

Specific methods are covered in the following chapters: (5) Construction of Monitoring Wells, (6) Collection of Ground Water Samples, (7) Sampling Subsurface Solids. Appendices of interest include: (A) Summary of Procedures Based on Parameters of Interest and (B) Sampling of Low Density Immiscible Organics).

Skoog, D. A. 1985. *Principles of Instrumental Analysis, 3rd Edition*. Saunders College Publishing, Philadelphia, Pennsylvania.

Presents a comprehensive text on laboratory methods for measurement of physical and chemical properties of materials.

Suffet, I. H., C. W. Carter, and G. T. Coyle. 1981. Test Protocols for the Environmental Fate and Movements of Toxicants. In *Proceedings of a Symposium of the AOAC*, G. Zweig, and M. Beroza, eds. Association of Official Analytical Chemists, Washington, D.C.

Suggests refinements to laboratory protocols for measuring hydrolysis rates outlined in Mill et al. (1982).

Theng, B. K. G. 1974. *The Chemistry of Clay-Organic Reactions*. Adam Hilger Ltd., London.

Reports on the chemistry of clay-organic reactions, with special emphasis on the use of infrared spectroscopy.

U.S. Environmental Protection Agency, 1989. *Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste: Summaries of Recent Research*. U.S. EPA 625/6-89-025b.

Presents in a standardized summary format the following research papers: (1) Apps (1988), (2) Apps et al. (1988), (3) Collins and Crocker

(1988), (4) Roy et al. (1989), and (5) Strycker and Collins (1987).

U.S. Environmental Protection Agency. 1976. *Minimal Requirements for a Water Quality Assurance Program*. EPA/440/9-75-010, NTIS PB 258 807.

Presents a guide for planning and developing a quality assurance program. Part II includes a typical Memorandum of Understanding (MOU) on quality assurance procedures between an EPA regional office and a state. Other parts cover overall requirements, basic elements to be implemented immediately, and basic elements to be implemented in the future.

U.S. Geological Survey. Various Dates. *Techniques of Water-Resources Investigations of the United States Geological Survey*.

Presents an ongoing compilation of water resource investigation methods. Some chapters of interest include: Book 5, Chapter A2 (Determination of Minor Elements in Water by Emission Spectroscopy), Chapter A3 (Methods for Analysis of Organic Substances in Water), Chapter D2 (Guidelines for Collection and Field Analysis of Groundwater Samples for Selected Unstable Constituents).

Warner, D. L., and J. H. Lehr. 1977. *An Introduction to the Technology of Subsurface Wastewater Injection*. EPA 600/2-77-240. NTIS PB 279 207.

Arguably the best single reference document covering all aspects of the design, construction, and operation of waste-injection wells. Chapter 6 (Wastewater Characteristics) discusses sampling in general and the parameters that should be considered in characterizing wastes.

Watkins, J. W. 1954. *Analytical Methods of Testing Waters to be Injected into Subsurface Oil-Productive Strata*. U.S. Bureau of Mines Report of Investigations 5031. 29 pp.

The main section of interest covers corrosion tests. It also describes procedures for measuring ten parameters of potential significance in assessing corrosivity of a liquid (dissolved oxygen, free carbon dioxide, hydrogen sulfide, pH, total and dissolved iron, alkalinity and carbonate stability, hardness, chlorides, residual chlorides, and turbidity).

Webster, J. J., G.J. Hampton, J.T. Wilson, W.C. Ghiorse, and F.R. Leach. 1985. Determination of Microbial Cell Numbers in Subsurface Samples. *Ground Water* 23:17-25.

Describes procedures for several methods (ATP measurements and AOINT counts) for determining microbial cell numbers in subsurface samples and reports results of applying the methods to samples from Oklahoma and Texas.

Wood, W. W. 1976. Guidelines for Collection of Field Analysis of Ground-Water Samples for Selected Unstable Constituents. Chapter D2 of *Techniques of Water-Resource Investigations of the United States Geological Survey*. Available from U.S. Geological Survey, Books and Open-File Reports Section, Federal Center, Box 25425, Denver, Colorado 80225.

Covers field methods for sampling and field analysis of specific conductance, temperature, pH, carbonate and bicarbonate, Eh, and dissolved oxygen.

ZoBell, C. E. 1946. Studies on Redox Potential of Marine Sediments. *Am. Ass. Petr. Geol. Bull.* 30:477-513.

Describes procedures for colorimetric and electrometric measurement of Eh (redox potential) of sedimentary materials.

CHAPTER SEVEN

CASE STUDIES OF DEEP-WELL INJECTION OF INDUSTRIAL WASTE

This chapter discusses how field studies can be used in geochemical fate assessment (Section 7.1) and includes six cases of deep-well-injection facilities, documenting the geochemistry of the hazardous and other industrial wastes injected as reported in the literature. Each case study is organized in the same format, with section headings as follows:

■ **Injection Facility Overview** describes the type of facility, its current status, and the characteristics of the injected wastes and presents a brief history of injection and monitoring activities, including distance traveled by the waste.

■ **Injection/Confining-Zone Lithology and Chemistry** provides information on the geology and chemistry of the injection zone formation fluids.

■ **Chemical Processes Observed** briefly describes the types of interactions and major physical effects that have been observed at the site and evaluates their significance.

Table 7-1 summarizes information about each study, including chapter reference, location of the well, lithology of the injection zone, waste characteristics, major geochemical processes observed, and sources of information.

Other case-study compilations of industrial-waste injection have been prepared by Donaldson (1964), Donaldson et al. (1974), and Reeder et al. (1977). The first two summarize information on source and nature of waste, geology, surface equipment, and well completion and operation for 15 companies. Reeder et al. (1977) describe about a dozen studies in a similar format, organized by EPA region. Companies and precise locations are not specified in these studies, and none particularly emphasize geochemical interactions between injected waste and the reservoir formation. Nevertheless, these compilations provide useful information on geologic characteristics of injection zones, waste pretreatment, and injection-well operating characteristics.

7.1 Use of Field Studies in Geochemical Fate Assessment

Field studies are an important complement to geochemical modeling, as discussed in Chapter Five, and to laboratory studies, as discussed in Chapter Six. Two ways to investigate interactions between injected wastes and reservoir material are (1) direct observation of the injection zone and overlying aquifers using monitoring wells and (2) backflushing the injected waste. In both instances, samples of the fluids in the zone are collected at intervals to characterize the nature of geochemical reactions and to track changes over time.

7.1.1 Monitoring Wells
Monitoring wells drilled into the injection zone at selected distances and directions from the injection well allow direct observation of formation water characteristics and the interactions that occur when the waste front reaches the monitoring well. When placed near the injection well in the aquifer above the confining layer, monitoring wells can detect the upward migration of wastes caused by casing or confining-layer failure. Foster and Goolsby (1972) describe detailed methods for constructing monitoring wells.

Monitoring wells have several advantages: time-series sampling of the formation over extended periods is easy and the passage of the waste front can be observed precisely. Disadvantages are cost and the potential for upward migration of wastes if monitoring well casings fail. A monitoring well at the Monsanto plant had to be plugged when unneutralized waste reached it because of fears that the casing would corrode (see Section 7.2.1). The three Florida case studies (Sections 7.2, 7.3, and 7.4) and the North Carolina case study (Section 7.5) illustrate the usefulness of monitoring wells.

| Table 7-1 | **Summary of Case Studies** | | | | |

Location	Lithology	Wastes	Processes Observed	Section	Sources
			Florida		
Pensacola (Monsanto)	Limestone	Nitric acid Inorganic salts Organic compounds	Neutralization Bacterial denitrification	7.2	Goolsby, 1971, 1972 Faulkner and Pascale, 1975 Pascale and Martin, 1978 Elkan and Horvath, 1977 Dean, 1965 Barraclough, 1966 Goolsby, 1971 Willis et al., 1975
Pensacola (American Cyanamid)	Limestone	Acrylonitrile Sodium salts (nitrate, sulfate thiocyanate)	Bacterial denitrification No retardation of thiocyanate ions	7.3	Ehrlich et al., 1979 Vecchioli et al., 1984
Belle Glade	Carbonate	Hot acid Organic plant wastes	Neutralization Bacterial sulfate reduction Methane production	7.4	Kaufman et. al., 1973 Kaufman and McKenzie, 1975 McKenzie, 1976 Garcia-Bengochea and Vernon, 1970
			North Carolina		
Wilmington	Sand Silty sand Limestone	Organic acids Formaldehyde Methanol	Neutralization Dissolution-precipitation Complexation Adsorption Bacterial sulfate and iron reduction Methane production	7.5	DiTommaso and Elkan,1973 Leenheer and Malcolm, 1973 Peek and Heath, 1973 Leenheer et al., 1976a,b Elkan and Horvath, 1977 Willis et al., 1975
			Illinois		
Tuscola	Dolomite	Hydrochlorite acid	Neutralization Dissolution CO_2 gas production	7.6	Kamath and Salazar, 1986 Panagiotopoulos and Reid, 1986 Brower et al., 1989
			Texas		
Not specified	Miocene sand	(1) Organic acids Organic compounds (2) Alkaline salts Organic compounds	Precipitation Adsorption (inferred)	7.7	Donaldson and Johansen, 1973

7.1.2 Backflushing of Injected Wastes

Backflushing of injected wastes can also be a good way to observe waste/reservoir geochemical interactions. Injected wastes are allowed to backflow (if formation pressure is above the elevation of the wellhead) or are pumped to the surface. Backflowed wastes are sampled periodically (and reinjected when the test is completed); the last sample taken will have had the longest residence time in the injection zone. Keely (1982) and Keely and Wolf (1983) describe this technique for characterizing contamination of near-surface aquifers and suggest using logarithmic time intervals for chemical sampling. The three Florida studies (Sections 7.2, 7.3 and 7.4) all present results from backflushing experiments.

The advantages of backflushing are reduced cost compared with that of monitoring wells and reduced sampling time (sampling takes place only during the test period). Disadvantages include less precise time- and distance-of-movement determinations and the need to interrupt injection and to have a large enough area for backflushed fluid storage before reinjection.

7.2 Case Study No. 1: Pensacola, Florida (Monsanto)

7.2.1 Injection-Facility Overview

Monsanto operates one of the world's largest nylon plants on the Escambia River about 13 miles north of Pensacola, Florida. The construction, operations, and effects of the injection-well system at this site have been extensively documented by the U.S. Geological Survey in cooperation with the Florida Bureau of Geology. Pressure and geochemical effects are reported by Goolsby (1972), Faulkner and Pascale (1975), and Pascale and Martin (1978). Additional microbiological data are reported by Willis et al. (1975) and Elkan and Horvath (1977). Major chemical processes observed at the site include neutralization, dissolution, biological denitrification, and methanogenesis. The geochemical fate of organic contaminants in the injected wastes, however, has not been reported.

The waste is an aqueous solution of organic monobasic and dibasic acids, nitric acid, sodium and ammonium salts, adiponitrile, hexamethylenediamine, alcohols, ketones, and esters (Goolsby, 1972). The waste also contain cobalt, chromium, and copper, each in the range of 1 to 5 mg/L. Waste streams with different characteristics, produced at various locations in the nylon plant, are collected in a large holding tank; this composite waste is acidic. The specific characteristics of the waste varied somewhat as a result of process changes, (e.g., after 1968 more organic acids and nitric acid were added). Until mid-1968, wastes were partially neutralized by pretreatment. After that, unneutralized wastes were injected. No reason was reported for suspending treatment. Goolsby (1972) reports pH measurements ranging from a high of 5.6 in 1967 (at which time the pH was raised before injection by adding aqueous ammonia) to a low of 2.4 in 1971, and Eh ranging from +300 mV in 1967 to +700 mV in 1971. The chemical oxygen demand in 1971 was 20,000 mg/L (see Section 3.1.2 for a discussion of this parameter).

Monsanto began injecting wastes into the lower limestone of the Floridan aquifer in 1963. In mid-1964, a second well was drilled into the formation about 1,000 ft southwest of the first. A shallow monitoring well was placed in the aquifer above the confining layer about 100 ft from the first injection well, and a deep monitoring well was placed in the injection zone about 1,300 ft south of both injection wells. The deep monitoring well (henceforth referred to as the near-deep monitoring well) was plugged with cement in 1969 (see below). In late 1969 and early 1970, two additional deep monitoring wells were placed in the injection formation, 1.5 miles south-southeast (downgradient) and 1.9 miles north-northwest (upgradient) of the site. From 1963 to 1977, about 13.3 billion gallons of waste were injected. During the same period, injection pressures ranged from 125 to 235 psi. Figure 7-1 shows the location of all wells as of 1977; since then, a third injection well has been added (Haberfeld, 1989a).

Ten months after injection of neutralized wastes began, chemical analyses (see Section 7.2.3) indicated that dilute wastes had migrated 1,300 ft to the nearest deep monitoring well. Injection of unneutralized wastes began in April 1968. Approximately 8 months later, unneutralized wastes reached the near-deep monitoring well, indicating that the neutralization capacity of the injection zone between the injection wells and the monitoring well had been exceeded. At this point, the monitoring well was plugged with cement from bottom to top because operators were concerned that the acidic wastes could corrode the steel casing and migrate upward (Goolsby, 1972). The rapid movement of the waste through the limestone indicated that most of it migrated through a more permeable section, which was about 65 ft thick. By mid-1973, 10 years after injection began, a very dilute waste front arrived at the south monitoring well, 1.5 miles away. As of early 1977, there was no evidence that wastes had reached the upgradient monitoring well. The shallow monitoring well remained unaffected during the same period.

Figure 7-1 Location of Three Monitoring and Two Injection Wells, Monsanto Facility (Pascale and Martin, 1978).
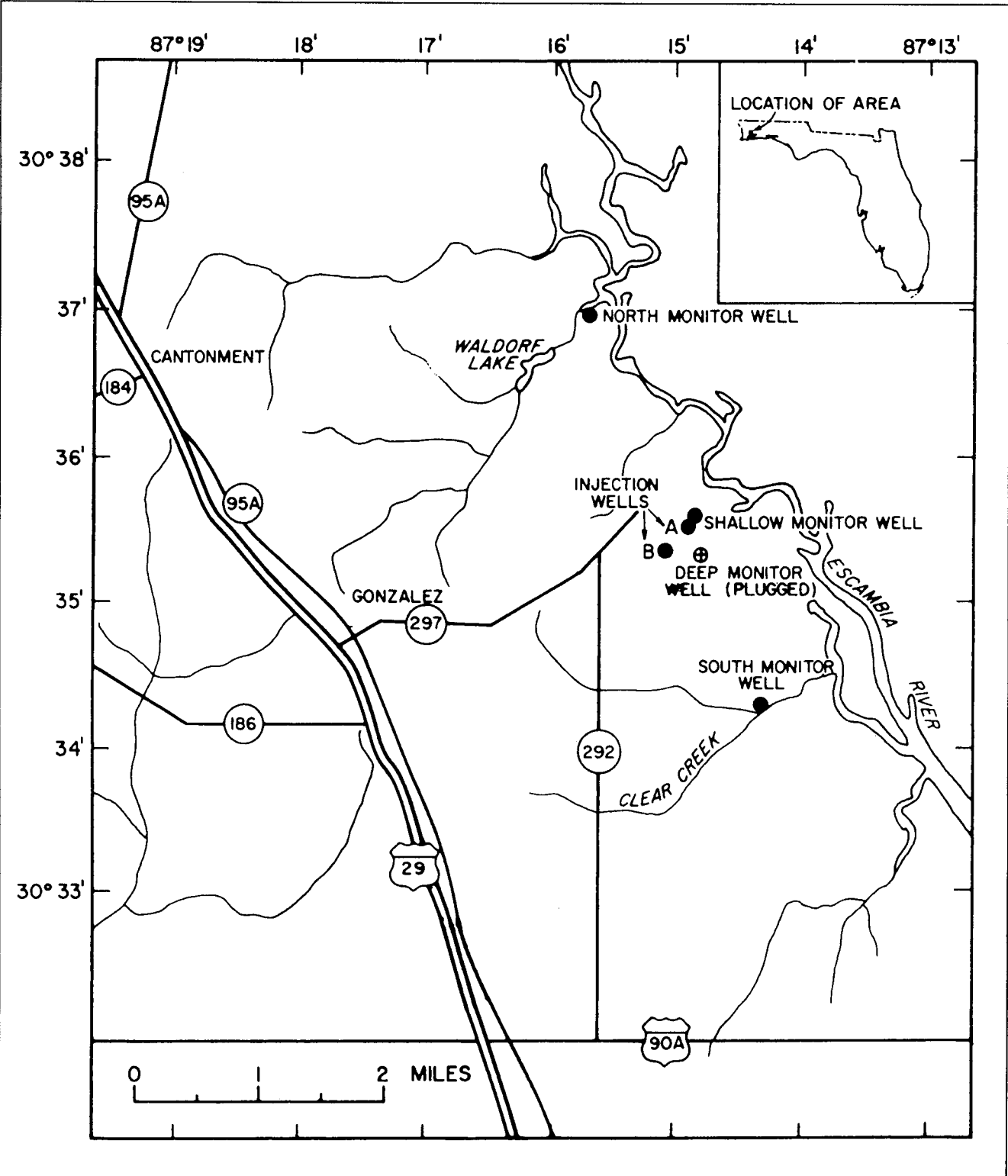
Increases in permeability caused by limestone dissolution approximately doubled the injection index (the amount of waste that can be injected at a specified pressure). As of 1974, the effects of the pressure created by the injection were calculated to extend more than 40 miles radially from the injection site (Faulkner and Pascale, 1975). An updip movement of the freshwater/saltwater interface in the injection-zone aquifer, which lies less than 20 miles from the injection wells, was also observed (see Figure 7-2).

7.2.2 Injection/Confining-Zone Lithology and Chemistry

The lower limestone of the Floridan aquifer is used as the injection zone (at 1,400 to 1,700 ft), and the Bucatunna clay member of the Byram formation (about 220 ft thick) serves as the confining layer. Figure 7-3 shows the stratigraphy of the area, and Figure 7-4 shows the local stratigraphy and the monitoring well installations. The formation water in the injection zone is a highly saline (11,900 to 13,700 mg/L total dissolved solids [TDS]) sodium-chloride solution. The Eh of

samples collected from two monitoring wells located in the injection formation ranged from +23 to -32 mV, indicating reducing conditions in the injection zone that would favor anaerobic biodegradation. Table 6-6 in Chapter Six contains additional data on the chemistry of the Floridan aquifer formation water.

The injection zone contains about 7,900 mg/L chloride, but less than 20 miles northeast of the injection site, chloride concentrations are less than 250 mg/L. Under natural conditions, water in the injection zone moves slowly south-southwestward toward the Gulf of Mexico, where it is assumed to discharge about 100 miles offshore. The preinjection hydraulic gradient was about 1.3 ft/mile (see Figure 7-2).

7.2.3 Chemical Processes Observed

As a result of dissolution of the limestone by the partly neutralized acid wastes, calcium concentrations more than doubled in the near-deep monitoring well 10 months after injection started in 1963 (Goolsby, 1972). In early 1966, however, they dropped to background levels (about 200 mg/L), possibly in response to biochemical decomposition of the waste. In September

Figure 7-2   Hydrogeology of the Lower Limestone of the Floridan Aquifer in Northwest Florida (Goolsby, 1972).

145
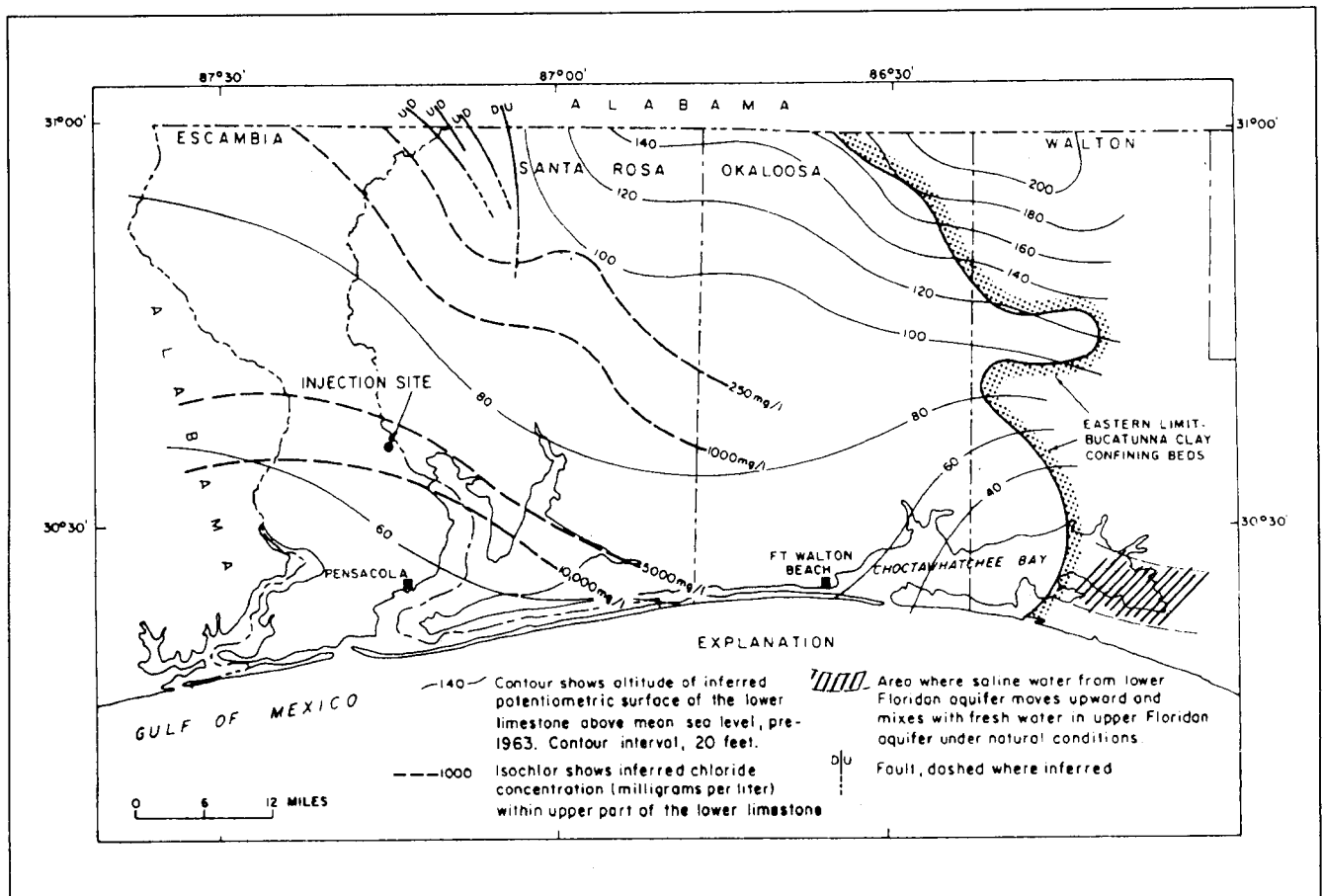
Figure 7-3 Generalized North-South Geologic Section Through Southern Alabama and Northwestern Florida (Goolsby, 1972).
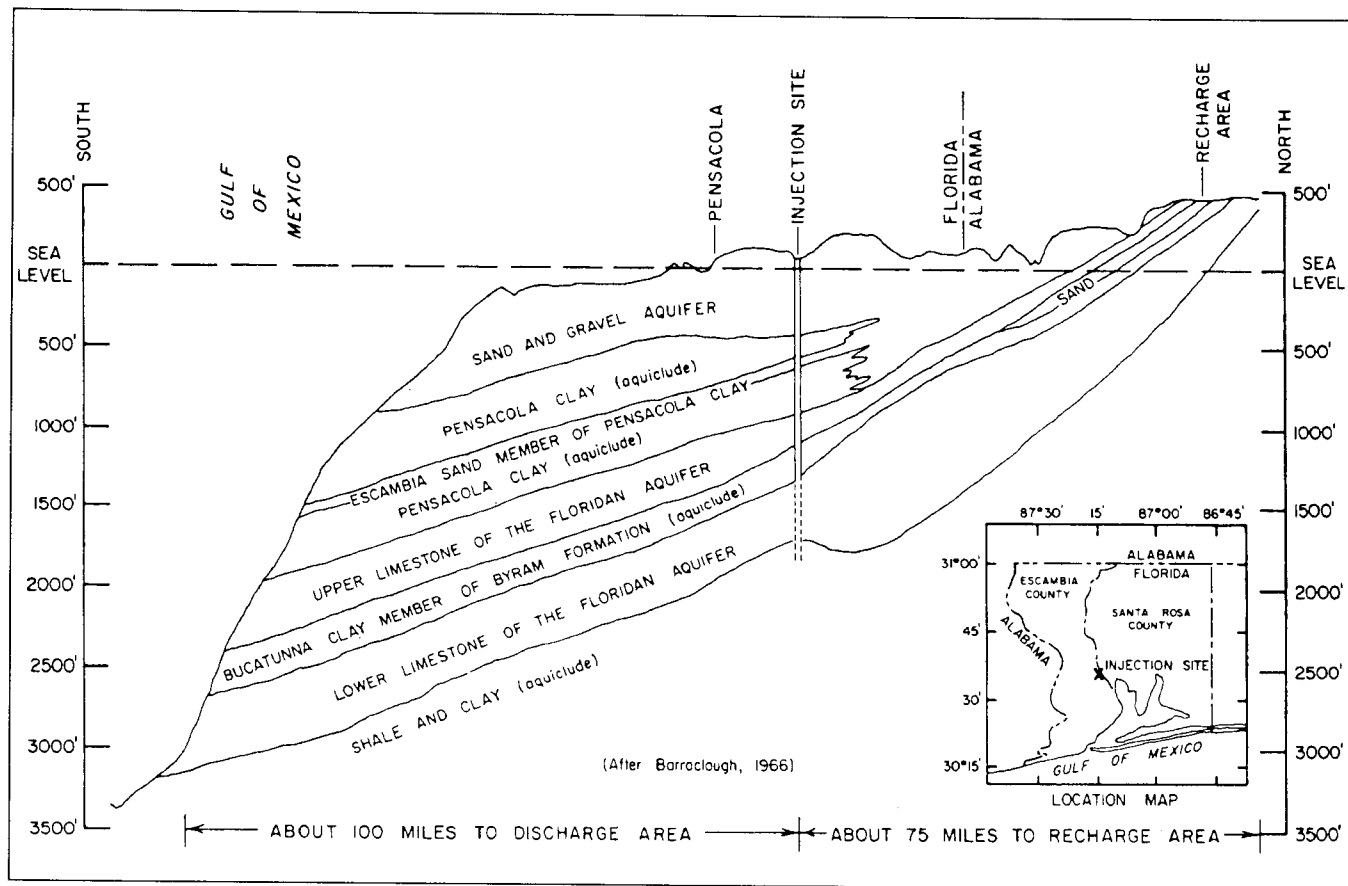
1968, after about 300 million gallons of the acidic, unneutralized waste had been injected, the calcium concentration began to increase again. An abrupt increase in calcium to 2,700 mg/L accompanied by a decrease in pH to 4.75 in January 1969 led to the decision to plug the near-deep monitoring well.

In an attempt to find out how fast the waste was reacting with limestone, a 3-hour backflushing experiment, in which waste was allowed to flow back out of the injection well, yielded some unexpected results. The increase in pH of the neutralized waste could not be fully accounted for by the solution of limestone as determined from the calcium content of the backflushed liquid; the additional neutralization apparently resulted from reactions between nitric acid and alcohols and ketones in the original waste induced by increased pressure in the injection zone compared to surface conditions (Goolsby 1971).

The lack of nitrates (which were present at levels of 545 to 1,140 mg/L in the waste) in the near-deep monitoring well, combined with the presence of nitrogen gas, indicated that degradation by denitrifying bacteria had taken place (Goolsby, 1972). Backflushing shortly before inject-

ing unneutralized wastes confirmed denitrification. Nitrate concentrations decreased rapidly as the backflushed waste was replaced by formation water. Similar backflushing experiments conducted after unneutralized wastes were injected, however, provided no evidence of denitrification, indicating that microbial activity was suppressed in the portion of the zone containing unneutralized wastes.

Elkan and Horvath (1977) performed a microbiological analysis of samples taken from the north and south deep monitoring wells in December 1974, about 6 months after the dilute waste front had reached the south well. Both denitrifying and methanogenic bacteria were observed. The lower numbers and species diversity of organisms observed in the south monitoring well compared with those in the north well indicated suppression of microbial activity by the dilute wastes.

Chemical analyses of the north and south monitoring wells were published for the period March 1970 to March 1977 (Pascale and Martin, 1978). Between September 1973 and March 1977 bicarbonate concentrations increased from 282 mg/L to 636 mg/L and dissolved organic carbon increased from 9 mg/L to

146

Figure 7-4 Monsanto Injection Facility Hydrogeologic Cross-Section (Faulkner and Pascale, 1975).
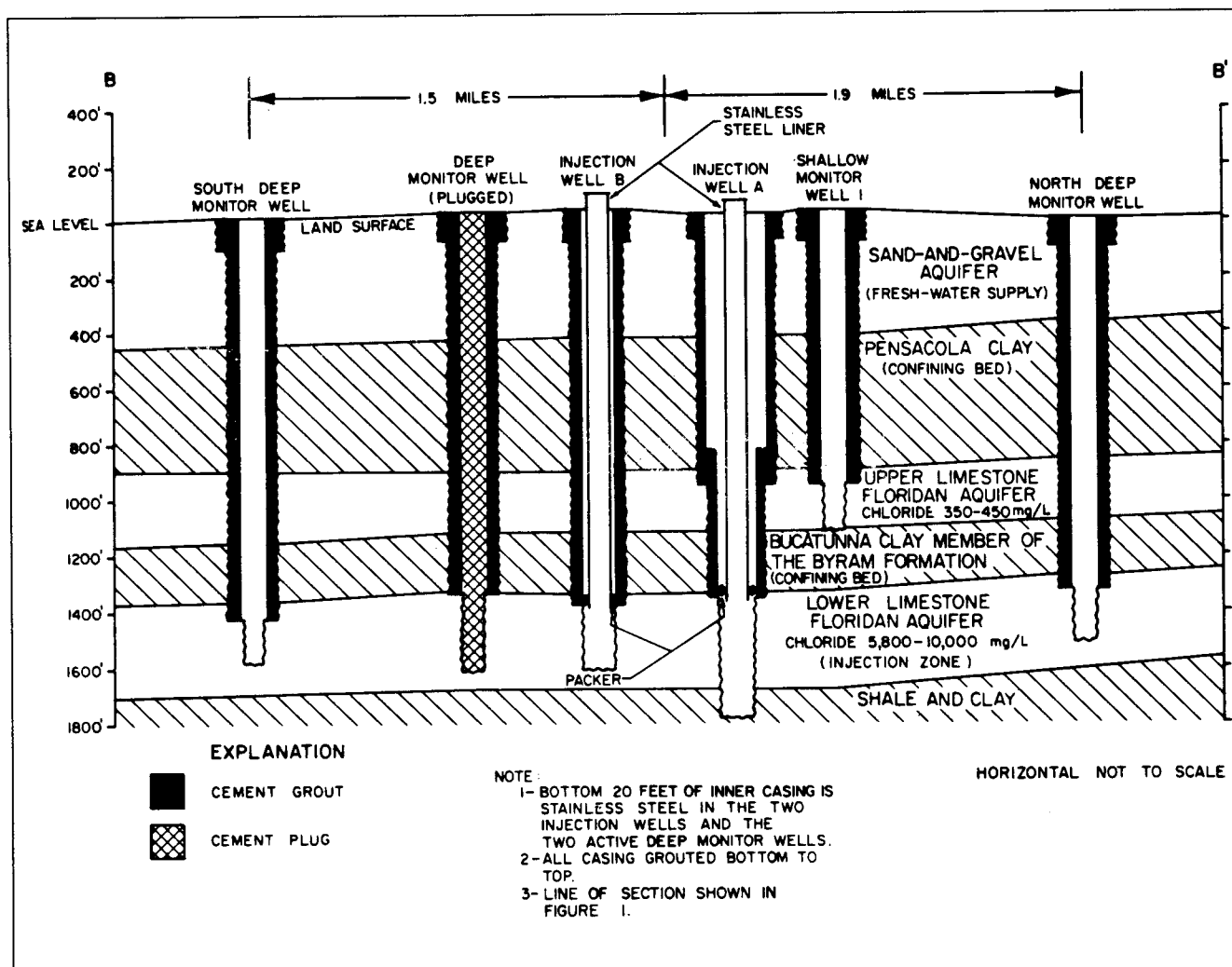
47 mg/L. These increases were accompanied by an increase in the dissolved-gas concentration and a distinctive odor like that of the injected wastes. The pH, however, remained unchanged. During the same period, dissolved methane increased from 24 mg/L to 70 mg/L, indicating increased activity by methanogenic bacteria. The observation of denitrification in the near-deep monitoring well and methanogenesis in the more distant south monitoring well fit the redox-zone biodegradation model discussed in Section 5.2.3.3 (see also Table 5-5).

Significant observations made at this site are: (1) organic contaminants (as measured by dissolved organic carbon) continue to move through the aquifer even when acidity has been neutralized, and (2) even neutralized wastes can suppress microbial populations.

7.3 Case Study No. 2: Pensacola, Florida (American Cyanamid)

7.3.1 Injection-Facility Overview

American Cyanamid Company operates a plant near Milton, Florida, which lies about 12 miles northeast of Pensacola and about 8 miles east of the Monsanto plant discussed in Section 7.2. Chemical changes caused by the injection of acidic wastes from this plant have been reported by Ehrlich et al. (1979) and Vecchioli et al. (1984), with the former citation providing the most complete information on the site. This case study illustrates the complexity of assessing the geochemical fate of mixed wastes. Acrylonitrile was detoxified by biological reduction, whereas sodium thiocyanate remained unaltered.

The facility combines acidic waste streams from various plant operations in a holding pond where they are mixed and aerated. The waste is pumped from the pond and neutralized with sodium hydroxide. The neutralized wastes are treated with alum to flocculate suspended solids and then passed through mixed-media filters. A small amount of hydrogen peroxide solution (amount unspecified) is added before filtration to inhibit microbial growth on the filters. The pretreated waste that is injected contains high concentrations of sodium nitrate, sodium sulfate, sodium thiocyanate (an inorganic cyanide compound), and various organic compounds, including acrylonitrile (a listed hazardous waste—see Table 4-10). The average pH of the waste is 5.8; average chemical oxygen demand is 1,690 mg/L.

A primary injection well and a standby well are situated about 1,500 ft apart. A shallow monitoring well is located near the primary injection well in the upper limestone Floridan aquifer that overlies the confining Bucatunna clay. Two deep monitoring wells in the injection zone are located 1,000 ft southwest, and 8,170 ft northeast of the primary injection well. Figure 7-5 shows the locations of the injection and monitoring wells.

Waste injection began in June 1975, and waste was first detected in the downgradient southwest deep monitoring well about 260 days later. To analyze the waste's physical and chemical properties after injection, the primary injection well was allowed to backflow into a holding pond for 5 days in November, 1977. This waste was sampled periodically (and reinjected when the test was completed). About 4 years after injection began (mid-1979), dilute waste arrived at the standby injection well 1,560 ft south of the primary well.

7.3.2 Injection/Confining-Zone Lithology and Chemistry

The injection well is in the same area as the Monsanto well, so the geology and native-water chemistry are very similar to that described in Section 7.2. Figure 7-6 shows the stratigraphy of the immediate area and distances between the injection and monitoring wells. The lower limestone of the Floridan aquifer is used as the injection zone (1,230 to 1,440 ft), and the confining Bucatunna clay is about 165 ft thick. TDS levels range from 12,000 to 12,700 mg/L, with chloride ion concentrations of 6,700 mg/L. The pH ranges from 7.3 to 7.6, and temperature, from 30° to 32°C. Table 6-6 contains additional data on the chemistry of the formation water. Caliper and flowmeter tests made in the injection wells suggest that the waste moves almost exclusively within the top 18 m (55 ft) of the lower limestone. As discussed in Section 7.2.2, the preinjection ground-water flow direction is south-southwest (see Figure 7-2).

7.3.3 Chemical Processes Observed

The Eh of the injected waste dropped rapidly from +40 mV to -80 mV in the first 40 hours after injection began and remained at about -80 mV thereafter. Denitrifying bacteria detoxified the acrylonitrile by mineralizing the compound, breaking it down into bicarbonate and ammonia. The nitrates were degraded to nitrogen gas. The backflow test described in Section 7.3.1 produced data indicating that these transformations were about 90% complete within 82 ft of the injection well and virtually 100% complete within 328 ft. These results are an example of a biodegradation-dispersion curve (see Figure 2-2 in Chapter Two). Denitrifying-bacteria densities increased from traces (10^1 organisms/100 mL in the native ground water) to large populations (10^7 to 10^8 organisms/100 mL) in injected wastes that had been in the aquifer for several days.

Sodium thiocyanate (NaSCN) was first detected in the closest monitoring well (1,000 ft away) 260 days after injection began. Ammonium ions (a reaction product of biomineralization) did not appear as a contaminant until 580 days after initial injection. This delay was probably the result of ion exchange or other adsorption processes and may be an example of an adsorption-dispersion curve (see Figure 2-2 in Chapter Two). Because sodium thiocyanate in the waste remained unchanged during its movement through the injection zone, it was used to detect the degree of mixing that took place between the waste liquid and native water in an observation well. Thus the appearance of sodium thiocyanate as well as an increase in chemical oxygen demand in the standby well 4 years after injection began signaled the arrival of wastes at that location.

This case study is interesting in that one hazardous waste (acrylonitrile) was quickly rendered nonhazardous after injection, whereas another (sodium thiocyanate) showed no evidence of decomposition during the duration of the study. The implication for geochemical fate assessment is that research should focus on the compounds likely to be most resistant to decomposition and/or immobilization, since they will be the ones most critical in demonstrating containment in a no-migration petition.

7.4 Case Study No. 3: Belle Glade, South-Central Florida

7.4.1 Injection-Facility Overview

The Belle Glade site, located southeast of Lake Okeechobee in south-central Florida (see Figure 7-7), illustrates some of the problems that can develop with acidic-waste injection when carbonate rock is the

Figure 7-5   Location of the American Cyanimid Injection Site and Monitoring Wells (Ehrlich et al., 1979).
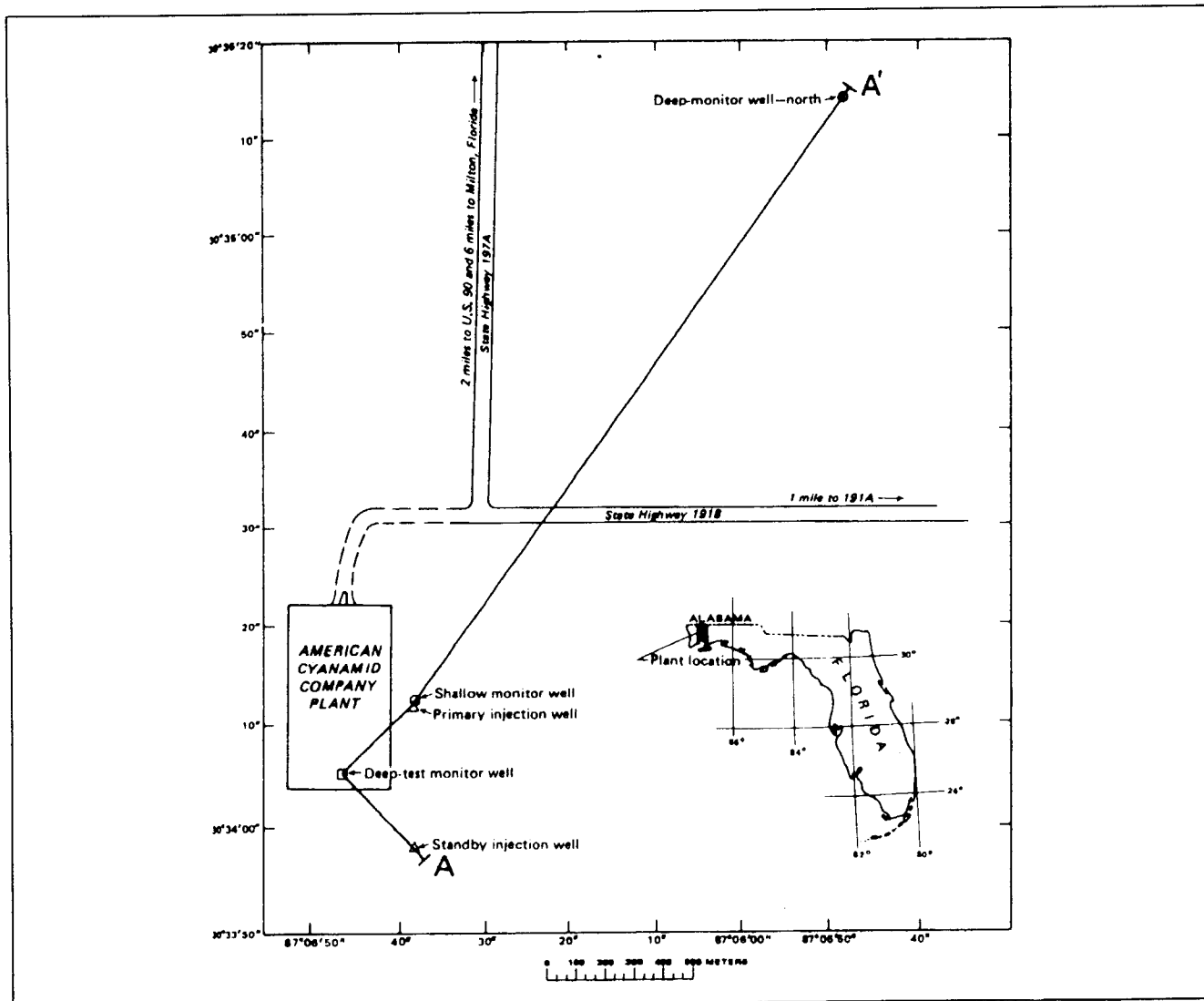
confining layer. Contributing factors to the contamination of the aquifer above the confining zone were the dissolution of the carbonate rock and the difference in density between the injected wastes and the formation fluids. The injected waste was less dense than the ground water because of its lower salinity and higher temperature (Kaufman et al., 1973).

The injected fluids include the effluent from a sugar mill and the waste from the production of furfural, an aldehyde processed from the residues of processed sugar cane. The waste is hot (about 75° to 93°C); acidic (pH 2.6 to 4.5); and has high concentrations of organics, nitrogen, and phosphorus (Kaufman and McKenzie, 1975). The waste is not classified as hazardous under 40 CFR 261, and the well is currently regulated by the State of Florida as a nonhazardous

injection well (Haberfeld, 1989b). The organic carbon concentration exceeds 5,000 mg/L.

The well was originally cased to a depth of 1,495 ft, and the zone was left as an open hole to a depth of 1,939 ft. The depth of the zone has been increased twice (see later discussion). Seasonal injection (fall, winter, and spring) began in late 1966; the system was inactive during late summer. Injection rates ranged from 400 to 800 gallons per minute, and wellhead injection pressures ranged from 30 to 60 psi. By 1973 injection had become more or less continuous. From 1966 to 1973, more than 1.1 billion gallons of waste were injected (Kaufman et al., 1973).

At the time injection began, a shallow monitoring well was placed 75 ft south of the injection well in the upper

Figure 7-6 American Cyanamid Injection Facility Hydrogeologic Cross Section (Ehrlich et al., 1979).
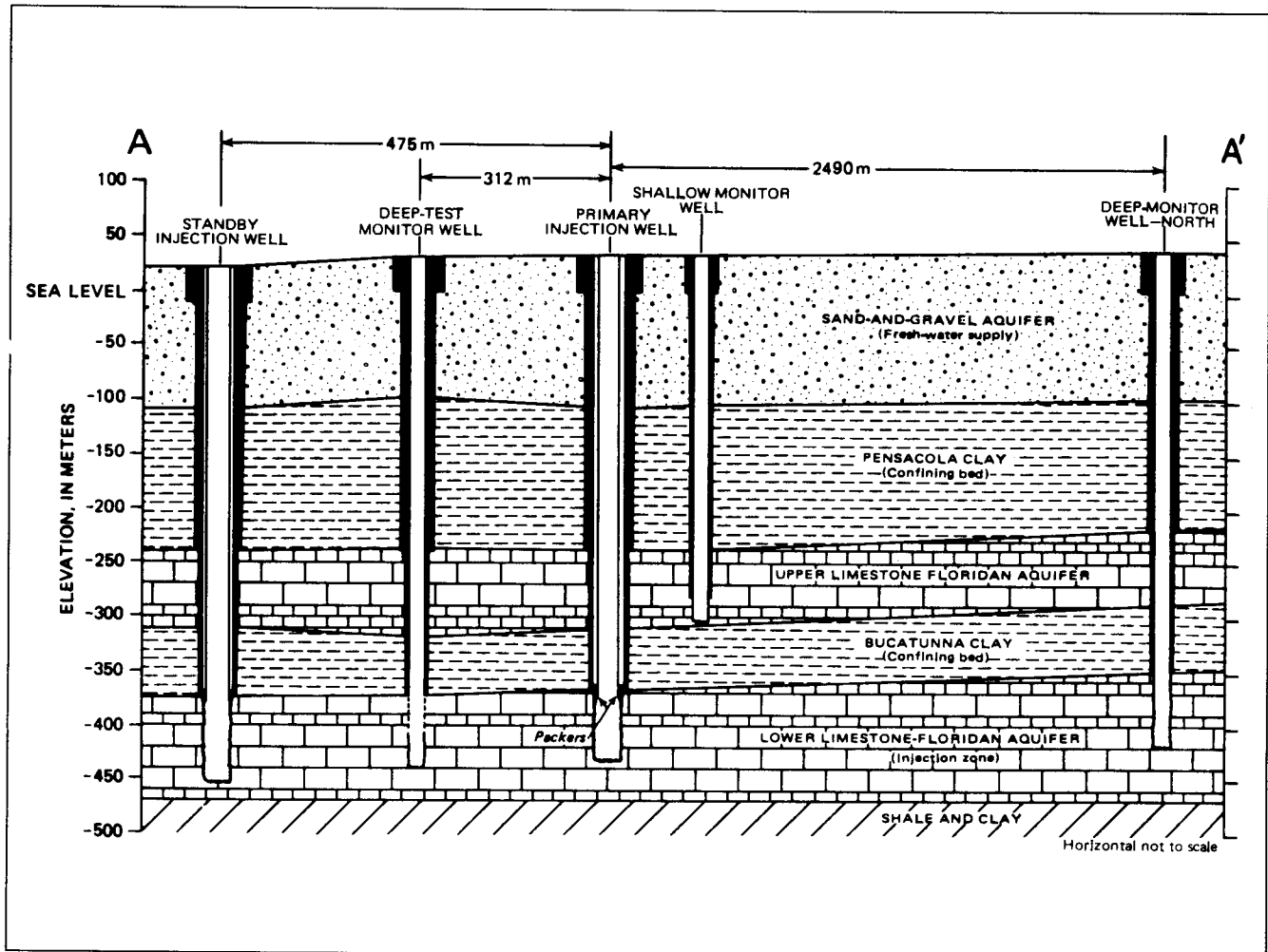
part of the Floridan aquifer above the confining layer. A downgradient, deep monitoring well was placed in the injection zone 1,000 ft southeast of the injection well (see Figure 7-7). Another shallow well, located 2 miles southeast of the injection site at the University of Florida's Everglades Experiment Station, has also been monitored for near-surface effects.

Acetate ions from the injected waste were detected in the deep monitoring well 1,000 ft southeast of the injection well in early 1967, a matter of months after injection began (Garcia-Bengochea and Vernon, 1970). In 1971, about 27 months after injection began, evidence of waste migration was detected at a shallow monitoring well in the upper part of the Floridan aquifer (see Section 7.4.3 for discussion of geochemical evidence). Dissolution of the carbonate confining layer by the acidic waste was the main reason for the upward migration. However, the lower density of the injected wastes compared with that of the formation waters

(0.98 g/mL vs. 1,003 g/mL) served to accelerate the rate of upward migration (Kaufman et al., 1973). In an attempt to prevent further upward migration, the injection well was deepened to 2,242 ft, and the inner casing was extended and cemented to 1,938 ft. When waste injection was resumed, evidence of upward migration to the shallow aquifer was observed only 15 months later. By late 1973, 7 years after injection began, the waste front was estimated to have migrated 0.6 to 1 mile from the injection well (Kaufman and McKenzie, 1975).

The injection well was deepened a third time, to a depth of 3,000 ft (McKenzie, 1976). A new, thicker confining zone of dense carbonate rock separates the current injection zone from the previous zone (see Figure 7-8—the current injection zone is not shown). As of early 1989, the wastes were still contained in the deepest injection zone (Haberfeld, 1989b).

7.4.2 Injection/Confining-Zone Lithology and Chemistry

The wastes are injected into the lower part of the carbonate Floridan aquifer, which is extremely permeable and cavernous (see Figure 7-8). The natural direction of ground-water flow is to the southeast (see Figure 7-7). The confining layer is 150 ft of dense carbonate rocks. The chloride concentration in the upper part of the injection zone is 1,650 mg/L, increasing to 15,800 mg/L near the bottom of the formation (Kaufman et al., 1973). The sources used for this case study did not provide any data on the current injection zone. The native fluid was basically a sodium-chloride solution but also included significant quantities of sulfate (1,500 mg/L), magnesium (625 mg/L), and calcium (477 mg/L). See Table 6-6 in Chapter Six for additional data on the chemistry of the formation water.

7.4.3 Chemical Processes Observed

Neutralization of the injected acids by the limestone formation led to concentrations of calcium, magnesium, and silica in the waste solution that were higher than those in the unneutralized wastes. Anaerobic decomposition of the organic matter in the injected waste apparently occurred through the action of both sulfate-reducing and methanogenic bacteria. Sulfate-reducing bacteria were observed in the injected wastes that were allowed to backflow to the surface. Sulfate levels in the native ground water declined by 45%, and the concentration of hydrogen sulfide increased by 1,600%. Methane fermentation (reduction of CO_2 to CH_4) was also inferred from the presence of both gases in the backflow fluid, but the presence of methanogenic bacteria was not confirmed. Increased hydrogen sulfide concentrations produced by the bacteria during biodegradation and the subsequent decrease in sulfate/chloride ratio in the observation wells were taken as indicators of upward and lateral migration. Migration into the shallow monitoring well was also indicated by a decline in pH from around 7.8 to 6.5, caused by mixing with the acidic wastes.

Chemical analyses of the backflowed injected waste that had been in the aquifer for about 2.5 months (for which some dilution had occurred) indicated that chemical oxygen demand (COD) was about half that of the

Figure 7-7   Index Map of Belle Glade Area and Potentiometric-Surface Map of the Floridan Aquifer in South Florida (Kaufman et al., 1973).
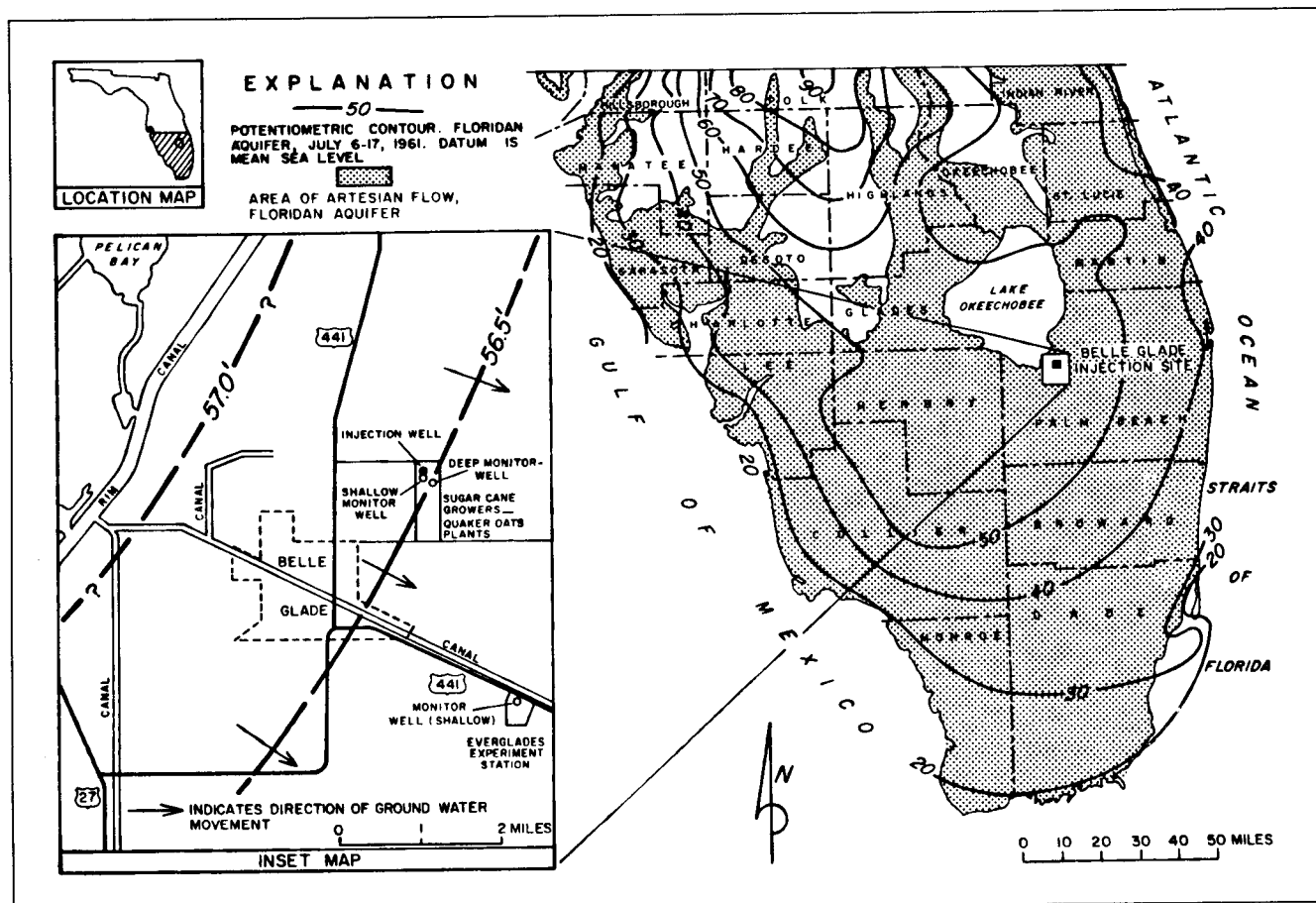
Figure 7-8 Generalized Hydrogeologic Section between Belle Glade and the Straits of Florida (Kaufman and McKenzie, 1975).
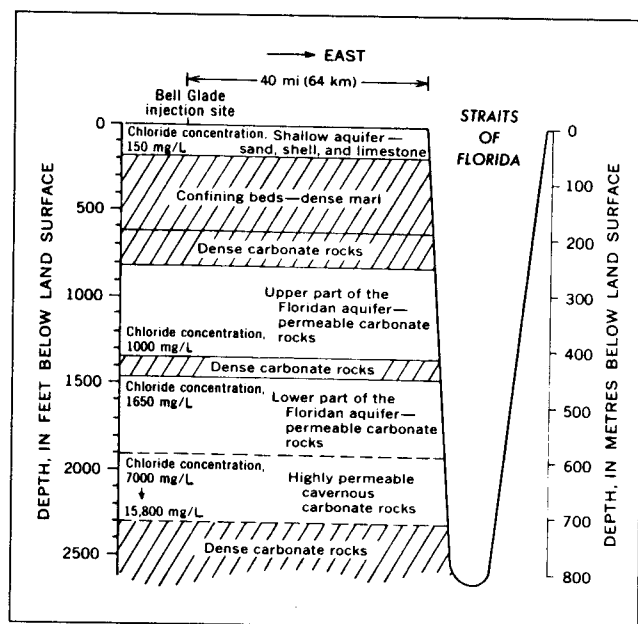
original waste. Samples that had been in residence for about 5 months had a COD approximately one-quarter that of the original waste (12,200 mg/L in the original waste compared with 4,166 mg/L in the samples). The percent reduction in COD resulting from bacterial action rather than dilution was not estimated.

7.5 Case Study No. 4: Wilmington, North Carolina

7.5.1 Injection-Facility Overview

The Hercules Chemical, Inc. (now Hercufina, Inc.), facility, 4 miles north of Wilmington, North Carolina, attempted deep-well injection of its hazardous wastes from May 1968 to December 1972, but had to discontinue injection because of waste-reservoir incompatibility and unfavorable hydrogeologic conditions. The U.S. Geological Survey conducted extensive geochemical studies of this site until the well was abandoned (Leenheer and Malcolm, 1973; Peek and Heath, 1973; Leenheer et al., 1976a,b). Biodegradation processes were also studied (DiTommaso and Elkan, 1973; Elkan and Horvath, 1977). More geochemical-fate processes affecting injected organic wastes have been documented at this site than at any other.

Hercules Chemical produced an acidic organic waste derived from the manufacture of dimethyl terphthalate, which is used in the production of synthetic fiber. The average dissolved organic carbon concentration was about 7,100 mg/L and included acetic acid, formic acid,

p-toluic acid, formaldehyde, methanol, terphthalic acid, and benzoic acid. The pH ranged from 3.5 to 4.0. The waste also contained traces (less than 0.5 mg/L) of 11 other organic compounds, including dimethyl phthalate, a listed hazardous waste (see Table 4-8 in Chapter Four).

From May 1968 to December 1972, the waste was injected at a rate of about 300,000 gallons per day. The first injection well (I-6) was completed to a depth of 850 to 1,025 ft (i.e., cased from the surface to 850 ft with screens placed in the most permeable sections of the injection zone to a depth of 1,025 ft). One shallow observation well (No. 3) was placed 50 ft east of the injection site at a depth of 690 ft. Four deep monitoring wells (Nos. 1, 2, 4, and 5) were also placed in the injection zone, one at 50 ft and three at 150 ft from the injection well (see Figure 7-9).

The injection well became plugged after a few months of operation because of the reactive nature of the wastes and the low permeability of the injection zone. The actual plugging process was caused both by reprecipitation of the initially dissolved minerals and by plugging of pores by such gaseous products as carbon dioxide and methane. When the first well failed, a second injection well (I-7A) was drilled into the same injection zone about 5,000 ft north of the first, and injection began in May 1971. Nine additional monitoring wells (three shallow, Nos. 8, 9, and 13, and six deep, Nos. 7, 11, 12, 14, 15, and 16) were placed at distances ranging from 1,500 to 3,000 ft from the second injection well (see Figure 7-9). Injection was discontinued in 1972 after the operators determined that the problems of low permeability and waste-reservoir incompatibility could not be overcome. Monitoring of the waste movement and subsurface environment continued into the mid-1970s in the three monitoring wells located 1,500 to 2,000 ft from the injection wells.

Within 4 months, the waste front had passed the deep observation wells located within 150 ft of the injection well (Nos. 1, 2, 4, and 5). About 9 months after injection began, leakage into the aquifer above the confining layer was observed (Well No. 3). This leakage was apparently caused by the increased pressures created by formation plugging and by the dissolution of the confining beds and the cement grout surrounding the well casing of several of the deep monitoring wells, caused by organic acids.

Eight months after injection began in the second injection well, wastes had leaked upward into the adjacent shallow monitoring well (Well No. 9). The leak apparently was caused by the dissolution of the cement grout around the casing. In June 1972, 13 months after

152

Figure 7-9   Map of Wilmington, North Carolina, Waste-Injection and Observation Wells (Leenheer and Malcolm, 1973).
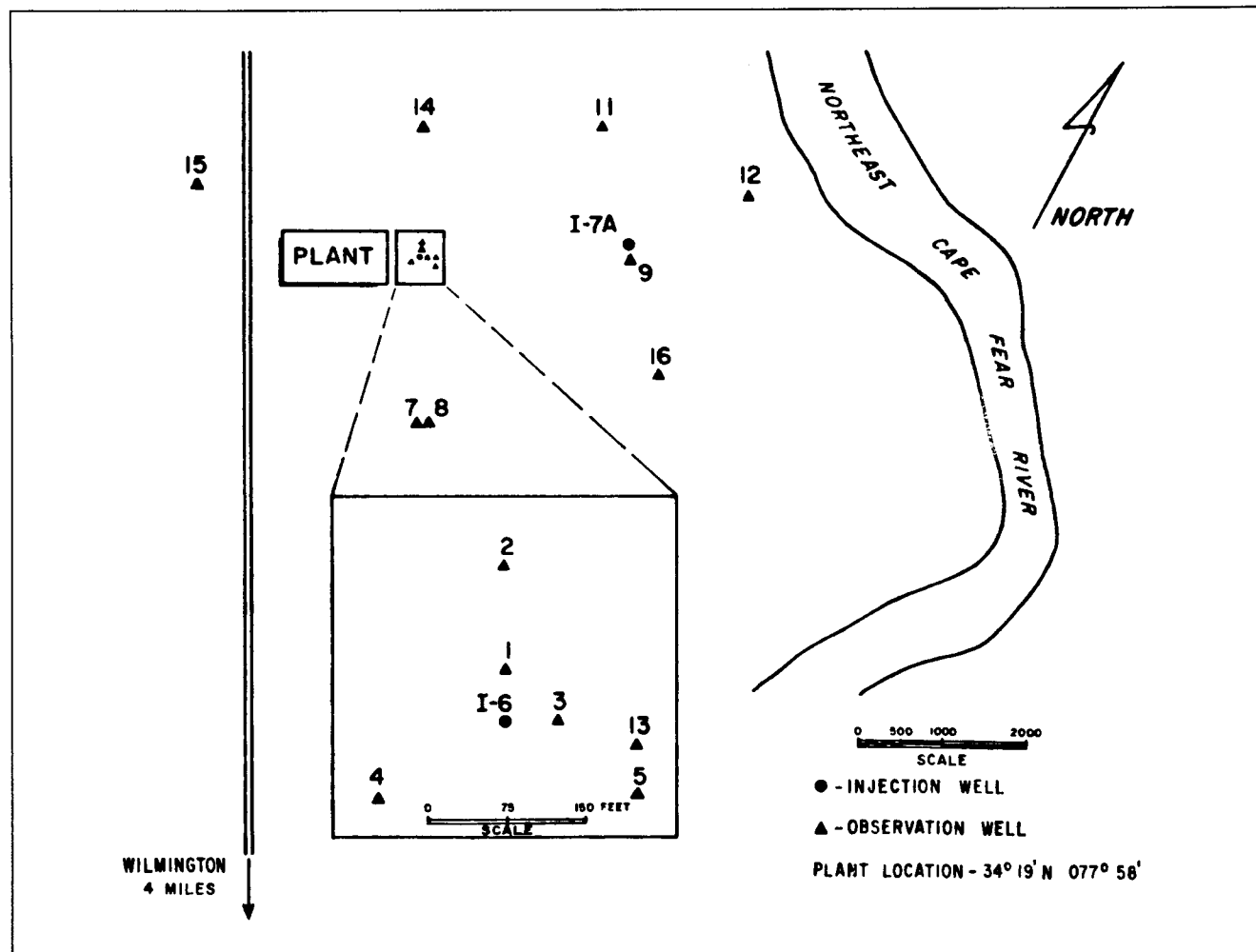
injection began in the second well, the waste front reached the deep monitoring well located 1,500 ft northwest of the injection well (No. 14), and in August 1972 waste was detected in Well No. 11 (about 1,000 ft north of injection well I-7A). Waste injection ended in December 1972. As of 1977, the wastes were treated in a surface facility (Elkan and Horvath, 1977).

7.5.2 Injection/Confining-Zone Lithology and Chemistry

The injection zone consisted of multiple Upper Cretaceous strata of sand, silty sand, clay, and some thin beds of limestone (see Figure 7-10). The clay confining layer was about 100 ft thick. The total-dissolved-solids concentration in the injection-zone formation water was 20,800 mg/L, with sodium chloride the most abundant constituent (see Table 6-6 in Chapter Six for additional data on the chemistry of the formation water).

7.5.3 Chemical Processes Observed

A number of chemical processes were observed at the site (Leenheer and Malcolm, 1976a,b):

■ The waste organic acids dissolved carbonate minerals, alumino-silicate minerals, and iron/manganese-oxide coatings on the primary minerals in the injection zone.

■ The waste organic acids dissolved and formed complexes with iron and manganese oxides. These dissolved complexes reprecipitated when the pH increased to 5.5 or 6.0 because of neutralization of the waste by the aquifer carbonates and oxides.

■ The aquifer mineral constituents adsorbed most waste organic compounds except formaldehyde. Adsorption of all organic acids except phthalic acid increased with a decrease in waste pH.

153

Figure 7-10 Diagram Showing Construction Features and Lithologic Log of Well 14, Wilmington, North Carolina (Leenheer and Malcolm, 1973).
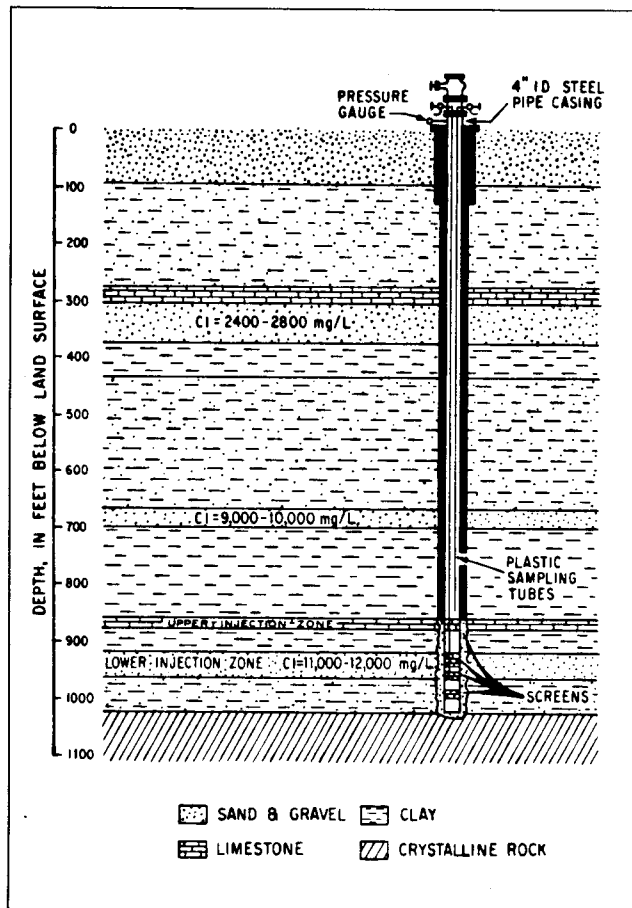
■ Phthalic acid was complexed with dissolved iron. The concentration of this complex decreased as the pH increased because the complex coprecipitated with the iron oxide.

■ Biochemical waste transformation occurred at low waste concentrations, resulting in the production of methane. Additional microbial degradation of the waste resulted in the reduction of sulfates to sulfides and ferric ions to ferrous ions.

When the dilute waste front reached Well No. 14, in June 1972, microbial populations rapidly increased in this well, with methanogenesis being the major degradative process (DiTommaso and Elkan, 1973). Elkan and Horvath (1977) found greater numbers and species diversity of microorganisms in Well No. 11, which contained dilute wastes, than in Well No. 7, which was uncontaminated. In laboratory experiments, however, DiTommaso and Elkan (1973) found that bacterial growth was inhibited as the concentration of

waste increased and could not decompose the waste at the rate it was being injected.

This case study illustrates the importance of dissolution/precipitation reactions in determining waste-reservoir compatibility. Adsorption was observed to immobilize most of the organic constituents in the waste except for formaldehyde. As with the Monsanto case study, biodegradation was an important process when wastes were diluted by formation waters, but the process became inhibited when undiluted waste reached a given location in the injection zone.

7.6 Case Study No. 5: Illinois Hydrochloric Acid-Injection Well

7.6.1 Injection-Facility Overview

This case study is an example of a well blowout resulting from the neutralization of acid by carbonate rock. Kamath and Salazar (1986) and Panagiotopoulos and Reid (1986) both discuss the same incident. Although they do not specify the location, Brower et al. (1989) identify the site as the Cabot Corporation injection well, near Tuscola, Illinois.

The waste hydrochloric acid (HCl) injected at the site was a byproduct of a combustion process at 2,972°F. When not recovered, the acidic stream was dumped into holding ponds where it was cooled to about 75°F before injection. The concentration of injected acid typically varied from 0.5 to 5% HCl, but ranged as high as about 30%. (The pH of injected acid that backflowed during one blowout incident ranged from 0.5 to 1.3.)

The injection well was cased to a depth of about 4,900 ft and extended into dolomite to a total depth of 5,300 ft. Injection began in the early 1960s and averaged around 90 gallons per minute (gpm). The natural fluid level was 200 ft below the wellhead, and wastes were injected using gravity flow, i.e., the pressure head of the well when filled to the surface with fluid was sufficient to inject fluids without pumping under pressure (Kamath and Salazar, 1986).

Between 1973 and 1975, several blowouts caused surface water pollution and fishkills. The most serious occurred in 1975 after unusually high concentrations of HCl (around 30%) were injected intermittently for several weeks. The well refused to accept additional acid under gravity flow. At first the operators thought the well bore had become plugged, and they pumped a concentrated calcium-chloride solution down the hole to dissolve precipitates that might have formed. Shortly thereafter the well tubing broke, pressure suddenly

154

rose to 450 psi, and a section of the upper tubing was ejected through the wellhead along with acid and annulus fluids. Backflow was stopped for a while by draining cold water from a fire hydrant into the well at 50 gpm. The well erupted again the next day, however, with a 10-ft gusher discharging at 250 gpm. The blowout was brought under control 2 days later when a blowout preventer was installed.

7.6.2 Injection/Confining-Zone Lithology and Chemistry

The injection zone was a cavernous dolomite, and the native ground water was very saline, with TDS levels ranging from 21,000 to 26,000 mg/L. No information was provided on the confining layer, but it is discussed in Brower et al. (1989) in detail.

7.6.3 Chemical Processes Observed

The HCl dissolved the dolomite, forming carbon dioxide (CO_2) gas. Under normal circumstances this gas remains in solution, but if the temperature of the acid and/or the acid concentration exceed certain limits, CO_2 evolves as a gas and accumulates in the upper portion of the cavity. The escape of even small amounts of CO_2 into the injection pipe can serve as a driving force to reverse the flow of the injected liquids, because as the CO_2 rises, pressure decreases and the gas expands.

There is some disagreement as to which parameter is most critical to gas blowout. Based on analysis of CO_2 phase behavior at different temperatures and pressures, Kamath and Salazar (1986) concluded that gas blowout becomes hazardous if the temperature of the injected HCl exceeds 88°F. Panagiotopoulos and Reid (1986) concluded that HCl concentration is the critical factor and that HCl concentrations exceeding 6% will evolve CO_2 gas and create a blowout hazard. Both sets of investigators explained the circumstances of this case study in terms of their respective models.

7.7   Case Study No. 6: Texas Petrochemical Plant

7.7.1 Injection-Facility Overview

This case study involves an unnamed petrochemical plant located about 15 miles inland from the Texas Gulf Coast, described by Donaldson and Johansen (1973). It illustrates two approaches to injecting incompatible waste streams to prevent well plugging by precipitation: surface treatment and multiple injection wells.

The plant began full-scale operation in 1962 and produced acetic, adipic, and propionic acids;

acetaldehyde; butanol; hexamethyldiamine; vinyl acetate; nylon; and other chemical products from petroleum-base stocks. The effluent was collected at waste treatment facilities as two separate mixtures. Because mixing two waste streams produced considerable precipitation, the waste streams were processed and injected separately into two wells.

Organic constituents in the first waste stream totaled about 14,000 mg/L (acetaldehyde, acetaldol, acetic acid, butanol-1, butyraldehyde, chloroacetaldehyde, crotonaldehyde, phenol, and propionic acid) and about 5,200 mg/L inorganic constituents. The pH ranged from 4 to 6, and TDS ranged from 3,000 to 10,000 mg/L.

The second waste stream contained amines and nitrates generated from the manufacture of nylon, hydrocarbon solvents used in processing, and other minor constituents. Organic constituents (amyl alcohol, cyclohexane, dodecane, hexanol, 1-hexylamine, 1,6-hexylamine, methanol, and valeric acid) totaled about 4,700 mg/L. Inorganic constituents in the second waste stream totaled about 21,350 mg/L, including 7,500 mg/L nitrate and 4,600 mg/L nitrite. The second waste stream was basic, with a pH from 8 to 10. The composition of the wastes changed over time when processes changed or a new unit was installed. Several new process wastes (unspecified) that were incompatible with either waste stream were made compatible by adjusting the pH and diluting them.

Injection began in both wells in mid-1963. The injection zone for Well No. 1 was 45 ft thick beginning at about 3,400 ft below the surface. Well No. 2 was located 2,700 ft north of Well No. 1, and the injection zone was located between 3,520 and 3,550 ft. Donaldson and Johansen (1973) mention no monitoring wells at the site. About 6 years after injection began, pressure interference from the two injection wells was observed. During the same period, the fluid front from Well No. 1 was about 730 ft from the well bore.

7.7.2 Injection/Confining-Zone Lithology and Chemistry

The injection formation was a loosely consolidated, fine-grained Miocene sand (see Figures 7-11 and 7-12). The confining strata between the base of the freshwater aquifer and the injection zone included about 1,200 ft of relatively impermeable shale and clay beds with individual zone thickness ranging from 10 to 245 ft.

7.7.3 Chemical Processes Observed

Wellhead pressures increased when injection was stopped at Well No. 1 for more than 24 hours, apparently

Figure 7-11. North-South Cross Section Showing Oil Wells and Inclination of Major Formations, Texas Petrochemical Plant (Donaldson and Johansen, 1973).

Figure 7-12. Texas Petrochemical Plant Injection Well (Donaldson and Johansen, 1973).
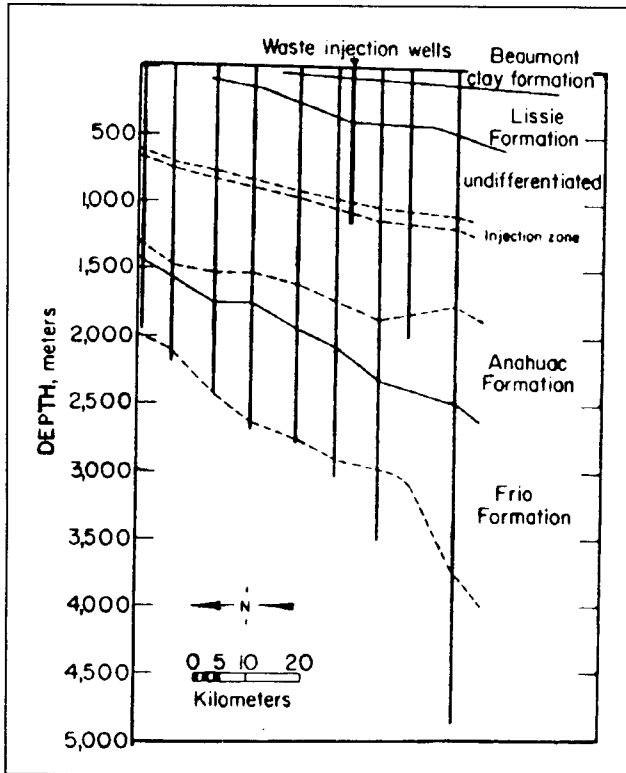
caused by a combination of precipitation reactions and backflow of sand. Injecting a slug of brine after every period of interrupted flow solved this problem. Movement of the main organic constituents (n-hexylamine, butanal, butanol, and phenol) was assumed to be slowed by adsorption. This conclusion was based on laboratory adsorption experiments by involving a different geologic formation (Cottage Grove sandstone); no direct observations were made of the injected waste. Section 5.2.2.1 and Table 5-4 in Chapter Five give additional information on the results of these adsorption experiments.

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APPENDIX A

SECTION AND TABLE INDEX FOR EPA PRIORITY POLLUTANTS

Appendix A. Section and Table Index for EPA Priority Pollutants

Compound	Group[a]	Section	Table
Acenaphthene[b]	PAH	4.3.5	4-9
Acenaphthylene	PAH	4.3.5	4-9
Acrolein[b]	P	4.3.7	4-11
Acrylonitrile[b]	N	4.3.6	4-10
Aldrin[b]	P	4.3.7	4-11
Anthracene[b]	PAH	4.3.5	4-9
Benzene[b]	MA	4.3.3	4-7
Benzidine	N	4.3.6	4-10
Benzo(a)anthracene[b]	PAH	4.3.5	4-9
Benzo(a)pyrene[b]	PAH	4.3.5	4-9
Benzo(b)fluoranthene	PAH	4.3.5	4-9
Benzo(ghi)perylene	PAH	4.3.5	4-9
Benzo(k)fluoranthene	PAH	4.3.5	4-9
Bromodichloromethane[b]	HAH	4.3.1	4-5
4-Bromodiphenyl ether	HE	4.3.2	4-6
Bromoform (see tribromomethane)[b]	HAH	4.3.1	4-5
Bromomethane (methyl bromide)	HAH	4.3.1	4-5
Carbon tetrachloride (see tetrachloromethane)[b]	HAH	4.3.1	4-5
Chlordane	P	4.3.7	4-11
Chlorodibromomethane (see dibromochloromethane)	HAH	4.3.1	4-5
4-Chlorodiphenyl ether	HE	4.3.2	4-6
Chlorobenzene[b]	MA	4.3.3	4-7
Chloroethane (ethyl chloride)[b]	HAH	4.3.1	4-5
Chloroethene (vinyl chloride)[b]	HAH	4.3.1	4-5
bis(2-Chloroethoxy) methane	HE	4.3.2	4-6
bis(2-Chloroethyl) ether[b]	HE	4.3.2	4-6
2-Chloroethyl vinyl ether	HE	4.3.2	4-6
Chloroform (see trichloromethane)[b]	HAH	4.3.1	4-5
bis(2-Chloroisopropyl) ether[b]	HE	4.3.2	4-6
p-Chloro-m-cresol	MA	4.3.3	4-7
Chloromethane (methyl chloride)	HAH	4.3.1	4-5
bis(Chloromethyl) ether	HE	4.3.2	4-6
2-Chlorophenol[b]	MA	4.3.3	4-7
Chrysene[b]	PAH	4.3.5	4-9
DDD	P	4.3.7	4-11
DDE[b]	P	4.3.7	4-11
DDT[b]	P	4.3.7	4-11
Dibenzo(a,h)anthracene	PAH	4.3.5	4-9
Dibromochloromethane (chlorodibromomethane)	HAH	4.3.1	4-5
1,2-Dichlorobenzene (o-dichlorobenzene)[b]	MA	4.3.3	4-7
1,3-Dichlorobenzene (m-dichlorobenzene)[b]	MA	4.3.3	4-7

Compound	Group[a]	Section	Table
1,4-Dichlorobenzene (p-dichlorobenzene)[b]	MA	4.3.3	4-7
3,3'-Dichlorobenzidine	N	4.3.6	4-10
Dichlorodifluoromethane	HAH	4.3.1	4-5
1,1-Dichloroethane (ethylidene chloride)[b]	HAH	4.3.1	4-5
1,2-Dichloroethane (ethylene chloride)[b]	HAH	4.3.1	4-5
1,1-Dichloroethene[b]	HAH	4.3.1	4-5
trans-1,2-Dichloroethene[b]	HAH	4.3.1	4-5
Dichloromethane (see methylene chloride)[b]	HAH	4.3.1	4-5
2,4-Dichlorophenol[b]	MA	4.3.3	4-7
1,2-Dichloropropane[b]	HAH	4.3.1	4-5
1,2-Dichloropropene	HAH	4.3.1	4-5
Dieldrin[b]	P	4.3.7	4-11
Diethyl phthalate[b]	PE	4.3.4	4-8
2,4-Dimethyl phenol (2,4-xylenol)	MA	4.3.3	4-7
Dimethylnitrosamine[b]	N	4.3.6	4-10
Dimethyl phthalate[b]	PE	4.3.4	4-8
Di-n-butyl phthalate	PE	4.3.4	4-8
4,6-Dinitro-o-cresol	MA	4.3.3	4-7
2,4-Dinitrophenol[b]	MA	4.3.3	4-7
2,4-Dinitrotoluene[b]	MA	4.3.3	4-7
2,6-Dinitrotoluene[b]	MA	4.3.3	4-7
Di-n-octyl phthalate	PE	4.3.4	4-8
Di-n-propyl nitrosamine	N	4.3.6	4-10
1,2-Diphenylhydrazine (hydrazobenzene)	N	4.3.6	4-10
Diphenylnitrosamine	N	4.3.6	4-10
Endosulfan and endosulfan sulfate[b]	P	4.3.7	4-11
Endrin and endrin aldehyde[b]	P	4.3.7	4-11
Ethylbenzene[b]	MA	4.3.3	4-7
Ethyl chloride (see chloroethane)[b]	HAH	4.3.1	4-5
Ethylene dichloride (see 1,2-dichloroethane)[b]	HAH	4.3.1	4-5
bis(2-Ethylhexyl) phthalate[b]	PE	4.3.4	4-8
Ethylidene chloride (see 1,1-dichloroethane)[b]	HAH	4.3.1	4-5
Fluoranthene[b]	PAH	4.3.5	4-9
Fluorene[b]	PAH	4.3.5	4-9
Heptachlor	P	4.3.7	4-11
Heptachlor epoxide	P	4.3.7	4-11
Hexachlorobenzene[b]	MA	4.3.3	4-7
Hexachlorobutadiene[b]	HAH	4.3.1	4-5
Hexachlorocyclohexane (lindane)[b]	P	4.3.7	4-11
Hexachlorocyclopentadiene	HAH	4.3.1	4-5

Compound	Group[a]	Section	Table
Hexachloroethane	HAH	4.3.1	4-5
Indeno(1,2,3-cd)pyrene	PAH	4.3.5	4-9
Isophorone	P	4.3.7	4-11
Lindane (see hexachlorocyclohexane)[b]	P	4.3.7	4-11
Methyl bromide (see bromomethane)	HAH	4.3.1	4-5
Methyl chloride (see chloromethane)[b]	HAH	4.3.1	4-5
Methylene chloride (see dichloromethane)[b]	HAH	4.3.1	4-5
Methyl chloroform (see 1,1,1-trichloroethane)[b]	HAH	4.3.1	4-5
Naphthalene[b]	PAH	4.3.5	4-9
Nitrobenzene[b]	MA	4.3.3	4-7
2-Nitrophenol[b]	MA	4.3.3	4-7
4-Nitrophenol[b]	MA	4.3.3	4-7
PCB (see polychlorinated biphenyls)[b]	PAH	4.3.5	4-9
Pentachlorophenol[b]	MA	4.3.3	4-7
Perchloroethylene (see tetrachloroethene)[b]	HAH	4.3.1	4-5
Phenanthrene[b]	PAH	4.3.5	4-9
Phenol[b]	MA	4.3.3	4-7
Polychlorinated biphenyls (PCB)[b]	PAH	4.3.5	4-9
Pyrene[b]	PAH	4.3.5	4-9
Tetrachlorodibenzodioxin	P	4.3.7	4-11
1,1,2,2-Tetrachloroethane[b]	HAH	4.3.1	4-5
Tetrachloroethene (perchloroethylene)[b]	HAH	4.3.1	4-5
Tetrachloromethane (carbon tetrachloride)[b]	HAH	4.3.1	4-5
Toluene[b]	MA	4.3.3	4-7
Tribromomethane (bromoform)[b]	HAH	4.3.1	4-5
1,2,4-Trichlorobenzene[b]	MA	4.3.3	4-7
1,1,1-Trichloroethane (methyl chloroform)[b]	HAH	4.3.1	4-5
1,1,2-Trichloroethane[b]	HAH	4.3.1	4-5
Trichlorethene[b]	HAH	4.3.1	4-5
Trichloromethane (chloroform)[b]	HAH	4.3.1	4-5
Trichlorofluoromethane[b]	HAH	4.3.1	4-5
2,4,6-Trichlorophenol[b]	MA	4.3.3	4-7
Vinyl chloride (see chlorethene)[b]	HAH	4.3.1	4-5
Vinylidiene chloride (see 1,1-dichloroethene)[b]	HAH	4.3.1	4-5
2,4-Xylenol (see 2,4-Dimethyl phenol)	MA	4.3.3	4-7

[a]HAH = halogenated aliphatic hydrocarbon, HE = halogenated ether, MA = monocyclic aromatic, PE = phthalate ester, PAH = polycyclic aromatic hydrocarbon, N = nitrogenous organic, P = pesticide.

[b]Others sources of information on partition coefficients and biodegradation for this compound can be found in Appendix B.

APPENDIX B

GROUND-WATER CONTAMINANT FATE (ADSORPTION AND BIODEGRADATION) AND TRANSPORT STUDIES INDEXED BY ORGANIC COMPOUND

This appendix lists organic compounds for which data on ground-water retardation/ partition coefficients and/or biodegradation have been cited in published scientific papers and reports. Over 150 organic compounds are listed. Compounds listed in Appendix A, for which information is available in other tables and in the text of this reference guide, are indicated with an asterisk.

A large body of literature is available on adsorption and biodegradation of pesticides, but only pesticides that are priority pollutants are included in this appendix. Some review papers that provide data on partitioning and biodegradation of other pesticides include: Hamaker and Thompson (1972), Hamaker

(1972), Crosby (1973), and Rao and Davidson (1980).

Compounds are listed in alphabetical order. The alphabetical location is arranged without the isomer (cis-, trans-, o-, m-, p-) and substituent-number designation; isomers and substituent numbers for compounds with the same chemical compositions are placed in alphabetical and numerical order.

References listed in this appendix are also coded to indicate whether they present data based on field studies (F), laboratory studies (L), and/or whether quantitative models were developed or tested in the study (M).

Appendix B   **Ground-Water Contaminant Fate (Adsorption and Biodegradation) and Transport Studies Indexed by Organic Compound**

Compound	Ground-Water Retardation / Partition Coefficient	Biodegradation
	Type of Study	
Acenaphthene*		Wilson et al. (1985b)
Acetonitrile		Grula and Grula (1976)
Acrolein*		Kobayashi and Rittmann (1982)
Acrylonitrile*		Ehrlich et al. (1979) Kobayashi and Rittmann (1982)
Aldrin*		Kobayashi and Rittmann (1982)
2-Aminoanthracene	Karickhoff (1984)	
6-Aminochrysene	Karickhoff (1984)	
m-Aminophenol		Aelion et al. (1987)
Aniline		Aelion et al. (1987)
Anisole	Chiou et al. (1983)	
Anthracene*	Karickhoff et al. (1979) Nkedi-Kizza et al. (1985) Rao et al. (1985)	Ehrlich et al. (1983) Kobayashi and Rittmann (1982) Evans et al. (1965) Abbot and Gledhill (1971) Jamison et al. (1971)
Benzene*	Schwarzenbach and Westall (1981) Rogers and McFarlane (1981) Piet and Smeenk (1985) Chiou et al. (1977) Chiou et al. (1983) Karickhoff et al. (1979) Rao et al. (1985) Barber et al. (1988)	Wood et al. (1985) Kobayashi and Rittmann (1982) Wilson, J. T., et al. (1986) Wilson, B. H., et al. (1987) Barker and Patrick (1985) Mahadevaiah and Miller (1986)
Benzo(a)anthracene*		Kobayashi and Rittmann (1982)
Benzo(a)pyrene*		Kobayashi and Rittmann (1982) Barnsley (1975)
Benzoate		Gibson and Suflita (1986)
Benzonitrile	Roberts et al. (1980)	
Biphenyl	Rao et al. (1985)	Kobayashi and Rittmann (1982)
Bromobenzene	Chiou et al. (1977) Rao et al. (1985) Barber et al. (1988)	
Bromochloromethane		Kobayashi and Rittmann (1982)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Bromodichloromethane*	Wilson et al. (1981)	Rittman et al. (1980) Bouwer et al. (1981) Bouwer and McCarty (1984) Wilson et al. (1983a) Wilson et al. (1985a) Wood et al. (1985) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982) Roberts et al. (1982)
Bromoform*	Roberts et al. (1985) Piet and Smeenk (1985) Roberts et al. (1986) Curtis et al. (1986) Roberts et al. (1982)	Rittmann et al. (1980) Bouwer and McCarty (1984) Wood et al. (1985) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982) Roberts et al. (1982) Roberts et al. (1986)
n-Butylbenzene	Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985)	
sec-Butylbenzene	Bedient et al. (1983)	
Butyronitrile		Grula and Grula (1976)
Carbon tetrachloride*	Rogers and McFarlane (1981) Chiou et al. (1977) Curtis et al. (1986) Roberts et al. (1986)	Bouwer and McCarty (1984) Wood et al. (1985) Bouwer and McCarty (1983a) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982) Parsons et al. (1985)
Chlorobenzene*	Roberts et al. (1985) Roberts et al. (1980) Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985) Chiou et al. (1977) Wilson et al. (1981) Roberts et al. (1982) Chiou et al. (1983) Winters and Lee (1987) Voice et al. (1983) Voice and Weber (1985) Rao et al. (1985) Barber et al. (1988)	Rittmann et al. (1980) Bouwer and McCarty (1984) Wilson et al. (1985a) Wood et al. (1985) Wilson et al. (1983a,b) Bouwer and McCarty (1983b) Wilson, J.T., et al. (1986)
Chlorobenzoate (various isomers)		Kobayashi and Rittmann (1982)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
3-Chlorobenzoate		Gibson and Suflita (1986)
4-Chlorobenzoate		Gibson and Suflita (1986)
4-Chlorobiphenyl	Winters and Lee (1987)	Kobayashi and Rittmann (1982)
Chlorocresol	Piet and Smeenk (1985)	
Chlorodibromomethane		Bouwer and McCarty (1984) Bouwer and McCarty (1983b) Wood et al. (1985) Bouwer et al. (1981) Kobayashi and Rittmann (1982) Roberts et al. (1982)
Chloroethane*		Wood et al. (1985) Kobayashi and Rittmann (1982)
Chloroethene (see Vinyl chloride)		
bis(2-Chloroethyl)- ether*	Wilson et al. (1981)	
Chloroform*	Roberts et al. (1985) Schwarzenbach and Giger (1985) Piet and Smeenk (1985) Chiou et al. (1977) Wilson et al. (1981) Roberts et al. (1982)	Rittmann et al. (1980) Bouwer and McCarty (1984) Wilson et al. (1985a) Wood et al. (1985) Bouwer et al. (1981) Wilson et al. (1983b) Bouwer and McCarty (1983a) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982) Roberts et al. (1982)
bis(2-Chloroisopropyl) ether*		Kobayashi and Rittmann (1982)
Chloromethane (see Methyl chloride)		
p-Chlorophenol		Aelion et al. (1987)
2-Chlorophenol*		Suflita and Miller (1985) Gibson and Suflita (1986)
3-Chlorophenol		Suflita and Miller (1985) Gibson and Suflita (1986)
4-Chlorophenol		Suflita and Miller (1985) Gibson and Suflita (1986) Dec and Bollag (1988) Kobayashi and Rittmann (1982)
Chlorophenoxyphenol	Johnson et al. (1985)	

| | Type of Study | |
Compound	Ground-Water Retardation / Partition Coefficient	Biodegradation
Chrysene*	Rao et al. (1985)	
Cresol (various isomers)	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984)	Smolenski and Suflita (1987) Kobayashi and Rittmann (1982) Goerlitz et al. (1985) Dobbins and Pfaender (1987) [m-] Aelion et al. (1987) [m-]
DDE*	Chiou et al. (1977)	
DDT*	Chiou et al. (1977)	Kobayashi and Rittmann (1982)
Dibenzanthracene		Kobayashi and Rittmann (1982)
Dibenzofuran		Wilson et al. (1985b)
Dibromochloromethane (see Chlorodibromomethane)		
1,2-Dibromomethane	Steinberg et al. (1987) Chiou et al. (1979)	Bouwer and McCarty (1984) Bouwer and McCarty (1983b) Wilson et al. (1983a) Wilson, B. H., et al. (1986) Aelion et al. (1987) Roberts et al. (1986)
Dibutyl phthalate	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984) Piet and Smeenk (1985) Barber et al. (1988)	
Dichlorobenzene	Bedient et al. (1983) Chiou et al. (1979) Hutchins et al. (1984) Tomson et al. (1985) Roberts et al. (1986) Barber et al. (1988)	Wood et al. (1985)
1,2-Dichlorobenzene*	Roberts et al. (1980) Hassett et al. (1980) Chiou et al. (1979) Chiou et al. (1983) Curtis et al. (1986)	Rittmann et al. (1980) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982) Kuhn et al. (1985)
1,3-Dichlorobenzene*	Roberts et al. (1980) Chiou et al. (1983)	Rittmann et al. (1980) Bouwer and McCarty (1983b)
1,4-Dichlorobenzene*	Roberts et al. (1980) Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985) Wilson et al. (1981) Chiou et al. (1983) Wu and Gschwend (1986)	Rittmann et al. (1980) Bouwer and McCarty (1984) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
2,3-Dichlorobenzene		Kobayashi and Rittmann (1982)
3,4-Dichlorobenzoate		Gibson and Suflita (1986) Kobayashi and Rittmann (1982)
3,5-Dichlorobenzoate		Gibson and Suflita (1986) Kobayashi and Rittmann (1982)
Dichlorobromomethane (see Bromodichloromethane)		
Dichloroethane		Kobayashi and Rittmann (1982)
1,1-Dichloroethane*		Wilson et al. (1985a) Wood et al. (1985) Wilson et al. (1983b) Wilson, B. H., et al. (1986)
1,2-Dichloroethane*	Wilson et al. (1981) Hassett et al. (1980) Chiou et al. (1979)	Bouwer and McCarty (1984) Wilson et al. (1985a) Wood et al. (1985) Bouwer and McCarty (1983a)
Dichloroethene	Barber et al. (1988)	
1,1-Dichlorethene*		Wood et al. (1985) Kobayashi and Rittmann (1982)
cis- and trans-1,2-Dichloroethene*		Wood et al. (1985)
1,1-Dichloroethylene		Kobayashi and Rittmann (1982) Barrio-Lage et al. (1986)
1,2-Dichloroethylene		Kobayashi and Rittmann (1982)
cis- and trans-1,2-Dichloroethylene		Barrio-Lage et al. (1986) [cis] Kobayashi and Rittmann (1982)
Dichloromethane (see Methylene chloride)		
2,3-Dichlorophenol	Schellenberg et al. (1984) Bedient et al. (1983)	
2,4-Dichlorophenol*	Schellenberg et al. (1984) Johnson et al. (1985)	Gibson and Suflita (1986) Dec and Bollag (1988) Suflita and Miller (1985)
2,5-Dichlorphenol		Gibson and Suflita (1986) Suflita and Miller (1985)
2,6-Dichlorophenol	Johnson et al. (1985)	
3,4-Dichlorophenol		Gibson and Suflita (1986)
1,2-Dichloropropane*	Chiou et al. (1979)	
1,3-Dichlorpropylene		Kobayashi and Rittmann (1982)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Dieldrin*		Kobayashi and Rittmann (1982)
Diethanolamine		Boethling and Alexander (1979)
Diethylamine		Boethling and Alexander (1979)
m-Diethylbenzene	Rao et al. (1985)	
Diethyl phthalate*	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984) Piet and Smeenk (1985)	
Dimethylamine		Beothling and Alexander (1979)
1,4-Dimethylbenzene	Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985)	
Dimethylnitrosamine*		Kobayashi and Rittmann (1982)
Dimethyl phthalate*	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984)	
2,4-Dinitrophenol*	Schwarzenbach et al. (1988)	
Dinitrotoluene	Piet and Smeenk (1985)	
2,4-Dinitrotoluene*		Kobayashi and Rittmann (1982)
2,6-Dinitrotoluene*		Kobayashi and Rittmann (1982)
Diphenyl ether	Chiou et al. (1977)	
Endosulfan*		Kobayashi and Rittmann (1982)
Endrin*		Kobayashi and Rittmann (1982)
Ethylbenzene*	Piet and Smeenk (1985) Rao et al. (1985) Chiou et al. (1983)	Bouwer and McCarty (1984) Horvath (1972) Bouwer and McCarty (1983b
Ethyl chloride (see Chloroethane)		
Ethylene dibromide	Rogers and McFarlane (1981)	
bis(2-Ethylhexyl) phthalate*	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984)	
o-Ethyltoluene	Bedient et al. (1983) Hutchins et al. (1984) Tomson et al. (1985)	
Fluoranthene*		Colwell and Sayler (1976) Kobayashi and Rittmann (1982) Barnsley (1975)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Fluorene*		Wilson et al. (1985b)
Fluorobenzene	Chiou et al. (1977) Rao et al. (1985)	
Heptaldehyde	Roberts et al. (1980)	Rittman et al. (1980)
Hexachlorobenzene*	Karickhoff (1984) Karickhoff and Morris (1985)	Kobayashi and Rittmann (1982)
Hexachlorobiphenyl	Karickhoff et al. (1979)	
Hexachlorobutadiene*	Schwarzenbach and Giger (1985)	
Hexachlorocyclohexane (see Lindane)		
Hexchloroethane	Schwarzenbach and Giger (1985) Curtis et al. (1986) Roberts et al. (1986)	Criddle et al. (1986)
Iodobenzene	Chiou et al. (1977) Rao et al. (1985) Barber et al. (1988)	
Isoquinoline		Pereira and Rostad (1987)
Lindane*	Chiou et al. (1985)	Kobayashi and Rittmann (1982)
Methoxychlor	Karickhoff et al. (1979)	Kobayashi and Rittmann (1982)
9-Methyl anthracene	Karickhoff et al. (1979)	
3-Methyl benzoate		Kobayashi and Rittmann (1982)
Methyl chloride*		Wood et al. (1985) Kobayashi and Rittmann (1982)
Methyl chloroform (see 1,1,1-Trichloroethane)		
Methyl naphthalene	Barber et al. (1988)	
1-Methyl naphthalene	Roberts et al. (1980) Bedient et al. (1983)	Wilson et al. (1985b)
2-Methyl naphthalene	Roberts et al. (1980) Karickhoff et al. (1979) Bedient et al. (1983) Hutchins et al. (1984) Tomson et al. (1985)	Wilson et al. (1985b)
Methylene chloride*		Wood et al. (1985) Kobayashi and Rittmann (1982)
Monochlorophenol		Kobayashi and Rittmann (1982)

Appendix B (Continued)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Naphthalene*	Bedient et al. (1983) Roberts et al. (1980) Tomson et al. (1985) Schwarzenbach and Westall (1981) Chiou et al. (1977) Karickhoff et al. (1979) Winters and Lee (1987) Voice et al. (1983) Voice and Weber (1985) Rao et al. (1985) Piet and Smeenk (1985) Barber et al. (1988) Hutchins et al. (1984)	Rittmann et al. (1980) Bouwer and McCarty (1984) Ehrlich et al. (1983) Bouwer and McCarty (1983b) Wilson et al. (1985b) Kobayashi and Rittmann (1982) Ehrlich et al. (1982) Davies and Evans (1964) Naumova (1960) Slavnina (1965)
Nitrilotriacetic acid		Ward (1985) Dunlap et al. (1982)
Nitrobenzene*	Wilson et al. (1981) Piet and Smeenk (1985)	Kobayashi and Rittmann (1982)
p-Nitrophenol		Grula and Grula (1976) Kobayashi and Rittmann (1982) Aelion et al. (1987)
2-Nitrophenol*	Schwarzenbach et al. (1988)	
4-Nitrophenol*	Schwarzenbach et al. (1988)	
Pentachlorobenzene	Wu and Gschwend (1986) Karickhoff and Morris (1985)	
Pentachlorophenol*	O'Connor et al. (1984) Choi and Aomine (1974a,b) Schellenberg et al. (1984) Johnson et al. (1985)	Dec and Bollag (1988) Kobayashi and Rittmann (1982)
Perchlorethylene (see Tetrachloroethene)		
Phenanthrene*	Karickhoff et al. (1979) Rao et al. (1985)	Kobayashi and Rittman (1982) Evans et al. (1965) Abbott and Gledhill (1971) Jamison et al. (1971)
Phenol*	Scott et al. (1983)	Scott et al. (1983) Suflita and Miller (1985) Gibson and Suflita (1986) Ehrlich et al. (1982) Ehrlich et al. (1983) Godsy et al. (1983) Grula and Grula (1976) Kobayashi and Rittmann (1982) Aelion (1987)

Appendix B (Continued)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Phthalate esters		Kobayashi and Rittmann (1982)
Polychlorinated biphenyls (PCBs)*	Weber et al. (1980) Schwarzenbach and Westall (1981) Chiou et al. (1977) Chiou et al. (1983) Gschwend and Wu (1985)	Colwell and Sayler (1976) Kobayashi and Rittmann (1982)
Propionitrile		Grula and Grula (1976)
Propylbenzene	Rao et al. (1985)	
Pyrene*	Schwarzenbach and Westall (1981) Karickhoff et al. (1979) Karickhoff (1984) Karickhoff and Morris (1985) Rao et al. (1985)	Ehrlich et al. (1983) Kobayashi and Rittmann (1982)
Quinoline		Pereira and Rostad (1987)
Styrene	Roberts et al. (1980) Bedient et al. (1983)	Wilson et al. (1983a,b) Wilson, B. H., et al. (1986)
Tetracene	Karickhoff et al. (1979)	
1,2,3,4-Tetra- chlorobenzene	Wu and Gschwend (1986) Scwharzenbach and Westall (1981)	
1,2,3,5-Tetra- chlorobenzene	Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985)	
1,1,1-Tetra- chloroethane	Hassett et al. (1980)	
1,1,1,2-Tetra- chloroethane	Hassett et al. (1980)	Kobayashi and Rittmann (1982)
1,1,2,2-Tetra- chloroethane*	Chiou et al. (1979)	Bouwer and McCarty (1983a) Bouwer and McCarty (1984)
Tetrachloroethene*	Wilson et al. (1981) Chiou et al. (1979) Barber et al. (1988)	Parsons et al. (1985)

Compound	Type of Study	
	Ground-Water Retardation / Partition Coefficient	Biodegradation
Tetrachloroethylene	Bedient et al. (1983) Giger and Molnar-Kubica (1978) Tomson et al. 1985 Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985) Chiou et al. (1977) Wilson et al. (1981) Curtis et al. (1986) Roberts et al. (1986) Hutchins et al. (1984)	Bouwer and McCarty (1984) Wilson et al. (1985a) Wood et al. (1985) Bouwer et al. (1981) Wilson and Wilson (1985) Wilson et al. (1983a,b) Bouwer and McCarty (1983a) Kobayashi and Rittmann (1982) Kuhn et al. (1985) Roberts et al. (1982) Roberts et al. (1986) Aelion et al. (1987)
Tetrachloromethane (see Carbon tetrachloride)		
2,3,4,5-Tetra- chlorophenol	Schellenberg et al. (1984)	
2,3,4,6-Tetra- chlorophenol	Schellenberg et al. (1984) Johnson et al. (1985)	
1,2,4,5-Tetra- methylbenzene	Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985)	
Toluene*	Bedient et al. (1983) Tomson et al. (1985) Schwarzenbach and Westall (1981) Piet and Smeenk (1985) Chiou et al. (1977) Wilson et al. (1981) Hutchins et al. (1984) Rao et al. (1985)	Wilson et al. (1985a) Wilson et al. (1983b) Kobayashi and Rittmann (1982) Wilson, J. T., et al. (1986) Barker and Patrick (1986) Mahadevaiah and Miller (1986)
Toxaphene		Kobayashi and Rittmann (1982)
Tribromomethane (see Bromoform)		
Trichlorobenzene		Kobayashi and Rittmann (1982)
1,2,3-Trichloro- benzene	Schwarzenbach and Westall (1981)	Kobayashi and Rittmann (1982)

| | Type of Study | |
Compound	Ground-Water Retardation / Partition Coefficient	Biodegradation
1,2,4-Trichloro-benzene*	Roberts et al. (1980) Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985) Wilson et al. (1981) Chiou et al. (1983) Wu and Gschwend (1986) Barber et al. (1988)	Bouwer and McCarty (1984) Bouwer and McCarty (1983b) Kobayashi and Rittmann (1982)
Trichloroethane		Kobayashi and Rittmann (1982)
1,1,1-Trichloroethane*	Roux and Althoff (1980) Chiou et al. (1979)	Rittmann et al. (1980) Bouwer and McCarty (1983b) Bouwer and McCarty (1984) Wilson et al. (1985a) Wood et al. (1985) Wilson et al. (1983b) Parsons et al. (1985) Barker et al. (1986) Vogel and McCarty (1987)
1,1,2-Trichloro-ethane*	Wilson et al. (1981)	Wilson et al. (1985a) Wood et al. (1985)
Trichloroethene*	Roberts et al. (1982) Barber et al. (1988) Barrio-Lage et al. (1987)	Parsons et al. (1985)
Trichloroethylene	O'Connor et al. (1984) Schwarzenbach and Giger (1985) Rogers and McFarlane (1981) Wilson et al. (1981)	Wilson and Wilson (1985) Wood et al. (1985) Bouwer et al. (1981) Wilson et al. (1983a,b) Kobayashi and Rittmann (1982) Wilson, B. H., et al. (1986)
Trichlorofluoromethane*		Kobayashi and Rittmann (1982)
Trichloromethane (see Chloroform)		
2,3,4-Trichlorophenol	Schellenberg et al. (1984)	
2,4,6-Trichlorophenol*	Schellenberg et al. (1984) Johnson et al. (1985)	Suflita and Miller (1985)
3,4,5-Trichlorophenol	Schellenberg et al. (1984)	Gibson and Suflita (1986) Dec and Bollag (1988)
1,2,3-Trimethylbenzene	Schwarzenbach and Westall (1981)	
1,2,4-Trimethylbenzene		Barker et al. (1986)
1,2,5-Trimethylbenzene	Schwarzenbach and Westall (1981) Schwarzenbach and Giger (1985)	

Appendix B (Continued)

| | Type of Study | |
Compound	Ground-Water Retardation / Partition Coefficient	Biodegradation
Vinyl chloride*		Wood et al. (1985)
Vinylidiene chloride (see 1,1-Dichlorethane)		
Xylene (various isomers)	Tomson et al. (1985) Bedient et al. (1983) Hutchins et al. (1984) Rao et al. (1985) Piet and Smeenk (1985)	Wilson, J. T.. et al. (1986) [o-,m-] Wilson, B. H., et al. (1986) [o-] Wilson, B. H., et al. (1987) [m-,p-] Kuhn et al. (1985) [o-,m-] Barker et al. (1985) [o-] Barker and Patrick (1986) [o-,m-] Mahadevaiah and Miller (1986)

*Priority pollutant; additional data can be found by referring to Appendix A.

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[*](F) = field study, (L) = laboratory study, (M) = model developed.

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*This paper presents data on degradation of 14 phenolic compounds of which only phenol is indexed in the appendix.

+Biodegradation data on 49 compounds in 10 organic groups are reported; only phenolic and nitrile compounds are indexed in the appendix.

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