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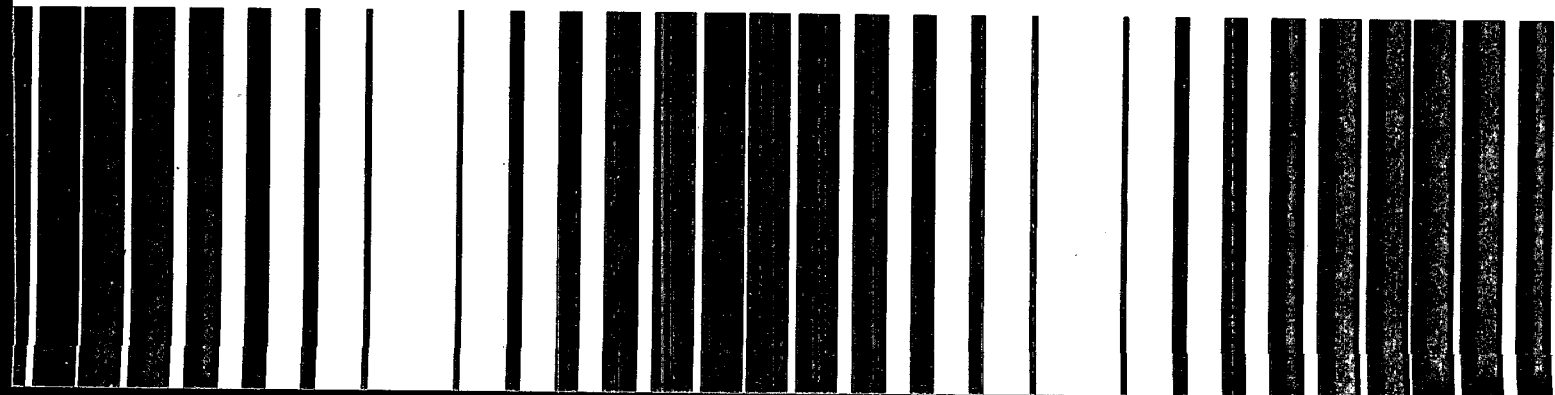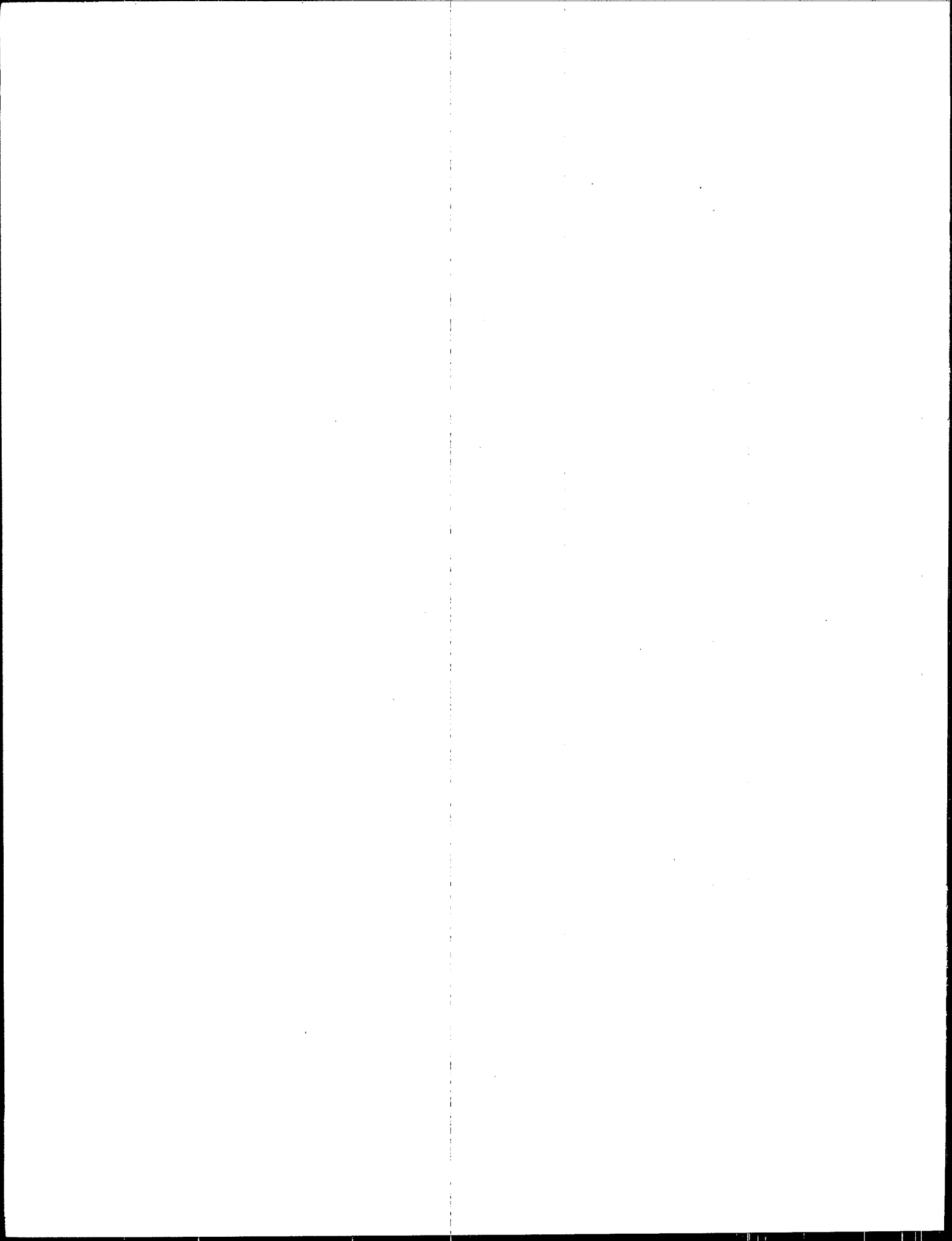# Assessing the Geochemical Fate of Deep-Well-Injected Hazardous Waste:

Summaries of Recent Research

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

Summaries of Recent Research

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CHAPTER ONE

EXECUTIVE SUMMARY

1.1 Overview

This report compiles and summarizes the results of recent research funded by the U.S. Environmental Protection Agency on topics related to geochemical-fate assessment of deep-well-injected hazardous wastes. Its purpose is twofold:

1. To make the results of this research available to a wider audience of scientists and professionals who are involved in various aspects of regulating and implementing the deep-well injection of hazardous wastes under federal and state Underground Injection Control programs.

2. To provide an overall assessment of the state of the art of predicting the geochemical fate of deep-well-injected wastes and to identify possible future directions for research in this area.

Chapters Two through Six summarize individual research reports. These five reports include two literature surveys (Arden Stryker and A. Gene Collins, *State-of-the-Art Report: Injection of Hazardous Wastes into Deep Wells*; John A. Apps, *Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of Deep Disposal Wells*); two reports focusing on laboratory procedures for predicting the geochemical fate of injected hazardous waste (J. Apps, L. Tsao, and O. Weres, *The Chemistry of Waste Fluid Disposal in Deep Injection Wells*; A. Gene Collins and M. E. Crocker, *Laboratory Protocol for Determining Fate of Waste Disposed in Deep Wells*); and one report comparing empirical data with the predictions from solution geochemistry models (W. R. Roy, S. C. Mravik, I. G. Krapac, D. R. Dickerson, and R. A. Griffin, *Geochemical Interactions of Hazardous Wastes with Geological Formations in Deep-Well Systems*).

This Executive Summary synthesizes the current understanding of the geochemistry of deep-well hazardous waste injection. It is drawn largely from information presented in the research summaries in this document, supplemented by additional literature review. These additional areas of study include the effects of organic matter on geochemical processes and biodegradation of hazardous organics in the deep-well environment. Since many of the conclusions of the additional literature are based on scientific data developed under near-surface environmental conditions, the similarities and differences between near-surface and deep-surface geochemical environments are noted where relevant.

The research summarized in this document represents an end to a 10-year hiatus in the study of the geochemical fate of deep-well-injected industrial wastes. The last period of active research on this subject took place from the late 1960s to the late 1970s. Most waste-reservoir interaction studies were published between 1972 and 1978, and virtually all reports of field studies of the geochemical fate of injected wastes appeared between 1971 and 1978. (The most recent citation, Vecchioli et al., 1984, reports no data after 1977.) Most of the post-1978 literature that is cited in Chapters Two and Six (the reports containing the most comprehensive literature reviews) does not relate directly to the geochemistry of deep-well waste injection, although it may provide insights into deep-well geochemical processes.

Thus, very little research specifically addresses the geochemical fate of deep-well-injected hazardous wastes, particularly in the context of the current federal and state regulatory environment for deep-well injection. A broad range of scientific literature is available on the geochemical fate of hazardous wastes in soil and near-surface groundwater systems. However, most of this literature is based on laboratory and/or field studies that do not simulate deep-well environmental conditions, and transferring results to estimate deep-well geochemical fate must be done cautiously.

The following uniform format is used for presenting material in this chapter and each of the five reports:

- **Section 1 (Overview)** presents the title and authors of the reports, where it can be obtained, a brief description of its contents, and a summary of its major conclusions.

- **Section 2 (Processes Affecting Geochemical Fate)** summarizes information on basic processes that may affect geochemical reactions between injected waste and fluids and solids in the injection zone. Specific chemical processes are classified into three categories:

— **Partition processes** affect the form or state of a compound but not its chemical structure or toxicity. These processes include: acid-base reactions, adsorption-desorption, immiscible phase separation and precipitation- dissolution.

— **Transformation processes** alter the chemical structure of a substance. These processes include biodegradation, complexation, hydrolysis, neutralization, oxidation-reduction, polymerization, and thermal degradation. Catalysis is included in this category.

— **Transport processes** carry wastes through the subsurface environment. Only those transport processes that significantly affect geochemistry (hydro-dynamic dispersion, osmotic potential, and particle migration) are covered.

- **Section 3 (Major Environmental Factors Affecting Geochemical Processes)** contains any information in the report related to the significance and effect of environmental factors such as pH, Eh, salinity, reservoir-matrix minerals, temperature, and pressure on geochemical processes. It includes any information on the actual environmental conditions that exist in deep-well injection zones.

- **Section 4 (Geochemical Characteristics of Hazardous Waste)** summarizes information on the chemical characteristics of specific organic and inorganic substances (both hazardous and nonhazardous) that may be injected into deep-well formations.

- **Section 5 (Methods and Models for Predicting Geochemical Fate)** summarizes information on basic approaches to geochemical modeling and specific methods or models for predicting adsorption, aqueous and solution geochemistry, biodegradation, hydrolysis, and transport.

- **Section 6 (Laboratory Procedures and Protocols)** summarizes any laboratory procedures described in the report for obtaining empirical data on waste-reservoir geochemical interactions.

- **Section 7 (Field Case Studies)** summarizes any information in the report on field observations of geochemical interactions between injected wastes and the injection zone.

- **Section 8 (Further Research Needs)** lists any recommendations for further research.

The Executive Summary provides an overview of the state of the art in geochemical fate assessment for deep-well injection of hazardous wastes. This chapter follows the same format used in the research-summary chapters to identify strengths and weaknesses in current knowledge. The conclusions in this chapter are drawn from a synthesis of information in the research summaries and additional review of relevant scientific literature.

The uniform format of each report is designed to facilitate locating information on specific topics. For example, any information on the processes of adsorption will be included under Partition Processes in Section 2 of each chapter. Similarly, any information on aqueous- and solution-gochemistry models will be found in Section 5 of each chapter.

Most of the reports summarized in this document contain some discussion of EPA's 1988 Final Underground Injection Control regulations concerning injection of hazardous wastes (53 Federal Register 28118-28157). Discussions specific to regulatory issues have not been included in the Research Summaries.

1.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

Environmental conditions in the deep-well environment (see also Section 1.3) restrict the number of basic chemical processes that may immobilize or transform hazardous wastes. For example, absence of sunlight and air-water interfaces means that photolysis and volatilization do not occur. The significance of geochemical processes that may affect deep-well-injected waste are briefly discussed below.

1.2.1 Partition Processes
Acid-base equilibria are fundamental to the aqueous geochemistry of injected waste and the injection zone. The high salinities of injection zones make predicting such reactions more difficult than predicting those occurring in the fresh or moderately saline waters typically found in near-surface environments (excluding marine environments).

Adsorption-desorption is likely to be a significant process affecting the mobility of heavy metals and organic wastes. The basic mechanisms for these processes are still not well

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understood. Such deep-well environmental conditions as increased temperature, pressure, and high salinities make the study and prediction of adsorption more difficult compared to those for near-surface environments. Organic-matter content is a major factor affecting adsorption in the near surface, but its significance in the deep-well environment has received little attention.

Precipitation-dissolution reactions are particularly important because incompatibilities between injected wastes and reservoir fluids commonly result in precipitation reactions that can plug or at least reduce the permeability of the injection zone. Both precipitation and dissolution reactions affect the dissolved species that are available for acid-base reactions.

Immiscible - Phase Separation is not a major process in the deep-well environment because deep-well injection is generally limited to waste streams that are soluble in water. Blowout, caused when gaseous carbon dioxide forms as a result of the injection of concentrated acids into carbonate formations, is an example of a process unique to the deep-well environment.

1.2.2 Transformation Processes

Neutralization of highly acidic wastes in injection zones with carbonate lithology is one of the few geochemical processes that can be predicted with any confidence. Neutralization of acidic and alkaline wastes in injection zones with other lithologies will also occur to varying degrees.

Complexation is likely to be an important process affecting the mobility of heavy metals in the deep-well environment. High salinities in the deep-well environment make prediction of complexation reactions more difficult. Humic substances can be major factors in complexation reactions, but their significance to such reactions in deep-well environments has received little attention.

Hydrolysis may be a significant process for a limited number of organic compounds in the deep-well environment (see Table 1-1). EPA's 10,000-year- no-migration standard establishes a time frame in which half-lives on the order of thousands of days may be adequate to allow hydrolysis to be a significant transformation process. The half-lives reported in Table 1-1 are based on rate constants measured at surface conditions and do not necessarily reflect what would occur under the temperatures, pressures, and salinities typical of the deep-well environment. The higher temperatures and pressures that exist may increase rates of hydrolysis; however, the high salinities may affect rate constants in unpredictable ways.

Oxidation-reduction (redox) reactions involving inorganic constituents in the deep-well environment will affect the

mobility of heavy metals and precipitation reactions and will strongly influence the type of microbiological activity. Many

Table 1-1 Listed Hazardous Organic Wastes for Which Hydrolysis May Be a Significant Transformation Process in the Deep-well Environment

Group Compound	Half-life[a]
Pesticides	
Aldrin	760
Dieldrin	3,830
DDT[b]	—
Endosulfan/Endosulfan sulfate[b]	21
Heptachlor[b]	1
Halogenated Aliphatic Hydrocarbons	
Chloroethane (ethyl chloride)[b]	38
1,2-Dichloropropane[b]	—
1,3-Dichloropropene[b]	—
Hexachlorocyclopentadiene[b]	14
Bromomethane (methyl bromide)[b]	20
Bromodichloromethane	5,000
Methyl chloride	
Halogenated Ethers	
bis(Chloromethyl)ether[b]	< 1
2-Chloroethyl vinyl ether	1,800
bis(2-Chloroethoxy) methane[b]	—
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
Polycyclic Aromatic Hydrocarbons	—
Nitrosamines and Misc. Compounds	—

[a]Half-life measured in days at pH 7 and ambient temperature.
[b]Hydrolysis identified as a significant process by Callahan et al. (1979).

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

organic compounds are degraded by biologically mediated redox reactions (see Biodegradation, below). Aerobic conditions may exist near the injection well when injected wastes contain dissolved oxygen. However, the deep-well environment is typically mildly to strongly reducing (anaerobic), and any oxygen in injected wastes is likely to be depleted rapidly.

Catalysis may increase the rate of other transformation reactions (such as hydrolysis, redox reactions, and polymerization). Catalytic reactions under the temperatures and pressures typical of the deep-well environment have received little attention in the literature.

Polymerization reactions of some monocyclic aromatic compounds (catalyzed by clays) may serve to enhance adsorption of these compounds. Such reactions under deep-well environmental conditions have not been studied.

Thermal-degradation reactions under deep-well environmental conditions have not received much study. In general, however, temperatures and pressures typical of deep-well injection zones are probably too low for initiating high-temperature reactions.

Biodegradation of at least some components of deep-well-injected wastes has been observed in all cases where mixtures of injected wastes and formation waters have been used to make direct observations of microbiological and/or geochemical effects (see Section 1.7). Degradation of organic wastes by denitrifying, sulfate-reducing, and methanogenic bacteria have been either observed directly or inferred from geochemical evidence. The conditions of the deep-well environment are well within the range of conditions to which anaerobic bacteria are adapted. Denitrifying and methanogenic bacteria have been observed to degrade a number of hazardous halogenated aliphatic and monocyclic aromatic hydrocarbon compounds in near-surface environments. Sulfate-reducing bacteria appear to be more abundant and adapted to a wider range of environmental conditions in the deep-well environment than denitrifying or methanogenic bacteria, but are less capable of degrading hazardous organic compounds; data are, however, very limited on this subject. The ecologies of denitrifying, sulfate-reducing, and methanogenic bacteria in both near-surface and deep-well environments are not well-understood, and this area of research has received little attention in the context of deep-well injection of wastes.

1.3 Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes

Every injection well has a unique set of enviromental factors that determine the chemical reactions that may occur when waste is injected. Compared to those of near-surface environments, the parameters that define the deep-well environment are much narrower in range.

1.3 Typical Range of Environmental Factors

pH and Eh (Redox Potential). The pH of most deep-well injection zones ranges from 5.0 to 8.5 and the Eh ranges from 0 to -400 mV. The pH range is well suited for neutralization reactions (although the lithology of the injection zone is an equally important factor affecting neutralization capacity). As noted in the previous section, the low Eh values of typical injection zones indicate that aneraboic, biologically mediated reducing reactions will predominate.

Salinity and Water Chemistry. The salinity of most deep-well injection zones ranges from 20,000 to 100,000 mg/L, although values as high as 350,000 mg/L are possible. Sodium chloride, a strong electrolyte, is a major constituent of water in deep-well injection zones. High salinities and electrolytic characteristics of waters in injection zones complicate the modeling and prediction of the aqueous geochemistry of injected-waste and formation-water mixtures (see Section 1.5).

Reservoir Matrix. Sedimentary rock forms the solid matrix of most deep-well injection zones. Many chemical reactions occurring when hazardous wastes are injected are largely determined by the physical and chemical properties of that rock. Approximately two-thirds of active waste-injection wells use sands and sandstones for the injection zone, and about one-third use carbonate rock (limestone and dolomite). Particle-size distribution influences the surface area available for waste-solid interactions. Mineralogy also strongly influences the types of chemical reactions that will occur at the waste-solid interface.

Silicate clays (particularly the smectite group, vermiculite, and illite) and hydrous-oxide clays are the most reactive minerals in deep-well formations because of their high surface area and cation-exchange capacity. Clays are particularly important in adsorption reactions and may catalyze other geochemical reactions. Organic matter composed of stable humic substances is even more reactive than clay

minerals in near-surface environments, but this material has not received much attention in the context of geochemical-fate assessment in the deep-well environment. Organic matter in sedimentary rocks (bitumin and kerogen) is derived largely from humic substances that originated at near-surface conditions, but it is possible that burial may alter the reactivity of these materials.

Temperature and Pressure. The temperatures of most deep-well injection zones range from 40° to 75°C with extremes from 20° to 150°C. Pressures most likely range from 50 to 150 bars. The rates of most acid-base and dissolution reactions increase with temperature, but the exact effect of the interactions among competing reactions is difficult to predict. Increased temperature usually *decreases* the rate of adsorption because these reactions are primarily exothermic. The separate or combined effects of temperature and pressure may result in different reactions from those occurring among wastes and the injection zone fluids and solids under near-surface conditions. Consequently, laboratory compatibility tests and evaluations of individual geochemical processes must simulate actual temperatures and pressures in the injection zone.

1.3.2 Influence of Environmental Factors on Waste-Reservoir Compatibility

Injected wastes tend to be less saline (on the order of 10,000 mg/L total dissolved solids), and their dissolved constituents usually have attained equilibrium at lower temperatures and pressures than those found in the injection zone. When such wastes are injected without considering possible incompatibilities, adverse chemical and physical reactions can occur near the injection site. Major operational problems that can occur in this situation include: (1) well plugging, (2) well-casing/confining-layer failure, and (3) well blowout. These problems are discussed below.

Well Plugging. Table 1-2 lists 10 possible causes of reduced permeability in the injection zone or plugging of well screens and possible remedial actions. The most common causes of plugging are (1) swelling and migration of water-sensitive clays (such as montmorillonite) when lower-salinity wastes replace the formation fluids, (2) precipitation reactions, and (3) biological clogging of well screens.

Well-Casing and/or Confining-Layer Failure. Corrosion of well casing and packing can threaten the integrity of a well if proper materials have not been used in construction (see U.S. EPA, 1989). Dissolution of the confining-layer formation by highly acidic or alkaline wastes may also allow upward migration of wastes. Chemically active injected fluids may reduce surface energy, surface cohesion, and breaking strength of a confining formation, and stresses from increased injection pressure may fracture rock to

create channels in a confining formation (Swolf, 1972). Carbonate-confining layers are most susceptible to breaching from dissolution by acidic wastes. Lower density and viscosity of injected wastes compared with those of the injection-zone fluids tend to increase the potential for waste-confining-layer interactions and upward migration.

Well Blowout. Injection of hot, concentrated hydrochloric acid into a carbonate zone can result in phase separation of carbon-dioxide gas. In this situation, formation pressures increase to the point where waste and reservoir fluids are forced up the injection well to the surface. This problem can be controlled readily by keeping temperatures and concentrations of the acidic waste within certain recommended limits: (1) less than 6% HCl (Pangiotopoulos and Reid, 1986) and (2) less than 88°F (Kamath and Salazar, 1986).

1.4 Geochemical Characteristics and Fate of Hazardous Waste

1.4.1 Sources and Composition of Deep-Well-Injected Wastes

An estimated 11.5 billion gallons of hazardous wastes were injected in 1983, of which about half (50.9%) came from the

Table 1-3   Estimated Volume of Deep-Well- Injected Wastes by Industrial Category, 1983

Industrial Category	Volume (MGY)	Percent of Total
Organic chemical	5,868	50.9
Petroleum refining and petrochemical products	2,888	25.0
Misc. 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	11,539	100.0

Source: U.S. EPA (1985).

Table 1-2 Causes of Well Plugging and Possible Remedial Actions

Cause	Possible Action
Failure to remove particulate solids and/or colloids before injection.	Filtration before injection.
Bacterial growth on well screen and formation.	Treatment 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.	Pretreatment; 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.	Preinjection neutralization to avoid dissolution.
Reprecipitation of dissolved material (iron or calcium sulfate).	Pretreatment.
Change in wettability or reduction in pore dimensions by adsorption (organics with large molecular weight).	Difficult to remedy.
Flow of unconsolidated sands into well-bore.	Gravel pack well screen. Inject a slug of brine after every period of interrupted flow.
Scaling on injection equipment by precipitation from injection fluid.	Pretreatment; flushing with solutions to remove accumulated scale.

Source: Adapted from Barnes (1972), Donaldson and Johanson (1973), Hower et al. (1972), Davis and Funk (1972), and Veley (1969).

production of organic chemicals and one-quarter (25.0%) came from the petroleum-refining and petrochemical-products industry (see Table 1-3). The remaining 24% came from six other industrial categories: miscellaneous chemical production (6.0%), agricultural chemical products (4.6%), inorganic chemical products (2.2%), commercial disposal (4.1%), metals and minerals (5.8%), and aerospace (1.5%).

Although no systematic data exist on the exact chemical composition of deep-well-injected wastes, EPA has gathered data for 108 wells (55% of total active wells) operating in 1983. Table 1-4 summarizes the total quantity of undiluted waste in six major categories, provides a breakdown of average concentrations of individual 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 (52.0%). Acids were the next most important constituent by volume (20.3%), followed by organics (17.4%). 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.

1.4.2 Geochemical Fate of Deep-Well-Injected Wastes

Several dozen inorganic elements and compounds are classified as hazardous or exhibit toxic characteristics at relatively low concentrations, and hundreds of organic compounds are classified as hazardous. Much of the data available on the geochemical properties of individual complexity of natural environments, where competing processes and chemical reactions may lead to outcomes different from those indicated by laboratory studies. Injected hazardous wastes tend to be complex mixtures of hazardous and nonhazadous organic and inorganic constituents. The number of possible chemical interactions increases factorially as the number of compounds in the waste stream increases, confounding geochemical fate predictions for specific substances. Variations in particle-size distribution and mineral composition of the injection zone (which is difficult to characterize from a few boreholes) further complicate predictions of geochemical reactions between a waste and the injection zone.

1.5 Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes

1.5.1 Specific Methods and Models

Aqueous-Geochemistry Computer Codes. Four general types of computer codes are used to model aqueous geochemistry:

1. **Thermodynamic codes** process empirical data so that thermodynamic data at a standard reference state (25°C and 1 bar) can be obtained for individual species. They are also used to recalculate thermodynamic properties of the species of interest at the temperatures, pressures, and ionic concentrations being simulated.

2. **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 is the theoretical distribution of the aqueous species for the dissolved elements.

3. **Reaction-progress codes**, also called **mass-transfer codes**, calculate both the equilibrium distribution of aqueous species (as in distribution-of-species codes) and the new composition of the solution, as selected minerals and compounds are precipitated or dissolved.

4. **Transport codes** model chemical transport by combining aqueous-geochemistry codes with physical-transport codes. Two major approaches have been used: integrated codes simultaneously solve all mass, momentum, and energy-transfer equations, including those in which chemical reactions participate, for each time step in the evolution of the system; **two-step models** first solve mass momentum and energy balances for each time step and then re-equilibrate the chemistry using a distribution-of-species code.

Dozens of codes have been developed to model aqueous geochemistry, but most have been developed for near-surface environments. Only a few are suitable for modeling the high salinities, temperatures, and pressures that exist in the deep-well environment. Thermodynamic, distribution-of-species, and reaction-progress codes that may be useful for modeling deep-well injection are listed and described in Table 1-5. Table 1-6 describes integrated and two-step

Table 1-4 Waste Characteristics of 108 Hazardous-Waste Wells Active in 1983 in the United States

Waste Type/ Components	Gallons[a]	Avg. Concentration (mg/L)	No. of Wells
Acids	44,140,900 (20.3)[b]		37
Hydrochloric acid		78,573	15
Sulfuric acid		43,000	6
Nitric acid		75,000	2
Formic acid		75,000	2
Unspecified acid		44,900	12
Heavy Metals	1,517,600 (0.7)		19 (17.6)
Chromium		1.4	11
Nickel		600	5
Unspecified metals		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
Other	22,964,600 (9.9)		33 (30.5)
Total	228,021,800[c]		108

[a]Gallons of undiluted wastes.
[b]Number in parentheses is percent of total.
[c]Excludes overlaps between organics and acids.

Source: U.S. EPA (1985).

Table 1-5   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, 1989
  Tanger and Helgeson, 1988
	Can be used to calculate dissolution-reaction constants at any specified temperature between 0° and 800°C and 1-5,500 bars.

PHAS20
  Haas, 1974
  Haas and Fisher, 1976
	Developed by USGS for thermodynamic calculations.

Distribution-of-Species Codes	
SOLMNEQ Kharaka and Barnes, 1973	Handles temperature of 0°-350°C, pressure from 1-1,000 bars, and salinities up to about 29,000 mg/L. It includes organic complexes and ion-exchange equilibria. The model has been used by Ehrlich et al.(1979) and Roy et al. (1988) to simulate injected waste-reservoir interactions.
Reaction-Progress Codes	

EQ3/6
  Wolery and Walters, 1975
  Wolery, 1979
  Wolery, 1983
  Jackson and Wolery, 1985
  Wolery, 1986
	Handles temperatures of 0°-350°C and pressures from 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 brines (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
  Plummer et al., 1983).
	Temperature range 20°-150°C, pressure range 50-300 bar, salinity range 10,000-350,000 TDS. Has successfully modeled the evolution of ground water with the mineralogy of a limestone and dolomite aquifer in Florida (Plummer et al., 1983).

PHREEQEP Crowe and Longstaffe, 1987	Incorporates Pitzer interaction electrolyte model into PHREEQE up to 150°C.
ECES[a] Scrivner et al., 1986	Temperature range is 0°-200°C; pressure range is 0-200 atm; and 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.

[a] Electrolyte Concentration of Equilibrium Solution

Sources: Nordstrom et al., 1979; Apps, 1988.

Table 1-6. Integrated Groundwater Chemical Transport Models

Developers	Description/Comments
Integrated Models	
Rubin and James, 1973	Simulates heterovalent ion exchange and changing concentrations of pore fluid ions in one-dimensional flow.
Valochi, Street, and Roberts, 1981 Valochi et al., 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, called CHMTRNS, 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 reversible and irreversible dissolution, and oxidation-reduction reactions. Has not been tested with complex multicomponent systems.
Two-Step Models	
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 incoporates distribution-of-species code MICROQL (Westall et al., 1976). Modeling of ion-exchange reactions in artificial recharge in Palo Alto Baylands project yielded same results as one-step analysis by Valocchi, Street, and Roberts (1981).
Kirkner et al., 1984, 1985 Their et al., 1984	Models multicomponent solute transport with adsorption and aqueous complexation.
Huyakorn et al., 1983 Krupka and Morrey, 1985	SATURN incorporates distribution-of-species code MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985).
Narashimhan et al., 1986 Liu and Narashimhan, 1989 a,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).

groundwater chemical-transport models. Of those listed, SOLMNEQ, EQ3/6, and ECES have actually been used to model the deep-well environment. Section 1.5.2 discusses deficiencies in available models.

Adsorption is a complex process involving one or more of a number of bonding mechanisms (ion exchange, protonation, hydrogen, Van der Waals, hydrophobic, and/or dipole bonding). Thermodynamically and kinetically sound models of simple systems are available (e.g., the Langmuir equation for adsorption of gases on homogeneous surfaces and the Stanford General Model for Adsorption [SGMA]—the triple-layer model—for simple oxides). However, no such model is available for modeling adsorption on more complex minerals such as aluminosilicates, complex oxides, and fixed-charge clay minerals, which are prevalent in the deep-well environment. Consequently, researchers are currently confined to using empirical Freundlich isotherms or distribution coefficients (in the unlikely event that adsorption exhibits a linear relationship to concentration) when trying to predict adsorption in the deep-well environment. Inherent problems with this empirical approach are discussed in detail in Section 6.5.2.3. If these approaches are taken, laboratory adsorption *must* be measured under deep-well temperatures and pressures.

Hydrolysis is easily predicted when the rate constants for a compound are known. However, few if any data are available on hydrolysis rate constants for compounds at the salinities, temperatures, and pressures existing in the deep-well environment.

Biodegradation. Several qualitative models for biodegradation in the deep-well environment have been suggested. These models do not allow quantitative predictions

Figure 1-1 Proposed geochemical model of waste after injection into subsurface.

to be made, but they indicate what types of biodegradation processes may occur. The conceptual geochemical model of acidic waste injected into the subsurface proposed by Leenheer and Malcolm (1973) involves a moving front of microbial activity. The moving front has five zones, as shown in Figure 1-1: (1) a dilute zone controlled by diffusion, (2) a zone where substrate concentrations are high enough 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.

Bouwer and McCarty (1984) have suggested a qualitative model based on redox zones for microbial degradation of trace organic constituents with increasing distance from the injection point. Table 1-7 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. The model implies that most compounds not degraded in their appropriate zone will move through the groundwater system without significant additional degradation, except for those compounds which are biodegraded methanogenically, for which complete biodegradation may occur. Other factors, such as pH and water chemistry (e.g., presence or absence of sulfates), tend to complicate the redox-zone model.

The most sophisticated model available for predicting biodegradation of organic contaminants in subsurface systems is the **biofilm model**, originally presented by Williamson and McCarty (1976a,b) and refined over several years 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 model predicts that biofilm development will be confined to within about a meter of the injection zone at near-surface artificial recharge wells. Where biological clogging is a potential problem, the biofilm model may be of value in deep-well-injection settings. However, where injected wastes are toxic to microbiota before dilution in the injection zone (see Figure 1-1), the biofilm model would not be applicable.
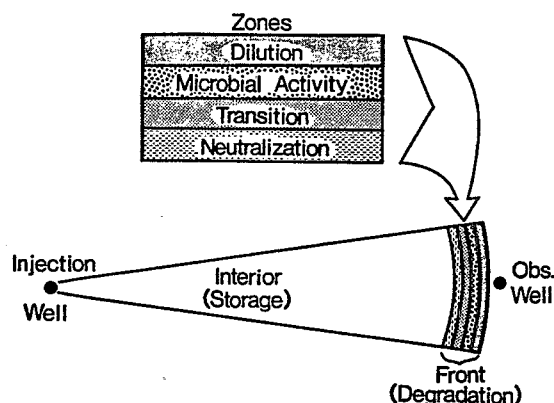
1.5.2 Deficiencies in Geochemical Models
The geochemical modeling of the fate of hazardous wastes in saline aquifers contained in deep sedimentary formations is in a preliminary stage. Computer codes have not been adequately tested, so fate predictions must be corroborated by laboratory and field studies. The major deficiencies in currently available geochemical codes for predicting the fate of deep-well-injected hazardous wastes include:

Table 1-7   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	None identified	C_1 and C_2 Halogenated aliphatics

Source: Adapted from Bouwer and McCarty (1984).

■ 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). Either solid-solution models 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 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 species between the adsorbed and aqueous state.

■ Calcium-sodium chloride brines (which typically occur 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. Precise modeling is limited to systems with relatively low salinities, where modeling a multitude of parameters is 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 to these codes can simulate nonequilibirum conditions, but the extent to which codes can be manipulated to simulate processes that are kinetically (rate) controlled is limited. The slow reaction rates in the deep-well environment relative to groundwater movement create particular problems for the simulation.

■ Little is known about the kinetics of dissolution, precipitation, and oxidation-reduction reactions in the natural environment. Consequently, simulating the kinetics of the complicated injection-zone chemistry is very difficult.

1.6 Laboratory Procedures and Protocols

1.6.1 General

Procedures for field and laboratory characterization of injected wastes, reservoir lithology, and formation water are well established. For geochemical fate assessment, researchers must pay more attention to characterizing reactive minerals in the injection zone (primarily clays) and solid and dissolved phases of organic matter, as well as to the microbial ecology of the injection zone (as evidenced by gaseous byproducts of microbial activity and direct observation of microbiota). Basic methods for sampling and identifying groundwater microorganisms are reasonably well established, but they require some refinement if they are to be used systematically to characterize deep-well-injection zones.

1.6.2 Waste-Reservoir Interaction Tests

Waste-reservoir-interaction tests serve at least three purposes: (1) to identify possible incompatibilities between reservoir components and wastes to be injected, (2) to identify types of chemical interactions, and (3) to provide empirical data for predicting the geochemical fate of injected wastes. Specific procedures for performing interaction tests described in the scientific literature vary considerably but can be grouped into two types: **batch tests** and **flowthrough tests**.

Batch tests are performed by mixing wastes and reservoir materials in the same proportions as those expected in the field. The materials are mixed in a series of reactors, which may be subjected to temperatures and pressures that simulate the deep-well environment. The reactors are opened in sequence at regular time intervals 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. Chapter Four describes procedures for batch tests in more detail.

Flowthrough tests, also called **dynamic coreflood tests**, 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 the experiment, and the injected fluid is monitored at the outflow end at specified intervals to observe changes in chemistry. In adsorption experiments, equilibrium adsorption is obtained when the outflow concentation 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. Chapter Four describes procedures for flowthrough tests in more detail.

Table 1-8 summarizes information on 11 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 of the experiment.

The following issues should be considered when selecting a laboratory method for evaluating interactions between wastes and reservoir materials:

- The results of any test method will contain uncertainties created by the sample chosen (which may not be representative of the injection zone) and by the possible alteration of in-situ properties caused by shaping.

Furthermore, because the duration of such experiments is usually measured in hours or days, only those reactions reaching equilibrium quickly will be measured. Reactions taking years to reach equilibrium will not be measured.

- Tests must simulate temperature and pressures in the injection zone unless preliminary tests show that these parameters do not significantly affect the process 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 normal atmospheric pressure. Subsequent experiments were then conducted at atmospheric pressure.

- Experimental results from tests using simulated sand cores or simulated waste solutions have lower confidence levels than those in which actual cores and waste streams are used.

- Batch experiments using disaggregated material are likely to overestimate adsorption rates because of the larger surface area that is created by disaggregation. Batch experiments using undisturbed cores are more likely to yield better results, but they still will not simulate subsurface conditons as effectively as flowthrough experiments in undisturbed cores.

- Flowthrough experiments on subsurface cores at simulated temperature and pressure conditions will probably yield the best results, although the uncertainties that affect all types of waste-reservoir-interaction experiments still apply.

1.7 Field Case Studies

The most extensive field studies of geochemical fate of deep-well-injected wastes have taken place at four sites. Three involved carbonate injection zones in Florida (Pensacola-Monsanto, Pensacola-American Cyanamid, and Belle Glade, all of which are still active) and one involved an injection zone of mixed lithology (now abandoned) near Wilmington, North Carolina. Section 2.7 in this document provides some information on these field studies. Table 1-9 summarizes information on these field case studies, including geochemical processes observed, and some additional literature references.

The published data for these field case studies are 10 to 15 years old. Additional geochemical field studies of deep-injection wells are needed in these and other

Table 1-8 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	25-55	0.1-11.7	Roy et al., 1988
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 et al., 1975
Flowthrough — Column					
Unspecified	Miocene sand	—	—	—	Hower et al., 1972
Acidic, organic	Cretaceous sand (simulated)	80	20	0.1	Elkan and Horvath, 1977
Flowthrough — Undisturbed					
Acidic (steel)	Mt. Simon sandstone	—	?	0.1	Bayazeed and Donaldson, 1973
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

Table 1-9 Summary of Case Studies

Location	Lithology	Wastes	Processes Observed	Additional Sources of Information
Florida Pensacola (Monsanto)	Limestone	Nitric Acid Inorganic Salts Organic compounds	Neutralization Bacterial dentrification	Barraclough, 1966 Dean, 1965 Goolsby, 1971 Goolsby, 1972 Faulkner and Pascale, 1975 Pascale and Martin, 1978 Elkan and Hovarth, 1977 Willis et al., 1975
Pensacola (American Cyanamid)	LImestone	Acrylonitrile Sodium salts (nitrate, sulfate, thiocyanate)	Bacterial dentrification No retardation of thiocyanate ions	Ehrlich et al., 1979 Vecchioli et al., 1984
Belle Glade	Carbonate	Hot acid Organic plant wastes	Neutralization Bacterial sulfate reduction Methane production	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 Adsorption Bacterial sulfate and iron reduction Methane production Complexation	DiTommaso and Elkan, 1973 Leenheer and Malcom, 1973 Peek and Heath, 1973 Leenheer et al., 1976a,b Elkan and Horvarth, 1977

geological areas and should be designed to consider current regulatory requirements.

1.8 Further Research Needs

This section compiles the research recommendations contained in the reports summarized in Chapters Two through Six and includes additional recommendations arising from the synthesis in this chapter (see Section 1.8.4). The section from which the recommendation comes is noted after each recommendation.

1.8.1 Thermodynamic- and Aqueous-Geochemistry Modeling

■ Continue to refine and add to the thermodynamic databases required for modeling, and develop data on thermodynamic properties of water-miscible organic compounds. (Section 3.8).

- Develop solid-solution models and the capability to model precisely the thermodynamic properties of strong mixed electrolytes (brines) for a diverse range of injection-zone conditions (Section 3.8). Accurately determine the activity coefficients of ions in strong mixed electrolytes (Section 6.8).

- Develop better data and understanding of the thermodynamic properties of clays, and develop thermodynamic data for minerals and organic aqueous species for which no data are currently available (Section 6.8).

- Perform more field validation studies of geochemical codes (Section 6.8).

1.8.2 Adsorption

- Develop an integrated compilation of data in the extensive literature describing adsorption of inorganic and organic species on clays (Section 6.8).

- Develop empirical models describing irreversible adsorption of water-miscible organic compounds on mineral surfaces in an injection zone (Section 3.8).

- Develop adsorption or ion-exchange models that can be used under the conditions of deep-well injection (Section 6.8).

1.8.3 Specific Laboratory and Field Studies

- Conduct dynamic coreflood (i.e., flowthrough) studies of selected phenols (a common hazardous constituent of injected wastes) and determine their short-term fate (30 to 60 days) under typical reservoir conditions created in the laboratory. Such parameters as solution pH, salt concentration, temperatures, clay composition, and waste concentration should be evaluated with respect to precipitation, adsorption, permeability reduction, and thermal degradation (Section 2.8).

- Conduct additional dynamic coreflood and/or related studies of selected hazardous wastes to determine their fate in subsurface environments. These studies might include: coreflood studies using different cores and other organic-waste compounds; studies of the interactions of phenols with confining-layer materials (using batch reactors rather than corefloods); and studies of the effects of microorganisms on the degradation of phenols (Section 2.8).

- Study further nonequilibrium in in-situ brines. The comparison of simulated and actual Gulf Coast brines in Section 3.5 suggest that in-situ brines are not in homogeneous or heterogeneous equilibrium (Section 3.8).

- Conduct field studies to compare results of laboratory experiments and computer modeling reported in Chapter Three. These studies could involve injecting a simulated waste stream containing variable amounts of sodium borate and cresol in an arenaceous (sandstone) formation. The injected stream could be left in place for an extended period of time, then recovered and changes in its composition measured. The formation fluids could be continually removed and measured for changes in borate and cresol, allowing the adsorptive-desorptive capacity of the rock, potential decomposition products, and various hydrologic parameters to be determined. The results could be correlated with laboratory studies and conclusions drawn regarding the scaling factors and more fundamental differences in mechanisms between laboratory and field conditions (Section 3.8).

1.8.4 Other Research Needs

- Measure hydrolysis rate constants of selected hazardous organic compounds at simulated deep-well-injection temperatures, pressures, and salinities. The selected halogenated aliphatic hydrocarbons and phthalate esters in Table 1-1 would be good candidates for such studies.

- Develop information on the amount and chemical characteristics of organic matter in typical deep-well-injection formations. (The Frio formation in Texas, which receives more injected wastes than any other formation, would be a good candidate.) Evaluate the significance of organic matter in deep-well injection as it affects adsorption and complexation as compared with its significance in near-surface environments.

- Perform general studies of the ecology of anaerobic bacteria in deep-well-injection formations to identify measurable environmental parameters (pH, Eh, salinity, inorganic substrates, etc.) that in combination might be used to predict which type of anaerobic microorganisms (denitrifying, sulfate-reducing, and methanogenic) are likely to be most active in degrading hazardous constituents of injected wastes. Perform more specific studies of the ability of sulfate-reducing bacteria to degrade hazardous organic wastes.

References

Apps, J. A. 1988. *Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of*

Deep Disposal Wells. Draft Report prepared for EPA, Lawrence Berkeley Laboratory, LBL-26007.

Apps, J., L. Tsao, and O. Weres. 1988. The Chemistry of Waste Fluid Disposal in Deep Injection Wells. *2nd Berkeley Symposium on Topics in Petroleum Engineering*, pp. 79-82. Lawrence Berkeley Laboratory, LBL-24337.

Barnes, I. 1972. Water-Mineral Reactions Related to Potential Fluid Injection Problems. In *Symposium on Underground Waste Management and Environmental Implications*, T.D. Cook, ed. Houston, Texas. Am. Ass. Petr. Geol. Mem. 18. pp. 294-297.

Barraclough, J. T. 1966. Waste Injection into a Deep Limestone in Northwestern Florida. *Ground Water* 4(1):22-24.
Bayazeed, A. F., and E. C. Donaldson. 1973. *Subsurface Disposal of Steel Pickle Liquor.* U.S. Bureau of Mines. Report of Investigation 7804, 31 pp.

Bouwer, E. J., and P. L. McCarty. 1984. Modeling of Trace Organics Biotransformation in the Subsurface. *Ground Water* 22(4):433-440.

Callahan, M. A., et al. 1979. *Water-Related Environmental Fate of 129 Priority Pollutants.* EPA Report 440/4-79-029a-b. Washington DC.

Carnahan, C. L. 1986. *Simulation of Uranium Transport with Variable Temperature and Oxidation Potential: The Computer Program THCC.* Lawrence Berkeley Laboratory, LBL-21639.

Carnahan, C. L. 1987. Simulation of Chemically Reactive Solute Transport under Conditions of Changing Temperature. In *Coupled Processes Associated with Nuclear Waste Repositories*, C.F. Tsang, ed. Academic Press, Orlando, Florida, pp. 249-257

Cederberg, G. A., R. L. Street, and J. O. Leckie. 1985. A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems. *Water Resources Research* 21:1095-1104.

Chang, H. T., and B. E. Rittmann. 1987a. Mathematical Modeling of Biofilm on Activated Carbon. *Environ. Sci. Technol.* 21(3):273-280.

Chang, H. T., and B. E. Rittmann. 1987b. Verification of the Model of Biofilm on Activated Carbon. *Environ. Sci. Technol.* 21(3) 280-288.

Collins, A. G., and M. E. Crocker. 1988. *Laboratory Protocol for Determining Fate of Waste Disposed in Deep Wells.*

EPA Report 600/8-88/008. National Institute for Petroleum and Energy Research, Bartlesville, OK.

Crowe, A. S., and F. J. Longstaffe. 1987. Extension of Geochemical Modeling Techniques to Brines: Coupling of the Pitzer Equations to PHREEQ. In *Solving Ground Water Problems with Models.* Conference on Solving Ground Water Problems with Models, Denver, CO. National Water Well Association, Dublin, Ohio, pp. 110-129.

Davis, K. E., and R. J. Funk. 1972. Control of Unconsolidated Sands in Waste Disposal Wells. In *Symposium on Underground Waste Management and Environmental Implications*, T. D. Cook, ed. Houston, Texas. Am. Ass. Petr. Geol. Mem. 18. pp. 112-118.

Dean, B. T. 1965. The Design and Operation of Deep-Well Disposal System. *Water Pollution Control Federation Journal* 37:245-254.

DiTommaso, A., and G. H. Elkan. 1973. Role of Bacteria in Decomposition of Injected Liquid Waste at Wilmington, North Carolina. In *International Symposium on Underground Waste Management and Artificial Recharge*, J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences, pp. 585-599.

Donaldson, E. C., and R. T. Johanson. 1973. History of a Two-Well Industrial-Waste Disposal System. In *International Symposium on Underground Waste Management and Artificial Recharge*, J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences. pp. 603-621.

Donaldson, E. C., M. E. Crocker, and F. S. Manning. 1975. *Adsorption of Organic Compounds on Cottage Grove Sandstone.* Bartlesville Energy Research Center, Oklahoma. BERC/RI-75/4.

Edwards, A. L. 1972. *TRUMP: A Computer Program for Transient and Steady State Temperature Distributions in Multi-Dimensional Systems*, Rev. 3. Lawrence Livermore National Laboratory Report 14754.

Ehrlich, G. G., E. M. Godsy, C. A. Pascale, and J. Vecchioli. 1979. Chemical Changes in an Industrial Waste Liquid During Post-Injection Movement in a Limestone Aquifer, Pensacola, Florida. *Ground Water* 17(6):562-573.

Elkan, G., and E. Horvath. 1977. *The Role of Microorganisms in the Decompositon of Deep Well Injected Liquid Industrial Wastes.* Prepared for National Science Foundation, NTIS PB-268 646.

Ellington, J. J., et al. 1988. *Measurement of Hydrolysis Rate Constants for Evaluation of Hazardous Waste Land Disposal, V. III: Data on 70 Chemicals.* EPA Report 600/3-88/028. PB88-234042.

Faulkner, G. L., and C. A. Pascale. 1975. Monitoring Regional Effects of High Pressure Injection of Industrial Waste Water in a Limestone Aquifer. *Ground Water* 13(2):197-208.

Felmy, A. R., D. Girvin, and E. A. Jenne. 1984. *MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria.* EPA Report 600/3-84-032. Washington DC.

Garcia-Bengochea, J. I., and R. O. Vernon. 1970. Deep-Well Disposal of Waste Waters in Saline Aquifers of South Florida. *Water Resources Research* 6(5):1464-70.
Goolsby, D. A. 1971. Hydrogeochemical Effects of Injecting Wastes into a Limestone Aquifer near Pensacola, Florida. *Ground Water* 9(1)13-17.

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*, T. D. Cook, ed. Houston, Texas. Am. Assn. Petr. Geol. Mem. 18. pp. 355-368.

Grove D. A., and W. W. Wood. 1979. Prediction and Field Verification of Subsurface-Water Quality Changes During Artificial Recharge, Lubbock, Texas. *Ground Water* 17:250-257.

Grula, M. M., and E. A. Grula. 1976. *Feasibility of Microbial Decomposition of Organic Wastes under Conditions Existing in Deep Wells.* Bartlesville Energy Research Center, BERC/RI-76/6.

Haas, J. L., Jr. 1974. *PHAS20, A Program for Simultaneous Multiple Regression of a Mathematical Model to Thermochemical Data.* NTIS AD-780 301.

Haas, J. L., Jr., and J. R. Fisher. 1976. Simultaneous Evaluation and Correlation of Thermodynamic Data. *American Journal of Science* 276:525-545.

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*, T. D. Cook, ed. Houston, Texas. Am. Assn. Petr. Geol. Mem. 18, pp. 287-293.

Huyakorn, P. S., S. D. Thomas, J. W. Mercer, and H. B. Lester. 1983. *SATURN: A Finite Element Model for Simulating Saturated-Unsaturated Flow and Radioactive Transport.* Prepared by GeoTrans for the Electric Power Research Institute, Palo Alto, California.

Jackson, K. J., and T. J. Wolery. 1985. Extension of the EQ3/6 Computer Codes to Geochemical Modeling of Brines. *Materials Research Society Symposium Proceeding* 44:507-513.

Jennings, A. A., K. J. Kirkner, and T. L. Theis. 1982. Multicomponent Equilibrium Chemistry in Groundwater Quality Models. *Water Resources Research* 18:1089-1096.

Kamath, K., and M. Salazar. 1986. The Role of the Critical Temperature of Carbon Dioxide on the Behavior of Wells Injecting Hydrochloric Acid into Carbonate Formations. In *Proc. Int. Symp. of Subsurface Injection of Liquid Wastes, New Orleans.* National Water Well Association. pp. 638-655.

Kaufman, M. I., D. A. Goolsby, and G. L. Faulkner. 1973. Injection of Acidic Industrial Waste Into a Saline Carbonate Aquifer: Geochemical Aspects. In *International Symposium on Underground Waste Management and Artificial Recharge*, J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences, pp. 526-55.

Kaufman, M. I., and D. J. McKenzie. 1975. Upward Migration of Deep-Well Waste Injection Fluids in Floridan Aquifer, South Florida. *J. Research U. S. Geological Survey* 3(3):261-271.

Kharaka, Y. K., and I. Barnes. 1973. *SOLMEQ: Solution-Mineral Equilibrium Computation.* U.S. Geological Survey, NTIS PB 215-899, 81 pp.

Kirkner, D. J., A. A. Jenning, and T. L. Theis. 1985. Multisolute Mass Transport with Chemical Interaction Kinetics. *J. of Hydrology* 76:107-117.

Kirkner, D. J., T. L. Theis, and A. A. Jennings. 1984. Multicomponent Solute Transport with Sorption and Soluble Complexation. *Advances in Water Resources* 7:120-125.

Krupka, K. M., and J. K. Morrey. 1985. MINTEQ Geochemical Reaction Code: Status and Applications. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste.* G. K. Jacobs and S. K. Whatley, eds. NUREG/CP0062, ORNL/TM-9585, p. 46-53. U.S. Nuclear Regulatory Commission, Washington DC.

Leenheer, J. A., and R. L. Malcolm. 1973. Case History of Subsurface Waste Injection of an Industrial Organic Waste. In *International Symposium on Underground Waste Management and Artificial Recharge*, J. Braunstein, ed.

Pub. No. 110, Int. Assn. of Hydrological Science, pp. 565-584.

Leenheer, J. A., R. L. Malcolm, and W. R. White. 1976a. *Physical, Chemical and Biological Aspects of Subsurface Organic Waste Injection near Wilmington, North Carolina.* U. S. Geol. Surv. Prof. Paper 987.

Leenheer, J. A., R. L. Malcolm, and W. R. White. 1976b. Investigation of the Reactivity and Fate of Certain Organic Compounds of an Industrial Waste After Deep-Well Injection. *Environ. Sci. Tech.* 10(5):445-451.

Liu, C. W., and T. N. Narashimhan. 1989a. Redox-Driven Multiple Species Reactive Chemical Transport in Groundwater Systems, Part 1: Model Development. Submitted to *Water Resources Research* 25:869-882.

Liu, C. W., and T. N. Narashimhan. 1989b. Redox-Driven Multiple Species Reactive Chemical Transport in Groundwater Systems, Part 2: Verification and Applicaton. Submitted to *Water Resources Research* 25:883-910.

McCarty, P. L., M. Reinhard, and B. E. Rittmann. 1981. Trace Organics in Groundwater. *Environ. Sci. Technol.* 15(1):40-51.

McKenzie, D. J. 1976. *Injection of Acidic Industrial Waste into the Floridan Aquifer near Belle Glade, Florida: Upward Migration and Geochemical Interactions.* U.S. Geol. Surv. Open File Report 76-626.

Miller, C. W., and L. V. Benson. 1983. Simulation of Solute Transport in a Chemically Reactive Heterogeneous System. *Water Resources Res.* 19(2):381-391.

Mills, W. B., et al. 1985. *Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants* (Revised 1985). EPA Report 600/6-85/002a-b. Athens, Georgia.

Morel, F., and J. Morgan. 1972. A Numerical Method for Computing Equilibria in Aqueous Chemical Systems. *Envrion. Sci. Technol.* 9(1):58-67.

Narashimhan, T. N., A. F. White, and T. Takunaga. 1986. Groundwater Contamination from an Inactive Uranium Mill Tailings Pile, 2. Application of a Dynamic Mixing Model. *Water Resources Research* 22(13):1820-1834.

Noorishad, J., and C. L. Carnahan. 1985. Development of a Kinetic Equilibrium Chemical Transport Code. *Trans. Am. Geophysical Union* 66:274.

Noorishad, J., C. L. Carnahan, and L. V. Benson. 1987. *A Report on the Development of the Non-Eqilibrium Reactive Chemical Transport Code CHMTRNS.* Lawrence Berkeley Laboratory Report, LBL-22361, 229 pp.

Nordstrom, D. K., et al. 1979. A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems. In *Chemical Modeling in Aqueous Systems,* E. A. Jenne, ed. *Advances in Chemistry* 110:857-892.

Panagiotopoulos, A. Z., and R. C. Reid. 1986. Deep-Well Injection of Aqueous Hydrochloric Acid. In *Proc. Int. Symp. of Subsurface Injection of Liquid Wastes, New Orleans.* National Water Well Association, pp. 610-637.

Parkhurst, D. L., D. C. Thorstensen, and L. N. Plummer. 1980. *PHREEQE A Computer Program for Geochemical Calculation.* U.S. Geological Survey Water Resources Investigation 80-96.

Pascale, C. A., and J. B. Martin. 1978. *Hydrologic Monitoring of a Deep-Well Waste-Injection System near Pensacola, Florida, March 1970-March 1977.* U.S. Geol. Surv. Water Res. Invest. 78-27.

Peek, H. M., and R. C. Heath. 1973. Feasibility Study of Liquid-Waste Injection into Aquifers Containing Salt Water, Wilmington, North Carolina. *International Symposium on Underground Waste Management and Artificial Recharge,* J. Braunstein, ed. Pub. No. 110, Int. Assn. of Hydrological Sciences, pp. 851-875.

Plummer, L. N., and D. L. Parkhurst. 1985. PHREEQE: Status and Applications. In *Proceedings of the Conferences on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment,* G. K. Jacobs and S. K. Whattley, eds. NUREG/CP-0062, ORNLY/TM-9585. U.S. Nuclear Regulatory Commission, Washington, DC, pp. 37-46.

Plummer, L. N., D. L. Parkhurst, and D. C. Thorstenson. 1983. Development of Reaction Models for Ground Water Systems. *Geochimica et Cosmochimica Acta* 47:665-686.

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. Research U.S. Geol. Survey* 6(1):1-9.

Reardon, E. J. 1981. Kd's—Can They Be Used to Describe Reversible Ion Sorption Reactions in Contaminant Migration? *Ground Water* 19 (3):279-286.

Rittmann, B. E., and P. L. McCarty. 1980a. Model of Steady-State Biofilm Kinetics. *Biotech. Bioeng* 22:2343-2357.

Rittmann, B. E., and P. L. McCarty. 1980b. Evaluation of Steady-State Biofilm Kinetics. *Biotech. Bioeng.* 22:2359-2373.

Rittmann, B. E., P. L. McCarty, and P. V. Roberts. 1980. Trace-Organics Biodegradation in Aquifer Recharge. *Ground Water* 18(3):236-242.

Roy, W. R., S. C. Mravik, I. G. Krapac, D. R. Dickerson, and R. A. Griffin. 1988. *Geochemical Interactions of Hazardous Wastes with Geological Formations in Deep-Well Systems.* Illinois Geological Survey, Champaign, Illinois.

Rubin, J., and R. V. James. 1973. Dispersion-Affected Transport of Reacting Solutes in Saturated Porous Media: Galerkin Method Applied to Equilibrium Controlled Exchange in Unidirectional Steady Water Flow. *Water Resources Res.* 9(5):1332

Schwarzenbach, R. P., and W. Geiger. 1985. Behavior and Fate of Halogenated Hydrocarbons in Ground Water. *Ground Water Quality,* C. H. Ward, W. Giger, and P. L. McCarty, eds. Wiley Interscience, New York. pp. 446-471.

Scrivner, N. C., K. E. Bennet, R. A. Pease, A. Kopatsis, S. J. Sanders, D. M. Clark, and M. Rafal. 1986. Chemical Fate of Injected Wastes. In *Proc. Int. Symp. on Subsurface Injection of Liquid Wastes, New Orleans.* National Water Well Association, pp. 560-609.

Shock, E., and H. C. Helgeson. 1988. Calculation of Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Prediction to 5 kb and 1000°C. Submitted to the *Am. J. Science.*

Shock, E., and H. C. Helgeson. 1989. Calculation of Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Standard Partial Molal Properties of Organic Species. Submitted to *Geochimica et Cosmochimica.*

Solomon, C. 1986. *Reaction Path Modeling of Interaction between Basalt and Groundwater in the Columbia Plateau, Washington.* Presented at Workshop of Geochemical Modeling, Fallen Leaf Lake, California, Sept. 14-17.

Swolf, H. S. 1972. Chemical Effects of Pore Fluids on Rock Properties. In *Symposium on Underground Waste Management and Environmental Implications,* T. D. Cook,

ed. Houston, Texas. Am. Assn. Petr. Geol. Mem. 18, pp. 224-234.

Tanger, J. C., and H. C. Helgeson. 1988. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperature: I. Revised Equation of State for the Standard Partial Molal Properties of Ions and Electrolytes. *American Journal of Science* 288:19-98.

Theis, T. L., D. J. Kirkner, and A. A. Jennings. 1984. *Multi-Solute Subsurface Transport Modeling for Energy Solid Wastes.* Report DOE/ER-0222, 8 pp.

U.S. Environmental Protection Agency. 1985. *Report to Congress on Injection of Hazardous Waste.* EPA Report 570/9-85-003. Washington DC. PB86-203056.
U.S. Environmental Protection Agency. 1989. *Injection Well Mechanical Integrity.* EPA Report 625/9-89/007.

Valocchi, A. J., P. V. Roberts, G. A. Parks, and R. L. Street. 1981. Simulation of the Transport of Ion-Exchanging Solutes Using Laboratory-Determined Chemical Parameter Values. *Ground Water* 19(6):600-607.

Valocchi, A. J., R. L. Street, and P. V. Roberts. 1981. Transport of Ion-Exchanging Solutes in Groundwater: Chromatographic Theory and Field Simulation. *Water Resources Research* 17(5):1517-1527.

Vecchioli, J., G. G. Ehrlich, E. M. Godsy, and C. A. Pascale. 1984. Alterations in the Chemistry of an Industrial Waste Liquid Injected into Limestone Near Pensacola, Florida. In *Hydrogeology of Karstic Terrains, Case Histories, V. 1.,* G. Castany, E. Groba, and E. Romijn, eds. International Association of Hydro- geologists, pp. 217-221.

Veley, C. D. 1969. How Hydrolyzable Metal Ions React with Clays To Control Formation Water Sensitivity. *J. Petroleum Tech.* September:1111-1118

Walsh, M. P., L. W. Lake, and R. S. Schechter. 1982. A Description of Chemical Precipitation Mechanisms and Their Role in Formation Damage during Simulation by Hydrofluoric Acid. *J. of Petroleum Technology* 34:2097-2112.

Westall, J. C., J. L. Zachary, and F. M. M. Morel. 1976. *MINEQL—A Computer Program for the Calculation of Chemical Equilibrium Compositions of Aqueous Systems.* MIT Technical Note No. 18, 91 pp.

White, A. F., J. M. Delany, T. N. Narashimhan, and A. Smith 1984. Groundwater Contamination from an Inactive

Uranium Mill Tailings Pile, 1: Application of a Chemical Mixing Model. *Water Resources Research* 20:1743-1752.

Williamson, K., and P. L. McCarty. 1976a. A Model of Substrate Utilization by Bacterial Films. *J. Water Poll. Control Federation* 48:9.

Williamson, K., and P. L. McCarty. 1976b. Verification Studies of the Biofilm Model for Bacterial Substrate Utilization. *J. Water Poll. Control Federation* 48:281.

Willis, C. J., G. H. Elkan, E. Horvath, and K. R. Dail. 1975. Bacterial Flora of Saline Aquifers. *Ground Water* 13(5):406-409.

Wolery, T. J. 1979. *Calculation of Chemical Equilibrium between Aqueous Solution and Minerals: The EQK3/6 Software Package.* Lawrence Livermore Laboratory Report UCRL-52658, 41 pp.

Wolery, T. J. 1983. *EQ3NR, A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation.* Lawrence Livermore Laboratory Report UCRL-53414, 191 pp.

Wolery, T. J. 1986. *Requirements for Development and Use of Scientific and Engineering Software (EQ3/6 Task).* Lawrence Livermore Laboratory Report, draft.

Wolery, T. J., and L. J. Walters, Jr. 1975. Calculation of Equilibrium Distribution of Species in Aqueous Solutions by Means of Monotone Sequences. *Mathematical Geology* 7(2):99-115.

CHAPTER TWO

RESEARCH SUMMARY NO. 1
STATE-OF-THE-ART REPORT: INJECTION OF HAZARDOUS WASTES INTO DEEP WELLS

2.1 Overview

2.1.1 Origin and Content
Source: *State-of-the-Art Report: Injection of Hazardous Wastes into Deep Wells.* EPA/600/8-87/013, February 1987. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. 55 pages. NTIS PB87-170551.

Authors: Arden Strycker and A. Gene Collins, National Institute for Petroleum and Energy Research, P.O. Box 2128, Bartlesville, Oklahoma 74005.

Contents: Literature review of 82 sources on: (1) processes affecting the geochemical fate of inorganic and organic hazardous wastes, (2) mathematical models used for predicting fate, and (3) field case studies involving deep-well injection of hazardous waste.

2.1.2 Major Conclusions
■ Many factors affect the ultimate fate of injected wastes. These factors include the pH and Eh of the waste and reservoir fluids, brine concentration of the waste fluids, clay type and amount in the reservoir, presence or absence of iron oxides, presence or absence of organic complexing agents, molecular characteristics of organic materials, and other factors that determine if the environment is anaerobic or aerobic. All these factors are interrelated and any mixing of different types of hazardous wastes in the reservoir further complicates the situation, making it difficult to predict exactly what occurs after wastes are injected. Relevant research conducted to date concerning this problem has been limited and is not sufficient to address the problem of predicting ultimate fate.

■ The basic compatibility test conducted by mixing waste fluids and reservoir fluids does not always give meaningful results. The test must be conducted under reservoir conditions. Precipitates, if

formed in the compatibility test, may or may not plug the well depending on the type formed.

■ For inorganic wastes, solution pH is critical for determining the ultimate fate. The identity of soluble species, solubility products, adsorption characteristics, and chemical interactions are some of the variables affected by pH.

■ The brine concentration, even though not listed as hazardous, can affect clay stability and adsorption characteristics.

■ The presence of organic complexing agents may or may not affect the mobility of heavy metals in the reservoir.

■ Adsorption of inorganic wastes depends on a number of factors, such as Eh, pH, clay type, and the presence or absence of iron oxide and hydroxides.

■ Hydrolysis is the major mechanism for degradation of certain halogenated hydrocarbons.

■ Microbial degradation processes can transform hazardous wastes after deep-well injection, but results are not always predictable.

2.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

2.2.1 Overview of Fate-Influencing Processes
Subsurface reservoir fluids have equilibrated with reservoir minerals and clays during geologic time. All the minerals, rocks, hydrocarbons, and gases are interrelated and contribute to the final stable solute/solvent matrix that exists in the reservoir. On the other hand, waste solutions considered for deep-well injection are generated in a different environment and have attained a thermodynamic equilibrium under different conditions. Consequently, when

wastes are injected into the formation, adjustments must occur in the reservoir before a new solute/solution equilibrium is reached.

2.2.2 Partition Processes

Acid/Base Reactions. See discussion of pH in Section 2.3.2.

Adsorption-desorption. Adsorption is a major mechanism affecting mobility of organic wastes. Factors affecting the degree of adsorption of a chemical include: molecular shape and configuration, pH, water solubility, charge distribution, polarity, molecular size, and polarizability. Molecular shape may increase or decrease adsorption energies of any particular compound even though the other chemical properties may be very similar (Bailey and White, 1970).

Adsorption mechanisms for organic chemicals include: ion exchange, protonation at the silicate surface, protonation in the solution phase with subsequent adsorption by ion exchange, and protonation by reaction with the disassociated protons from residual water present on the surface or in coordination with the exchangeable cation; organic cations are most easily adsorbed by ion exchange and the process is similar to that for inorganic materials (Bailey and White, 1970). Other adsorption mechanisms include Van der Waals forces, hydrogen bonding, and the formation of metal complexes.

Ion exchange is a very common adsorption mechanism for organic wastes (Bailey and White, 1970). At high salinity levels, ion-exchange rates tend to be slow (Veley, 1969). Complex polyvalent metal ions tend to adsorb strongly to clay particles so that ion exchange is less extensive than in clays with adsorbed calcium and sodium particles (Veley, 1969). The effect of complexing agents on adsorption depends on energy levels in relationship to ion-exchange processes; slight difference in conditions may have a major impact on the overall results (Champlin, 1969).

Adsorption processes in soil depend on: the structural characteristics of the molecule, organic content of the soil, pH of the medium, particle size, ion-exchange capacity, and temperature. Generally, as the solubility of the adsorbate decreases, adsorption increases, and as organic content of soil increases, adsorption increases (Haque et al., 1980).

Once materials are adsorbed, other processes that lead to their degradation may take place: microorganisms may metabolize wastes and clays, or minerals attached to clays may catalytically initiate other such reactions. Mortland (1985) discusses organic-adsorption mechanisms that in-clude: replacement of metals with cationic molecules, replacement of metals by neutral molecules that are protonated to become cationic, ion exchange with polyvalent metals attached to the clay, coordination with metal cations, and hydrogen bonding. This last occurs when esters hydrolyze (McAuliffe and Coleman, 1955). Other examples of adsorption are also discussed by Mortland (1985).

Temperature affects adsorption. Since adsorption processes are generally exothermic and desorption generally endothermic, an increase in temperature would normally reduce adsorption processes. EPTC (Theis et al., 1980) and pentachlorophenol (Choi and Aomine, 1974a,b) are exceptions.

The relative energies associated with complexing agents, ion-exchange processes, and adsorption processes will affect the degree of adsorption. Energies associated with some chelating agents are approximately the same as those of cation-silicate interactions, in which case slight differences in conditions may have a major impact on the amount of adsorption (Champlin, 1969). Chelating agents that enhance the solubility of uranium, cobalt, strontium, and cesium do not necessarily decrease adsorption. In the presence of clays, cobalt is less strongly adsorbed, strontium and cesium are not affected, and uranium is more strongly adsorbed. The higher uranium/acid-complex adsorption may be caused by additional electrostatic and molecular dipole-attractive forces (Means, 1982).

The amount of organic and inorganic materials adsorbed depends on the amount and type of clay present in the formation because different clays have different surface areas and charge densities. Since clays possess an overall negative charge, cations such as moderately soluble metal wastes are attracted to these clays. The more-soluble ions previously attached to the clays may resolubilize when other, less-soluble ions replace them on the clay surface, i.e., ion exchange (Wilson, 1980). Two types of clay, montmorillonite and vermiculite, have very high adsorption capacities, whereas kaolinite has a very low capacity and illite and chlorite have intermediate capacities. The adsorptive properties of clay have been attributed to the available surface area for the respective clays (Bailey and White, 1970). The interactions between waste fluids and formation clays have been difficult to characterize.

Clays become saturated with a particular ion when all the adsorption sites are filled; no further adsorption can occur. The saturation level depends on the amount and type of clay and whether iron and manganese oxides are present as additional adsorption surfaces. The net negative

charge of clays comes from the replacement of aluminum and silicon ions with other ions having lower oxidation states within the structure of the clay. Different clays behave in different ways because throughout a clay or between different clays ion replacement is not uniform, with consequent variations in the degree of negative charge (Scrivner et al., 1986a,b). Low-salinity or high-pH solutions cause water molecules to be adsorbed. When adsorbed, they separate the crystal layers of clay, causing it to swell. The realigned layers usually will not return to their original state even if higher-salinity solutions are again added.

Complex (polyvalent) metal ions adsorb strongly to clay particles. Strong adsorption behavior may immobilize metals and protect clays from swelling and fines migration. At high salinity levels, complex metal ions that are adsorbed onto unattached, fine clay particles may migrate in suspension (Champlin, 1969).

Certain metals (particularly heavy metals) associated with the clay may bond so tightly that they may be considered immobile or permanently adsorbed. On the other hand, metals that do not adsorb tightly may desorb at a later time when a different waste is injected.

A number of experiments show the variability of adsorption:

- Choi and Aomine (1974a,b) report that ion exchange and Van der Waals forces were the adsorption mechanisms acting on pentachloro- phenol. The degree of adsorption was highly pH-dependent and the temperature effects were not those anticipated.

- O'Connor et al. (1985) report that lesser amounts of trichloroethylene and pentachlorophenol adsorbed on Missouri soils as pH increased.

- Rogers and McFarlane (1981) report that adsorption of carbon tetrachloride, ethylene dibromide, and chloroform on montmorillonite clay depends on the degree of saturation by such cations as calcium and aluminum.

- Schwarzenbach and Giger (1985) report that at near-surface conditions adsorption of chlorinated benzenes increases as organic carbon increases.

See Section 2.5.2 for discussion of methods for predicting adsorption, and the Wilmington, North Carolina, case study (Section 2.7.2) for an example of adsorption involving injected wastes.

Precipitation-dissolution. Reactions between injected and interstitial fluids can produce precipitates in deep wells: (1) alkaline earth metals (calcium, barium, strontium, and magnesium) can precipitate as insoluble carbonates, sulfates, orthophosphates, fluorides, and hydroxides; (2) other metals (such as iron, aluminum, cadmium, zinc, manganese, and chromium) can precipitate as insoluble carbonates, bicarbonates, hydroxides, orthophosphates, and sulfides, and (3) oxidation-reduction reaction products, such as hydrogen sulfide with chromium (VI), may precipitate (Warner, 1966; Selm and Hulse, 1960). Ferric hydroxide, which is gelatinous, appreciably blocks the flow of fluids through a porous matrix; barium sulfate and calcium sulfate, which are finely crystalline, do not (Warner, 1966). A buffer zone of nonreactive water may prevent plugging due to precipitation (Warner, 1966). Precipitation reactions are more sensitive to temperature than pressure (Grubbs et al., 1972). Reeder et al. (1975) and Elkan et al. (1975) discuss an injection well in the Arbuckle formation that is an example of a well becoming plugged with precipitates. Scale indices have been developed to predict potential precipitation problems (Browne, 1984).

Above pH 10, calcium, barium, strontium, magnesium, and iron will form gelatinous hydroxide precipitates. Lower-pH solutions containing bicarbonates will convert to carbonates if the pH is raised and precipitates of iron, calcium, and magnesium carbonates result.

High-pH solutions can dissolve silica and release fines that may migrate and plug pores. Re-precipitation of dissolved silica in another section of the reservoir may reduce permeability (Thornton and Radke, 1985; Thornton and Lorenz, 1987). Certain low-pH solutions initially may leach some formation minerals; the solutions may also cause other minerals to precipitate and reduce permeability rather than increase it (Grubbs et al., 1972). Low-pH solutions may lead to the formation of silica gels or the dissolution of some clays and carbonates (either as a matrix or as cements); these problems are not as evident in carbonate formations, but later deposition of materials caused by changes in pH may also be a problem in carbonate formations.

Toxicity is a function of solubility, and solubility determines the relative mobility of materials. The more soluble the metal, the greater the rate of transport and the greater the magnitude of toxicity. Simple solution properties such as pH and Eh affect solubility. Concentrations also affect solubility; when ferric ion is present in low concentrations, natural organics such as humic acids form true solutions due to organometallic complexes. Pentachlorophenol

precipitates in solutions at pH less than 5 (Choi and Aomine, 1974a,b).

An injection well in the Magothy aquifer in New York exhibited a nearly 10-fold increase in ferrous ions over either injected or native fluids. Apparently the underground environment changed from a reducing to an oxidizing environment, leading to the dissolution of pyrite (iron sulfide). The ferrous ions produced by this process precipitated as ferric hydroxide in the presence of oxygen (Ragone et al., 1973). The chemistry of these reactions is complicated by the pH and Eh of the solution, the presence of Fe^{+3}, partial oxygen pressure, and the presence of organics. See the Wilmington, North Carolina, case study (Section 2.7.2) for examples of precipitation involving injected wastes.

2.2.3 Transformation Processes

Biological Transformation. See discussion of microbial degradation in this section.

Complexation. Organic chemicals can form complexes with metals that increase the solubility of the metal (Means and Hubbard, 1985; Means, 1982; Francis, 1985). The solubility of most metals is much higher when they are in the form of organometallic complexes. Naturally occurring chemicals that can partially complex with metal compounds and increase their solubility include: aliphatic acids, aromatic acids, alcohols, aldehydes, ketones, amines, aromatic hydrocarbons, esters, ethers, and phenols (Means and Hubbard, 1985). Natural organics such as humic acids form solutions of organometallic complexes when the ferric-ion concentration is low. At higher concentrations, colloidal suspensions are formed from the same humic acids, which may reduce intermolecular repulsion forces in the metal-complexed molecule. As a result, the organic material may recoil and become less hydrated in the solution, since all of the polar sites are taken up by the metal, and may remain suspended or precipitate, depending on the particle size (Means, 1982). Bacteria can degrade the organic components of organometallic complexed particles and may also convert some non-complexing materials into complexing agents. Depending on the conditions, mobility of metals in this situation may be increased or decreased (Francis, 1985). See the Wilmington, North Carolina, case study (Section 2.7.2) for an example of complexation involving injected wastes.

Cyclization. See discussion of thermal degradation in this section.

Hydrolysis. Hydrolysis is the chemical process by which a functional group attached to a molecule is replaced by an -OH functional group originating from a water molecule. Potentially, hydrolysis can either detoxify organic hazard-

ous waste, rendering it nonhazardous, or increase the toxicity of certain wastes. For organic materials, such factors as pH, temperature, and the presence of other ions affect the rate of hydrolysis. At low pH the hydronium ion predominates and at high pH the hydroxide ion is more prevalent. The magnitude of temperature effects on different compounds is not always known.

Hydrated polyvalent metal ions hydrolyze and form multiple associations with other metals. When these complex polynuclear ions associate with clay particles, a very tight structure forms around the clay crystal, and months or years may be required before true equilibrium is reached among all these different metal associations.

Hydrolysis can be catalyzed by either an acid or a base. The presence of certain alkaline earth and heavy-metal ions may also catalyze hydrolysis for a variety of esters (Mabey and Mill, 1978). Most hazardous wastes that potentially can undergo hydrolysis reactions are halogenated hydrocarbons. Since these compounds are not normally biodegradable, hydrolysis is expected to be the main mechanism of transformation. Hydrolysis half-lives at conditions that exist near the surface range from days to thousands of years (see discussion of carbon tetrachloride, ethylene dibromide, and chloroform in Section 2.4.2). Subsurface environments, with their increased temperatures and pressures and reduced Eh, may contribute to shorter half-lives.

Aliphatic and alkylic halides can hydrolyze under neutral or basic conditions to give alcohols, but these compounds are not likely to undergo the same process under acidic conditions. Different halides (phenyl dichloromethane, dichloromethane, and chlorobenzene) have very different hydrolysis rates. Section 2.5.2 discusses how to predict hydrolysis half-lives.

Microbial Degradation. Biodegradation can result from a variety of processes (Alexander, 1980, 1981; Crosby, 1973). Biological transformation may render organic hazardous wastes nonhazardous but for certain wastes actually increase toxicity. Biodegradation processes include: mineralization (conversion of organic to inorganic wastes), detoxification (conversion of toxic compounds to nontoxic compounds), co-metabolism (conversion of one organic compound to another without the microorganism's using this process as a nutrient), activation (conversion of a nontoxic compound to a toxic compound), and defusing (conversion of a compound capable of becoming hazardous to another, nonhazardous compound by circumventing the hazardous intermediate). Defusing has been observed in the laboratory but not identified in the environment.

Bacteria can degrade the organic components of organometallic complexed particles and may also covert some noncomplexing materials into complexing agents. Depending on conditions, mobility of metals may be increased or decreased (Francis, 1985).

Whether the environment is aerobic determines what biodegradation process will predominate. Some wastes are more easily degraded by aerobes (e.g., chlorobenzenes) and others are more easily degraded by anaerobes (e.g., carbon tetrachloride) (Jackson et al., 1985). Aerobic degradation is usually more efficient than anaerobic degradation, and higher temperatures are not so limiting for aerobes. Some compounds such as aromatics can be degraded only by aerobes (Grula and Grula, 1976).

Anaerobic degradation is a multistep process in which complex compounds are broken down by certain facultative bacteria, and the resulting short-chain acid anions are broken down by methanogenic bacteria (Novak and Ramish, 1975). Other mechanisms for anaerobic degradation have been proposed (Means and Hubbard, 1985). In anaerobic conditions, pH affects the extent to which methanogenic bacteria or sulfate-reducing bacteria proliferate. The two types of bacteria do not degrade the same compounds (Horvath, 1977).

A number of studies have looked at the effects of environmental conditions on microorganisms. Christofi et al. (1985) report that microorganisms exist in water samples taken from underground coal mines in Germany at all depths (600 to 3,000 ft) but greatest variety was found in the least-saline aquifer. Several studies indicate that, in general, growth and reproduction processes of bacteria occurring at near-surface conditions decrease with increasing pressures to 600 atmospheres (about 8,800 psi), whereas bacteria isolated from the marine environment at depths normal to these same pressures grow well in laboratory studies (ZoBell and Johnson, 1949; ZoBell and Oppenheimer, 1950; ZoBell and Cobet, 1962; Morita and ZoBell, 1956). The effects of high pressures on microorganism metabolic rates are unknown at present. At least one study has looked at the effects of temperature on microorganisms. In this study, aliphatic acids (acetate ions) were found to be degraded by methanogenic bacteria in oilfield waters with temperatures lower than 80° (Carothers and Kharaka, 1978).

When hazardous-waste injection begins, other microorganisms that can utilize the waste often appear and remain in the reservoir during injection. After organic wastes are injected, the reservoir tends to become more anaerobic and dominated by methanogenic and sulfate-reducing

bacteria (Elkan and Horvath, 1975; Elkan, 1975). Laboratory model studies found microbial populations increased by seven or more orders of magnitude when waste was introduced into the model. Degradation of formic acid in the laboratory model increased as pressure increased to 500, but decreased when pressures were increased to 4,000 psi (Grula and Grula, 1976). Before injection at one site, aerobic bacteria (3,000 organisms/m) dominated a saline aquifer at 850-1,000 ft. After injection of mostly acidic wastes (acetic acid, formic acid, and methanol), anaerobic methanogenic bacteria were predominant (DiTommaso and Elkan, 1972).

Some compounds (certain chlorinated alkanes and alkenes) are not degraded in the materials normally found in deep subsurface environments; others are readily degraded (toluene and styrene), although not equally in different environments (Wilson et al., 1985). Consequently, Wilson et al. (1985) recommend that biodegradation should not be depended on for waste degradation unless the particular waste has been tested in the materials encountered and at the likely downhole conditions. Naphthalene and heptaldehyde may be degraded, whereas haloforms are not (Rittman et al., 1980). Horvath (1977) has summarized processes involving biodegradation of acetate, formate, methanol, formaldehyde, and aromatic acids. See the Wilmington, North Carolina, case study (Section 2.7.2) for an example of microbial degradation involving injected wastes.

Neutralization. See the Wilmington, North Carolina, case study (Section 2.7.2) for an example of neutralization involving injected wastes. See also pH effects.

Thermal Degradation. Thermal degradation processes include pyrolysis, condensation reactions, cyclization, and intramolecular rearrangements. Most of these processes occur only under very high temperatures or in the presence of other chemicals. Reservoir temperatures and pressures commonly existing in the injection zones of hazardous-waste-injection wells are normally too low for initiating high-temperature reactions, but if the right chemicals (not necessarily hazardous) are present, thermal degradation might be initiated. For example, phenols can react with formaldehyde to form phenolic resins. The number and types of these reactions are almost limitless; each reservoir and waste should be evaluated individually. Thermal decarboxylization is probably the mechanism for acetate degradation in oilfield waters with temperatures greater than 200°C (Carothers and Kharaka, 1978).

2.2.4 Transport Processes
Dilution. Dilution by mixing with other waters contributes to low concentrations of aliphatic acids (acetate) in oilfield

waters at temperatures of less than 80°C (Carothers and Kharaka, 1978).

Dispersion. Mixing of fluids and precipitation reactions depend on hydrodynamic- dispersion properties (Warner, 1966). Advective and dispersive properties must be measured in the underground environment to predict adsorption processes (Roberts et al., 1985).

Fluid Migration. There are at least five ways a waste material may migrate and contaminate potable ground water (*Water Well Journal*, 1974).

1. Wastes may escape through the well bore into a underground source of drinking water (USDW) because of insufficient casing or failure of the injection-well casing due to corrosion, excessive injection pressure, etc.

2. Waste may escape vertically outside the well casing from the injection zone.

3. Waste may escape vertically from the injection zone through confining beds that are inadequate because of high primary permeability, solution channels, joints, faults, or induced fractures.

4. Wastes may escape vertically from the injection zone through nearby wells that are improperly cemented or plugged or that have insufficient or leaky casing.

5. Wastes may contaminate a USDW directly by lateral travel of the injected waste water from a region of saline water to a region of fresh water within the same aquifer.

Particle Migration. Clay swelling and clay-particle migration are possible with any injected fluid. In secondary and/or tertiary petroleum-recovery operations, engineers usually avoid injecting alkaline solutions and sometimes all aqueous solutions when water-sensitive clays are present. Damage to clays can result in drastically reduced permeabilities, and to prevent damage to reservoirs, specialized products that stabilize clays are often used to treat injected fluids.

Low concentrations of salts can lead to clay migration, and high-pH solutions tend to dissolve silica and release fines that can migrate and plug pores, reducing permeability (Hower et al., 1972). Low salinity leads to the loosening of the clay structure, with swelling (usually irreversible) and migration (Veley, 1969). Sodium ions bind less strongly to clay than do calcium ions and are more likely to result in reduction in permeability from clay swelling and migration. Complex metal ions may bind so strongly with clay particles that there will be little ion exchange with sodium, so that

swelling and migration are less likely under reduced-salinity conditions (Veley, 1969). Complex metal ions that are adsorbed onto very small particles of clay may migrate as metal-clay particles depending on the physical forces affecting particle-particle interactions, particle-matrix interactions, and gravitational effects (Champlin, 1969). Laboratory flow experiments found that at low salinity levels in a sand core, ion-clay particles were retained by the sand, whereas at high salinity levels ion-clay particles passed through the core (Champlin, 1969).

Oxidation-Reduction. Oxidation-reduction (redox) processes can render organic hazardous waste nonhazardous but increase toxicity for certain wastes. The exact species of oxygen radicals in aqueous and soil environments that initiate oxidation will depend on environmental conditions; the importance of this process at typical conditions for hazardous organic-waste injection has not been evaluated. Changes in oxidation state may render metals nonhazardous. Compounds such as phenols, aromatic amines, olefins, dienes, alkyl sulfides, and eneamines are particularly susceptible to oxidation reactions (Mill, 1980). Oxidation is more likely to be important in wastes containing chromium (VI). See the Wilmington, North Carolina, case study (Section 2.7.2) for an example of reduction of injected wastes.

2.3 Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes

2.3.1 Geochemical Characteristics of Deep-Well Zones
A typical injection well might be described as having the following characteristics. The well is 3,925 ft deep with an injection zone more than 200 ft thick. The injection zone is composed of sandstone/sand/silt, the confining zone of clay/shale. The median wellhead pressure and injection flow are 285 psig and 150 gallons per minute (Huff, 1986). Most facilities treat the waste before injection, with common pretreatment including solids removal, equalization, and pH adjustment. About 96 percent of the total volume injected is water.

2.3.2 Specific Environmental Factors
pH. When injected and reservoir solutions have different pH values, plugging problems can develop. The pH of these solutions is important because ion concentrations are linear functions of the fluid proportions, but the equilibrium constants are not. For example, injected and interstitial fluids that are saturated with carbonate may be incompatible due to different pH values. Above pH 10, calcium, barium, strontium, magnesium, and iron will form gelatinous hydroxide precipitates. Lower-pH solutions

containing bicarbonate will convert to carbonates if the pH is raised, and iron, calcium, and magnesium carbonates may precipitate (Barnes, 1972).

Certain low-pH solutions initially may leach some formation minerals but may also cause other minerals to precipitate, actually reducing permeability rather than increasing it (Grubbs et al., 1972). High-pH solutions tend to dissolve silica and release fines that may migrate and plug pores (Hower et al., 1972). Low-pH solutions may produce silica gels or dissolve some clays and carbonates (either in the matrix or in the well-casing cement). The pH of a solution strongly influences the formation of organometallic complexes. High-pH solutions tend to cause clays to swell.

Arsenic cations are more mobile than selenium, cadmium, and lead under anaerobic conditions when pH is neutral to alkaline (Fuller, 1977). At higher pH values, cadmium exists as various hydroxides (Fuller, 1977). In acidic solutions, pentachlorophenol concentrations decrease by precipitation; when pH values are greater than 5, the concentration decreases in the presence of clay because of adsorption. O'Connor et al. (1985) found that lesser amounts of trichloroethylene and pentachlorophenol adsorb on Missouri soils as pH increases.

Hydrolysis rates are also affected by pH. Aliphatic and alkylic halides can hydrolyze under neutral or basic conditions to give alcohols, but they are not likely to hydrolyze under acidic conditions. Under anaerobic conditions, pH strongly affects whether methanogenic or sulfate-reducing bacteria predominate (Horvath, 1977).

Temperature. Compatibility testing of solutions should be kept at reservoir temperature. Temperature is generally a more important factor than pressure in causing plugging when incompatible fluids are present (Grubbs et al., 1972). Subsurface temperatures affect the presence or absence of acetate ions in formation water samples in California and Texas (Carothers and Kharaka, 1978). The effect of temperature on the solubility of thorium sulfides depends on the hydrate being tested (Goldschmidt, 1958). Adsorption processes are generally exothermic, so an increase in temperature normally reduces adsorption, but a number of exceptions have been found (Theis et al., 1985). The pesticide EPTC and pentachlorophenol are examples of substances that are adsorbed more easily at higher temperatures (Theis et al, 1985; Choi and Aomine, 1974a). Temperature also influences hydrolysis rate, but the magnitude of this influence on different compounds is not always known. Increased temperatures in subsurface environments may lead to shorter hydrolysis half-lives for organic materials.

Pressure. Compatibility testing of solutions should be kept at reservoir pressure. Pressure is generally less important than temperature in causing plugging when incompatible fluids are present (Grubbs et al., 1972). Increased pressures in subsurface environments may lead to shorter hydrolysis half-lives for organic materials. Degradation rates of formic acid increase as pressure increases to 500 psi but decrease when pressures are further increased, to 4,000 psi (Elkan and Horvath, 1977; Elkan, 1975). In general, bacterial growth and reproduction decrease with increasing pressure to 600 atmospheres (about 8,000 psi) except for bacteria isolated from deep marine environments, which are adapted to high pressure (ZoBell and Cobet, 1962; ZoBell and Johnson, 1949; ZoBell and Oppenheimer, 1950; Morita and ZoBell, 1956).

2.4 Geochemical Characteristics and Fate of Hazardous Waste

A 1983 EPA survey of 108 active hazardous-waste wells found that most of the wastes categorized as hazardous contained either acid solutions or organic materials (U.S. EPA, 1985). The report by Callahan et al. (1979) provides a good summary of the expected fate of 129 nonorganic and organic hazardous-waste compounds. Although that report addresses the aquatic environment, and not deep-well-injection zones, the information is useful.

2.4.1 Specific Data on Inorganic Substances
Alkaline Earth Metals. Calcium, barium, strontium, and magnesium may react with injected fluids and precipitate as insoluble carbonates, sulfates, orthophosphates, fluorides, and hydroxides.

Alkaline Solutions. Alkaline solutions injected into reservoirs containing water-sensitive clays can drastically reduce permeabilities.

Arsenic. Arsenic is generally more mobile under anaerobic than aerobic conditions. It is more mobile than selenium, cadmium, and lead under aerobic conditions when the pH is neutral to alkaline. Some microorganisms can convert arsenic hydroxide to an organic compound (Fuller, 1977). Certain forms react with limestone to produce carbon dioxide; certain forms adsorb onto shales with varying amounts of clay (Stone et al., 1975).

Barium Sulfate. Barium sulfate does not appreciably block the flow of fluids through a porous matrix (Warner, 1966).

Cadmium. Cadmium may react with injection fluid and precipitate as insoluble carbonates, bicarbonates,

hydroxides, orthophosphates, and sulfides. This metal is less soluble than many others, but more so than lead. At higher pH values, mixtures of hydroxides will exist in various concentrations (Fuller, 1977; Jurinak and Santillan-Medran, 1974; Fugii, 1978; Stone et al., 1975). The presence of oxides and hydrous oxides of iron increases adsorption properties, and maximum adsorption of cadmium depends on Eh and pH (Ku et al., 1978). Some forms of cadmium react with limestone to produce carbon dioxide and adsorb onto certain shales containing varying amounts of clays (Stone et al., 1975). Cadmium will precipitate as cadmium sulfide in the presence of hydrogen sulfide.

Calcium Sulfate. This compound does not appreciably block the flow of fluids through a porous matrix (Warner, 1966).

Cesium. The solubility of chelated organic compounds containing cesium is not affected by the presence of clays (Means, 1982).

Chromium. Chromium (VI) is an excellent oxidizing agent. This compound reacts with hydrogen sulfide to form a precipitate. Chromates in a waste stream reacting with barium sulfate, hydrogen sulfide, and soluble iron form precipitates that eventually plugged a well in the Arbuckle formation (Reeder et al., 1975). Under neutral-to-alkaline conditions, chromium (VI) is more mobile than most of the metals listed. Under oxidizing conditions in soils, chromium (VI) will form insoluble precipitates with resident biological materials. Chromium (III) can adsorb strongly in acid solutions and will precipitate at pH values above 6 (as hydroxide, carbonate, or sulfide), whereas chromium (VI) does not (Fuller, 1977). Chromium (VI) can adsorb onto oxides and hydrous oxides of iron (Ku et al., 1978).

Cobalt. Solubility of chelated organic compounds containing cobalt increased in the presence of clays (Means, 1982).

Ferric Hydroxide. This compound appreciably blocks the flow of fluids through a porous matrix (Warner, 1966).

Lead. The solubilities for lead are lower and the tendencies to adsorption higher than for most of the other metals listed (Fuller, 1977). Typical precipitates are lead hydroxide and lead carbonate (Jurinak and Santillan-Medran, 1974). Sodium chloride somewhat increases the solubility of lead (Stone et al., 1975).

Mercury. Bacteria can convert inorganic mercury compounds to the more toxic and volatile dimethyl mercury (Fuller, 1977). A major problem in soil environments is the volatility of mono- and dimethyl-mercury compounds

(Stone et al., 1975). This metal strongly adsorbs onto iron oxides if present. Whether bioconversion and hazardous volatilization of mercury occur in injection zones is not known.

Nickel. Nickel adsorbs strongly in the presence of iron and manganese oxides. It is not very soluble in the presence of carbonates, hydroxides, or sulfides (Fuller, 1977). Soluble salts include nickel acetate, chloride, nitrate, and sulfate (Stone et al., 1975). Nickel oxides may be solubilized in strong acid, but as strong acids are neutralized in the reservoir, these oxides may then precipitate. Nickel carbonyl is very toxic and potentially explosive when concentrated; it is stable in dilute acid or basic solutions but will produce carbon monoxide and nickel metal when heated (Ku et al., 1978).

Selenium. Some selenium compounds adsorb more strongly in the presence of iron oxides (Nebergall et al., 1968). Selenium dioxide is readily soluble in water and forms selenous acid in aqueous solutions (Partington, 1966). Many selenium compounds can be reduced to produce selenium metal when exposed to organic matter in the subsurface environment (Goldschmidt, 1958).

Strontium. The solubility of chelated organic compounds containing strontium is not affected by the presence of clays (Means, 1982).

Thorium. Thorium salts are not very soluble in neutral-pH natural waters. Soluble salts include sulfates, chlorides, and some sulfides, but as the solution becomes basic, these salts precipitate as hydroxide (Goldschmidt, 1958). The effect of temperature on solubility of thorium sulfides depends on the hydrate: some hydrates increase in solubility with increasing temperature, others decrease (Goldschmidt, 1958).

Uranium. The solubility of chelated organic compounds containing uranium decreased in the presence of clays because of adsorption (Means, 1982).

2.4.2 Specific Data on Organic Substances
Acetic Acid/Acetate. Acetic acid and acetate are present in oilfield waters (Carothers and Kharaka, 1978). Thermal decarboxylation occurs at temperatures greater than 200°C (Kharaka, 1978). Microbial degradation by methanogenic bacteria occurs at temperatures less than 80°C (Means and Hubbard, 1985). Horvath (1977) summarizes biodegradation processes for these compounds. Anaerobic methanogenic bacteria replaced aerobic bacteria after injection of wastes containing acetic acid, formic acid, and methanol (DiTommaso and Elkan, 1973). See the Wilmington, North Carolina, case study (Section 2.7.2) for

an example of the degradation of acetic acid in an injection zone.

Acidic Wastes. See Belle Glade, Florida, case study (Section 2.7.1).

Alcohols. Alcohols partially complex with metal compounds (Means and Hubbard, 1985). The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures were studied by Grula and Grula (1976).

Aldehydes. Aldehydes partially complex with metal compounds (Means and Hubbard, 1985). The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures were studied by Grula and Grula (1976).

Aliphatic Acids. Aliphatic acids partially complex with metal compounds (Means and Hubbard, 1985).

Aliphatic Halides. Aliphatic halides can hydrolyze under neutral or basic conditions to give alcohols, but this reaction is not likely under acidic conditions. The hydrolysis rate depends on the type of halide.

Alkyl Sulfides. Alkyl sulfides are particularly susceptible to oxidation (Mill, 1980).

Alkylic Halides. Alkylic halides can hydrolyze under neutral or basic conditions to give alcohols, but this reaction is not likely under acidic conditions. The hydrolysis rate depends on the type of halide.

Amines. Amines partially complex with metal compounds (Means and Hubbard, 1985). Aromatic amines are particularly susceptible to oxidation (Mill, 1980). The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures were studied by Grula and Grula (1965).

Aromatic Acids. Aromatic acids partially complex with metal compounds (Means and Hubbard, 1985). Horvath (1977) summarizes the biodegradation processes affecting aromatic acids.

Aromatic Compounds. Aromatic compounds can be degraded only by aerobic bacteria; higher temperatures are not a limiting factor for biodegradation of these compounds.

Aromatic Hydrocarbons. Aromatic hydrocarbons partially complex with metal compounds (Means and Hubbard, 1985).

Benzoic Acids. The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures were studied by Grula and Grula (1976). See also the Wilmington, North Carolina, case study (Section 2.7.2).

Carbon Tetrachloride. Carbon tetrachloride, a halogenated hydrocarbon, does not adsorb onto calcium-saturated montmorillonite clay (Rogers and McFarlane, 1981). It is not normally biodegradable, and it has a hydrolysis half-life of 700 to 7,000 years at near-surface conditions; subsurface conditions *may* lead to shorter half-lives with the increased temperatures, pressures, and Eh present in this environment.

Carboxylic Acids. The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures were studied by Grula and Grula (1976).

Chlorinated Alkanes and Alkenes. These compounds are not biodegraded in materials normally found in deep subsurface environments (Wilson et al., 1985).

Chlorinated Benzenes. At the concentrations typical in the natural environment, a linear- adsorption isotherm can be used to represent the adsorption of chlorinated benzenes in the injection zone. Adsorption increases as organic carbon increases (Schwarzenbach and Giger, 1985).

Chlorobenzene. Chlorobenzene is virtually resistant to hydrolysis under normal circumstances.

Chloroform.. Chloroform, a halogenated hydrocarbon, does not adsorb onto calcium-saturated montmorillonite clay but showed 17 percent adsorption onto aluminum-saturated montmorillonite clay. The mechanism for this difference is not understood (Rogers and McFarlane, 1981); chloroform is not normally biodegradable, and it has a hydrolysis half-life intermediate between ethylene dibromide (5 to 10 days) and carbon tetrachloride (700 to 7,000 years) at near-surface conditions. Subsurface conditions, with their increased temperatures, pressures, and Eh, *may* lead to shorter hydrolysis half-lives.

Dichloromethane. The hydrolysis rate constant for dichloromethane is about five orders of magnitude lower than that for phenyl dichloromethane.

Dienes. Dienes are particularly susceptible to oxidation (Mill, 1980).

Diethylenetriaminepentaacetic Acid (DPTA). DPTA is a chelating agent that can increase the mobility of metals in an underground environment (Means and Hubbard, 1985; Means, 1982; Francis, 1985).

Enamines. Enamines are particularly susceptible to oxidation (Mill, 1980).

EPTC. EPTC is a pesticide for which adsorption increases with temperature (Theis et al., 1980).

Esters. Esters partially complex with metal compounds (Means and Hubbard, 1985). Clay or minerals attached to the clays can catalytically initiate the hydrolysis of adsorbed esters (McAuliffe and Coleman, 1955). The presence of certain alkaline-earth and heavy-metal ions may catalyze hydrolysis for a variety of esters (Mabey and Mill, 1978).

Ethers. Ethers partially complex with metal compounds (Means and Hubbard, 1985).

Ethylenediaminetetraacetic Acid (EDTA). EDTA is a chelating agent that can increase the mobility of metals in an underground environment (Means and Hubbard, 1985; Means, 1982; Francis, 1985).

Ethylene Dibromide (EDB). Rogers and McFarlane (1981) present data on adsorption of ethylene dibromide on montmorillonite clay. This compound is normally biodegradable and has a hydrolysis half-life of 5 to 10 days at near-surface conditions. Subsurface conditions, with their increased temperatures, pressures, and Eh, *may* lead to shorter hydrolysis half-lives.

Formaldehyde. The biodegradation processes affecting formaldehyde are summarized by Healy and Daughton (1986). Phenols can react with formaldehyde to form phenolic resins. This was the only waste organic compound *not* adsorbed onto aquifer mineral constituents (see the Wilmington, North Carolina, case study, Section 2.7.2).

Formate. Biodegradation of formate is summarized by Healy and Daughton (1986).

Formic Acid. Anaerobic methanogenic bacteria replaced aerobic bacteria after wastes containing acetic acid, formic acid, and methanol were injected (DiTommaso and Elkan, 1973). See also the Wilmington, North Carolina, case study (Section 2.7.2).

Haloforms. Haloforms are not subject to biodegradation (Rittman et al., 1980).

Halogenated Hydrocarbons. These compounds are not normally biodegradable; hydrolysis is expected to be the main mechanism of transformation. Most data on hydrolysis are derived under conditions most likely to occur in the near-surface environment. See also carbon tetrachloride, ethylene dibromide, and chloroform in this section.

Heptaldehyde. Heptaldehyde is subject to biodegradation (Rittman et al., 1980).

Ketones. Ketones partially complex with metal compounds (Means and Hubbard, 1985). The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures on ketones were studied by Grula and Grula (1976).

Methanol. Biodegradation processes affecting methanol are summarized by Healy and Daughton (1986). Anaerobic methanogenic bacteria replaced aerobic bacteria after wastes containing acetic acid, formic acid, and methanol were injected (DiTommaso and Elkan, 1973). See also the Wilmington, North Carolina, case study (Section 2.7.2).

Naphthalene. Naphthalene is subject to biodegradation (Rittman et al., 1980).

Nitrate. See the Pensacola, Florida (American Cyanamid), case study (Section 2.7.3).

Nitric Acid. See the Pensacola, Florida (Monsanto), case study (Section 2.7.4).

Nitriles. The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures on nitriles were studied by Grula and Grula (1976).

Nitro-aromatic Compounds. The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures on nitro-aromatic compounds were studied by Grula and Grula (1976).

Nitrotriacetic Acid (NTA). Nitrotriacetic acid is a chelating agent that can increase the mobility of metals in an underground environment (Means and Hubbard, 1985; Means, 1982; Francis, 1985).

Olefins. Olefins are particularly susceptible to oxidation (Mill, 1980).

Organonitrile Compounds. See the Pensacola, Florida (American Cyanamid), case study (Section 2.7.3).

Pentachlorophenol. This compound is adsorbed through a combination of ion-exchange and Van der Waals forces. A pH greater than 5 results in adsorption; adsorption decreases with an increase in the concentration of other salts in solution. Adsorption is greater at higher tempera-

tures, e.g., 33°C (Choi and Aomine, 1974a,b). Precipitation occurs at pH less than 5 (Choi and Aomine, 1974a,b). Pentachlorophenol adsorbs on several Missouri soils more readily than tricholorethylene. O'Connor et al. (1985) noted that adsorption of pentachlorophenol decreased as pH increased.

Phenols. Phenols partially complex with metal compounds (Means and Hubbard, 1985). They are particularly susceptible to oxidation (Mill, 1980) and can react with formaldehyde to form phenolic resins. The effects of enriched cultures of microorganisms, temperature, pressures, and mixed cultures on phenols were studied by Grula and Grula (1976).

Phenyl Dichloromethane. The hydrolysis rate constant of phenyl dichloromethane is about five orders of magnitude greater than that for dichloromethane.

Phthalic Acid. Adsorption of phthalic acid does *not* increase with a decrease in the pH of the waste (see the Wilmington, North Carolina, case study, Section 2.7.2).

p-Toluic Acid. See the Wilmington, North Carolina, case study (Section 2.7.2).

Sodium Thiocyanate. This compound remained unaltered during movement through the injection zone (see the American Cyanamid case study, Section 2.7.3).

Terephthalic Acid. See the Wilmington, North Carolina, case study (Section 2.7.2).

Toluene. Toluene biodegrades readily in materials normally found in deep subsurface environments; the rate varies with conditions (Wilson et al., 1985).

Trichloroethylene. This compound adsorbed less readily than pentachlorophenol on several Missouri soils. O'Connor et al. (1985) found that adsorption of trichloroethylene decreases as pH increases.

Styrene. Styrene biodegrades readily in materials normally found in deep subsurface environments; the rate varies with conditions (Wilson et al., 1985).

2.5 Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes

2.5.1 Basic Approaches
Before the fate of a hazardous waste is assessed, all major chemical and biological pathways for movement or trans-

formation must be described. The description should predict concentration as a function of time for the original chemical and all subsequent products.

Many factors affect the ultimate fate of injected wastes: the pH and Eh of the waste and reservoir fluids, brine concentrations of the waste fluids, clay type and amount in the reservoir, presence or absence of iron oxides, presence or absence of complexing agents, molecular characteristics of organic materials, and other factors that determine if the environment is aerobic or anaerobic. All these factors are interrelated, and any mixing of different types of hazardous wastes in the reservoir further complicates the situation, making it difficult to predict exactly what occurs after the wastes are injected. Research is not sufficient to address the problem of predicting the fate of injected wastes.

Hazardous wastes are complex mixtures and their combination with other mixed waste streams increases factorially the potential number of interactions; knowledge of these interactions is limited. Further, since subsurface environments often take many years to reach chemical and biological equilibrium, prediction may be impossible. Examples of the difficulties are:

- A model using the simple mixing of injection fluids and reservoir fluids does not adequately represent the complexities that often occur. This problem is illustrated by examples of fluids that appear incompatible in the laboratory but cause little trouble in the field, while apparently compatible fluids have plugged injection wells.

- Predicting how much waste will be adsorbed, how long the waste will remain immobile, and under what circumstances the waste will be desorbed is difficult.

- Theoretical and laboratory studies are not sufficient to predict the transport of wastes in an underground aquifer. The underground environment contains variables that have not been studied extensively. Consequently, the degree of uncertainty in modeled predictions is large, and tracer and pilot tests in the field must still be performed.

- Data on degradation processes are more limited for organic wastes than for inorganic wastes because hardly any definitive work has been done and the number of possible interactions is much greater.

- Data on the origin of bacteria in subsurface environments, their activity levels, and the importance of nonbiological processes are not adequate to

predict the fate of organic wastes (Healy and Daughton, 1986). Unless pilot studies have established the existence of biodegradation in the subsurface environment, the modeler cannot depend on these processes to detoxify waste. Further, for each injection system, the relative importance of organometallic interactions and the possible presence of bacteria capable of generating complexing materials should be considered in detail.

2.5.2 Specific Methods and Models

Adsorption Methods and Models. Techniques that can be used to study and demonstrate mechanisms by which organic chemicals are adsorbed include adsorption isotherms, calorimetry, X-ray diffraction, UV-visible spectroscopy, electron-spin-resonance spectroscopy, and infrared spectroscopy (Mortland, 1985).

The Freundlich isotherm is often used to evaluate adsorption of chemical compounds to soil particles (Haque et al., 1980), as given by:

$$x/m = KC^n$$

where

x = amount of chemical adsorbed
m = mass of soil
C = equilibrium concentration of the chemical
K = constant describing the extent of adsorption
n = constant describing the nature of adsorption

Ionic compounds or compounds capable of becoming ionic do not necessarily follow the Freundlich-isotherm concept.

Aqueous- and Solution-Geochemistry Models. Schechter et al. (1985) present a good review of aqueous-geochemistry and solution-geochemistry models. If a particular situation can be defined as containing specified components, equilibrium constants can be approximated and overall results predicted. Certain thermodynamic parameters are known for many of the materials of interest and provide a reasonable starting point. Some of the popular models discussed include: WATQF, SOLMNEQ, PHREEQE, EQ3/EQ6, PATH1, MINEQLI, MINEQLI- STANFORD, PHASEQL/FLOW, and REDEQL.

Biodegradation Models. Although bacteria are documented to exist in subsurface environments, other factors necessary for predicting fate remain undetermined. These factors include: origin of the bacteria, level of activity, and the importance of other, nonbiological processes.

Laboratory-model studies allow the behavior of microbial populations to be predicted when certain organic wastes are introduced. Increases in populations of seven or more orders of magnitude have been predicted (Elkan and Horvath, 1977; Elkan, 1975).

A biofilm model can be used to predict biodegradation of some compounds. The model presumes the formation of a film of microorganisms that degrade the waste chemicals near the point of injection. Correlation of results with model predictions supports the concept (Rittman et al., 1980).

Hydrolysis Models. Hydrolysis half-lives for organic wastes that undergo this process can be estimated fairly accurately if rate constants are known for the compound at the appropriate temperature, pH, ionic strength, etc. However, the amount of data available on rate constants under varying conditions is limited. Extrapolations made from one temperature to another can introduce large errors (Mabey and Mill, 1978).

Precipitation Methods and Models. Various methods for testing the compatibility of injection fluids and reservoir fluids have been described (Warner, 1977; Wolbach et al., 1984; Kaufman et al., 1973; Donaldson, 1972). Generally, two fluids are simply mixed together and allowed to stand. The formation of precipitate usually indicates fluid-fluid incompatibility. The solutions should be kept at the temperatures and pressures of the reservoir. Synthetic solutions are not as reliable as native reservoir fluids for accurate results. Sufficient time (hours to days) for incubation should be allowed; true thermodynamic equilibrium may be slow for some systems.

The Warner sand-pack model (Warner, 1966) for predicting chemical reactions between injection wastes and reservoir fluids includes theoretical and laboratory work. The amount of mixing between different fluids depends on hydrodynamic dispersion. Once the dispersive property of a porous medium is characterized, the amount of chemical reaction can be accurately predicted. The type of precipitate determines the degree of permeability reduction (see discussion of ferric hydroxide, barium sulfate, and calcium sulfate in Section 2.4.1). The laboratory model showed that a sufficiently large buffer zone of nonreactive water would effectively prevent a precipitation problem (Warner, 1966).

Transport Models. Roberts et al. (1985) review mathematical models for simulating waste transport in underground aquifers. These models are designed to predict the advection, dispersion, and adsorption of non-degradable organic solutes. Actual field cases were examined and compared with theoretical and laboratory

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results. The study showed that adsorption can be predicted with some accuracy, but that advective and dispersive properties must be measured in the underground environment; theoretical and laboratory studies were *not* sufficient to predict behavior.

Mills et al. (1985) summarize five models that can be used to predict groundwater contamination. These models calculate contaminant concentrations as a function of time for a given set of conditions. Two models are radial one-dimensional, one model is cartesian one-dimensional, and two models are cartesian two-dimensional. Parameters such as boundary conditions, aquifer dimensions, dispersivity coefficients, porosity, initial contaminant concentrations, and retardation factors are needed.

Kayser and Collins (1986) summarize four types of models relevant to groundwater contamination from enhanced oil recovery (EOR) or other fluids: groundwater-flow model, solute-transport model, heat-transport model, and deformation model. Each type of model is based on different dependent variables and is particularly useful for answering different types of questions.

2.6 Laboratory Procedures and Protocols

Detailed laboratory procedures and protocols are not discussed in this report. Section 2.5.2 (Precipitation Methods and Models) lists references describing laboratory methods for testing compatibility of injected fluids with reservoir fluids.

2.7 Field Case Studies

2.7.1 Field Case Study: Belle Glade, Florida (McKenzie, 1976)

Waste Characteristics. The waste injected at this facility is a hot acidic liquid generated at a furfural plant.

Aquifer Geology/Characteristics. The injection zone is a saline carbonate aquifer.

Injection Activities. In 1966, wastes were injected into the lower part of the aquifer, between depths of 1,485 and 1,939 ft. When near-surface contamination was detected, the injection depth was increased to 2,200 ft, and later to 3,000 ft.

Processes Observed. The injected acids were neutralized by the limestone formation, resulting in higher concentrations of calcium, magnesium, and silica in the waste solution. Sulfate-reducing bacteria present in the formation converted sulfates to sulfides. The hydrogen sulfide produced by the bacteria and the subsequent decrease in sulfate/chloride ratio was one indication of fluid migration.

Effects of Injection. The carbonate aquifer could not contain the hot acid wastes. Within 27 months, the effects of wastes were detected at a shallow monitoring well in the upper part of the aquifer. Both upward and lateral migrations were indicated by a decrease in the sulfate/chloride ratio and a corresponding increase in the hydrogen-sulfide concentration in the observation well. Increasing the injection depth to 2,200 ft did not prevent upward migration. The effectiveness of increasing the injection depth to 3,000 ft has not been reported. No extensive work was performed to determine the extent of the contamination zone.

2.7.2 Field Case Study: Wilmington, North Carolina (Peek and Heath,1973; Leenheer and Malcolm, 1973; Leenheer et al., 1976a,b)

Waste Characteristics. Organic waste derived from the manufacture of dimethyl terphthalate was injected at this facility. The waste was composed of acetic acid, formic acid, p-toluic acid, formaldehyde, methanol, terphthalic acid, and benzoic acid, with an average dissolved organic carbon of about 7,100 mg/L. Before injection, the waste was neutralized to pH 4 by adding lime, resulting in a calcium content of about 1,300 mg/L.

Aquifer Geology/Characteristics. The injection zone was a sedimentary aquifer with saline water. Sodium chloride was the major dissolved-solid constituent in the native ground water, and average dissolved-solids concentration was about 28,800 mg/L.

Injection Activities. From May 1968 to December 1972, waste was injected at a rate of about 300,000 gal./day. The injection zone consisted of multiple zones ranging in depth from about 850 to 1,000 ft. Injection was discontinued in 1972 after the operators determined that waste disposal into the reservoir was not desirable. Monitoring of the waste movement and subsurface environment continued into the mid-1970s. Samples were taken from three observation wells located 1,500 to 2,000 ft from the injection wells.

Processes Observed. A number of processes were observed:

- The waste organic acids dissolved carbonate minerals, aluminosilicate minerals, and the sesquioxide 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 because of neutralization of the waste by the aquifer carbonates and oxides.

- The aquifer mineral constituents adsorbed all waste organic compounds except formaldehyde. Adsorption of all organic acids except the phthalic acid was increased with a decrease in waste pH.

- Phthalic acid formed complexes with dissolved iron. The concentration of this complex decreased as 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 the reduction of ferric ions to ferrous ions.

Effects of Injection. Wells became plugged after a few months of injection because of waste reactivity. The plugging resulted from precipitation of the initially dissolved minerals and from the formation of such gases as carbon dioxide and methane. The combination of plugging in the formation and the dissolution by the organic acids of the bond between the cement grout surrounding the well casing and confining beds resulted in leakage of waste upward into the shallower zone.

2.7.3 Field Case Study: Pensacola, Florida (American Cyanamid) *(Ehrlich et al., 1979; Vecchioli et al., 1984)*
Waste Characteristics. Industrial waste liquid containing organonitrile compounds, nitrate, and sodium thiocyanate was injected at this facility.

Aquifer Geology/Characteristics. The injection-zone aquifer was a limestone formation.

Injection Activities. No details were given on the injection activities themselves. One observation well was constructed in the zone.

Processes Observed. Microbiological degradation converted organic compounds to carbon dioxide, and nitrate was reduced to elemental nitrogen. These transformations were virtually complete within a short distance from the well. Sodium thiocyanate remained unaltered during movement through the injection zone and was used to detect the degree of mixing of waste liquid with native water at an observation well. An 80% reduction in chemical oxygen demand was observed.

Effects of Injection. The waste liquid was free from organonitriles and nitrate by the time it reached the monitoring well. Sodium thiocyanate remained as a contaminant.

2.7.4 Field Case Study: Pensacola, Florida (Monsanto) *(Pascale and Martin, 1978)*
Waste Characteristics. Liquid waste containing nitric acid, inorganic salts, and numerous organic compounds was injected at this facility.

Aquifer Geology/Characteristics. The injection-zone aquifer was saline limestone.

Injection Activities. Data on injection rates, volumes, pressures, water levels, and laboratory analyses of waste samples taken from three monitoring wells were collected between 1970 and 1977. Wellhead pressure averaged 180 psi in March 1977, and the hydraulic pressure gradient was 0.53 psi/ft of depth at the top of the injection zone.

Processes Observed. Microbial degradation of waste in the injection zone is inferred from observed increases in bicarbonate, dissolved organic carbon, and gas content in the deeper monitoring well.

Effects of Injection. No effects were observed in the shallower observation well. The deeper monitoring well to the south showed an increase in concentrations of bicarbonates, dissolved organic carbon, and gas.

2.8 Further Research Needs

All areas need to be investigated further. The following could be the most productive in the near-term:

- Conduct dynamic coreflood studies of selected phenols to determine their short-term fate (30 to 60 days) under typical reservoir conditions created in the laboratory. Such parameters as solution pH, salt concentrations, temperatures, clays, and waste concentration should be evaluated with respect to precipitation, adsorption, permeability reduction, and thermal degradation.

- Conduct additional dynamic coreflood and/or related studies of selected hazardous wastes to determine their fate in subsurface environments. These studies might include: coreflood studies

using different cores and other organic waste compounds; studies of the interactions of phenols with confining-layer materials (using hydrothermal reactors rather than corefloods); and studies of the effects of microorganisms on phenols.

References

Alexander, M. 1980. Biodegradation of Toxic Chemicals in Water and Soils. In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals*. R. Haque, ed. Ann Arbor Science, pp. 179-190.

Alexander, M. 1981. Biodegradation of Chemicals of Environmental Concern. *Science* 211:132-138.

Andes, F. P. 1986. Implementation of the 1984 Hazardous and Solid Waste Amendments. *Underground Injection* 1(1):6-7.

Bailey, G. W., and J. L. White. 1970. Factors Influencing the Adsorption, Desorption and Movement of Pesticides in Soil. In *Residue Reviews*, Vol. 32, F. A. Gunther, ed. Springer-Verlag, New York, pp. 29-92.

Barnes, I. 1972. Water-Mineral Reactions Related to Potential Fluid-Injection Problems. *Underground Waste Management and Environ. Impl.*, Mem. 18, publ. Am. Assoc. Petr. Geo., pp. 294-297.

Browne, G. 1984. *Incompatible Water*. Kansas Univ. Drilling and Prod. Inst., Liberal, Kansas, 12 pp.

Callahan, M. A., M. W. Slimak, N. W. Gabel, I. P. May, C. F. Fowler, J. R. Freed, P. Jennings, R. L. Durfee, F. C. Whitmore, B. Maestri, W. R. Mabey, B. R. Holt, and C. Gould. 1979. *Water-Related Environmental Fate of 129 Priority Pollutants*, Volume II. EPA Report 440/4-79-029b, Washington, D.C., December.

Carothers, W. W., and Y. K. Kharaka. 1978. Aliphatic Acid Anions in Oil-Field Waters—Implications for Origin of Natural Gas. *Am. Assoc. Petr. Geol. Bull.* 62(12):2441-2453.

Champlin, J. B. F. 1969. *The Transport of Radioisotopes by Fine Particulate Matter in Aquifers*. NTIS Report PB-232 179, December, 187 pp.

Choi, J., and S. Aomine. 1974a. Mechanisms of Pentachlorophenol Adsorption by Soils. *Soil Sci. Plant Nutr.* 20(4):371-379.

Choi, J., and S. Aomine. 1974b. Adsorption of Pentachlorophenol by Soils. *Soil Sci. Plant Nutr.* 20(2):135-144.

Crosby, D. G. 1973. The Fate of Pesticides in the Environment. *Ann. Rev. Plant Physiol.*, 24:467-492.

Christofi, N., J. M. West, and J. C. Philp. 1985. *The Geomicrobiology of European Mines Relevant to Radioactive Waste Disposal*. British Geological Survey Report FLPU 85-1, January, 21 pp.

DiTommaso, A., and G. H. Elkan. 1973. Role of Bacteria in Decomposition of Injected Liquid Waste at Wilmington, North Carolina. *Underground Waste Management and Artificial Recharge Prep.* Vol. 1, pp. 585-599.

Donaldson, E. C. 1972. Injection Wells and Operations Today. *Underground Waste Management and Environ. Impl.*, Mem. 18, publ. Am Assoc. Petr. Geol., pp. 24-46.

Dowd, R. M. 1986. Groundwater Protection Programs. *Environ. Sci. Technol.* 20(9):862.

Elkan, G. H. et al. 1975. *The Role of Microorganisms in the Decomposition of Deep-Well Injected Industrial Wastes*. EPA Report 600/2-77-029. Cited in Wilson (1980).

Elkan, G. 1975. *Role of Microorganisms in the Decomposition of Deep Well Injected Liquid Industrial Wastes*. NSF/RA/E-75-059, 45 pp.

Elkan, G., and E. Horvath. 1977. *Role of Microorganisms in the Decomposition of Deep Well Injected Liquid Industrial Wastes*. NSF/RA-770107. NTIS PB 268 646.

Ehrlich, G. G., E. M. Godsy, C. A. Pascale, and J. Vecchioli. 1979. Chemical Changes in an Industrial Waste Liquid During Post-Injection Movement in a Limestone Aquifer, Pensacola, Florida. *Ground Water* 17(6):562-573.

Francis, A. J. 1985. *Microbial Transformations of Natural Organic Compounds and Radionuclides in Subsurface Environments*. U.S. Department of Energy Report DE86 003631, October, 12 pp.

Fugii, R. 1978. *The Complexing and Adsorption of Cadmium in Soils in the Presence of EDTA and NTA*. NTIS Report PB-290 809, 112 pp.

Fuller, W. H. 1977. *Movement of Selected Metals, Asbestos, and Cyanide in Soil: Applications to Waste Disposal Problems*. EPA Report 600/2-77-020, Cincinnati, Ohio, April, 243 pp.

Goldschmidt, V. M. 1958. *Geochemistry*, A. Muir, ed., Oxford University Press, London.

Grubbs, D. M., C. D. Haynes, T. H. Hughes, and S. H. Stow. 1972. *Compatibility of Subsurface Reservoirs with Injected Liquid Wastes.* NTIS Report PB-211 326, June, 121 pp.

Grula, M. M., and E. A. Grula. 1976. *Feasibility of Microbial Decomposition of Organic Wastes under Conditions Existing in Deep Wells.* Bartlesville Energy Technology Report BERC/RI-76/6, Bartlesville, Oklahoma, 55 pp.

Haque, R., J. Falco, S. Cohen, and C. Riordan. 1980. Role of Transport and Fate Studies in the Exposure, Assessment and Screening of Toxic Chemicals. In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals*, R. Haque, ed. Ann Arbor Science, 1980, pp. 47-67.

Healy, J. B., Jr., and C. G. Daughton. 1986. *Issues Relevant to Biodegradation of Energy-Related Compounds in Ground Water, A Literature Review.* U.S. Department of Energy Report UCB/SEEHRL 86-10, September, 42 pp.

Horvath, E. 1977. *Interactions of Aquifer Flora and Industrial Waste in a Model Deep Well Disposal System.* PhD thesis, North Carolina State University, 111 pp.

Hower, W. F., R. M. Lasater, and R. G. Migham. 1972. Compatibility of Injection Fluids with Reservoir Components. *Underground Waste Management and Environ. Impl.*, Mem. 18, Am. Assoc. Petr. Geo., pp. 287-293.

Huff, P. 1986. Survey Shows Reliability. *Underground Injection* 1(1):2-4.

Jackson, R. E., R. J. Patterson, B. W. Graham, J. Bahr, D. Belanger, J. Lockwood, and M. Priddle. 1985. *Contaminant Hydrogeology of Toxic Organic Chemicals at a Disposal Site, Gloucester, Ontario.* IWD Scientific Series No. 141, NHRI Paper No. 23, 74 pp.

Jurinak, J. J., and J. Santillan-Medran. 1974. *The Chemistry and Transport of Lead and Cadmium in Soils.* Utah State University Research Report 18, Utah State University Agricultural Experiment Stations, Logan, Utah, June.

Kaufman, M. I., D. A. Goolsby, and G. L. Faulkner. 1973. Injection of Acidic Industrial Waste into a Saline Carbonate Aquifer: Geochemical Aspects. *Underground Waste Management and Artificial Recharge*, J. Braunstein, ed. Vol. 1, pp. 526-551.

Kayser, M. B., and A. G. Collins. 1986. *Computer Simulation Models Relevant to Ground Water Contamination from EOR or Other Fluids—State of the Art.* National Institute for Petroleum and Energy Research Report NIPER-102, Bartlesville, Oklahoma, March, 84 pp.

Kharaka, Y. K., W. W. Carothers, and R. J. Rosenbauer. 1983. Thermal Decarboxylation of Acetic Acid: Implications for Origin of Natural Gas. *Geochimica et Cosmochimica Acta* 47:397-402.

Ku, H. F. H., B. G. Katz, D. J. Sulam, and R. K. Krulikas. 1978. Scavenging of Chromium and Cadmium by Aquifer Material—South Farmingdale-Massapequa Area, Long Island, New York. *Ground Water* 16(2):112-118.

Leenheer, J. A., and R. L. Malcolm. 1973. Case History of Subsurface Waste Injection of an Industrial Organic Waste. *Underground Waste Management and Artificial Recharge Symp. Prep.* 1:565-584.

Leenheer, J. A., R. L. Malcolm, and W. R. White. 1976a. *Physical, Chemical, and Biological Aspects of Subsurface Organic Waste Injection near Wilmington, North Carolina.* U.S. Geological Survey Professional Paper 987, 51 pp.

Leenheer, J. A., R. L. Malcolm, and W. R. White. 1976b. Investigation of the Reactivity and Fate of Certain Organic Compounds of an Industrial Waste after Deep-Well Injection. *Environ. Sci. Tech.* 10(5):445-451.

Mabey, W., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compounds in Water under Environmental Conditions. *J. Phys. Chem. Ref. Data* 7(2):383-415.

McAuliffe, C., and N. T. Coleman. 1955. H-Ion Catalysis by Acid Clays and Exchange Resins. *Soil Sci. Soc. Am. Proc.* 19:156-160.

McKenzie, D. J. 1976. *Injection of Acidic Industrial Waste into the Floridan Aquifer Near Belle Glade, Florida: Upward Migration and Geochemical Interactions.* U.S. Geological Survey Open-File Report 76-626, 54 pp.

Means, J. L. 1982. *The Importance of Organic Compounds in Ground Water as Radionuclide-Mobilizing Agents.* NTIS Report ONWI-348, December.

Means, J. L., and N. J. Hubbard. 1985. *The Organic Chemistry of Deep Ground Waters from the Palo Duro Basin, Texas: Implications for Radionuclide Complexation,*

Ground-Water Origin, and Petroleum Exploration. NTIS Report BMI/ONWI-578, May, 83 pp.

Mill, T. 1980. Data Needed to Predict the Environmental Fate of Organic Chemicals. In *Dynamics, Exposure and Hazard Assessment of Toxic Chemicals,* R. Haque, ed. Ann Arbor Science, pp. 297-321.

Mills, W. B., D. B. Porcella, M. J. Ungs, S. A. Gherini, K. V. Summers, L. Mok, G. L. Rupp, and G. L. Bowie. 1985. *Water Quality Assessment: A Screening Procedure for Toxic and Conventional Pollutants,* Part II. EPA Report 600/6-85/002b, Athens, Georgia, September, 474 pp.

Morita, R. Y., and C. E. ZoBell. 1956. Effect of Hydrostatic Pressure on the Succinic Dehydrogenase System in *Escherichia Coli. J. Bacteriol.* 71: 668-672.

Mortland, M. M. 1985. Interaction Between Organic Molecules and Mineral Surfaces. *Ground Water Quality,* Ward, C. H., W. Giger, and P. L. McCarty, eds. John Wiley & Sons, New York, pp. 370-385.

Nebergall, W. H., F. C. Schmidt, H. F. Holtzclaw, and S. C. Bailer. 1968. *College Chemistry,* 3rd ed. D. C. Heath and Company, Boston.

Novak, J. T., and M. S. Ramish. 1975. Stimulation in Anaerobic Degradation. *Water Research* 9:963-967.

O'Connor, J. T., M. M. Ghosh, S. K. Banerji, D. Piontek, E. Aguado, and T. M. Prakash. *Organic Groundwater Contamination Evaluation and Prediction.* U.S. Department of Interior. NTIS PB85-23006/8, 69 pp.

Partington, J. R. 1966. *General and Inorganic Chemistry,* 4th ed. St. Martin's Press, New York.

Pascale, C. A., and J. B. Martin. *Hydrologic Monitoring of a Deep-Well Waste-Injection System near Pensacola, Florida.* U.S. Geological Survey Water Resources Investigation 78-27, 61 pp.

Peek, H. M., and R. C. Heath. 1973. Feasibility Study of Liquid-Waste Injection into Aquifers Containing Salt Water, Wilmington, North Carolina. *Underground Waste Management and Artificial Recharge Symp. Prep.* 2: 851-875.

Ragone, S. E., J. Vecchioli, and H. F. H. Ku. 1973. Short-Term Effect of Injection of Tertiary-Treated Sewage on Iron Concentration of Water in Magothy Aquifer, Bay Park, New York. *Waste Management and Artificial Recharge, Prep.,* 1:273-290.

Reeder, L. R., J. H. Cobbs, J. W. Field, Jr., W. D. Finley, S. C. Vokurka, and B. N. Rolfe. 1975. *Review and Assessment of Deep-Well Injection of Hazardous Waste.* EPA Report 600/2-77-029, Cincinnati, Ohio, Vols. 1-4, July.

Rich, L. A. 1986. Hazardous Waste Management: New Rules Are Changing the Game. *Chem. Week* 139(8):26-64.

Rittmann, B. E., P. L. McCarty, and P. V. Roberts. Trace-Organics Biodegradation in Aquifer Recharge. *Ground Water* 18(3):236-243.

Roberts, P. V., M. Reihnhard, G. D. Hopkins, and R. S. Summers. 1985. Advection-Dispersion-Sorption Models for Simulating the Transport of Organic Contaminants. *Ground Water Quality,* Ward, C. H., W. Giger and P. L. McCarty, eds. John Wiley & Sons, New York, pp. 425-445.

Rogers, R. D., and J. C. McFarlane. 1981. Sorption of Carbon Tetrachloride, Ethylene Dibromide, and Trichloroethylene on Soil and Clay. *Environ. Monitoring and Assessment,* 1:155-162.

Schechter, R. S., L. W. Lake, and M. P. Walsh. 1985. *Development of Environmentally Attractive Leachants,* Geochemical Flow Modeling, Vol. III. Mining Research Contract Report, Bureau of Mines, Washington, D.C., March, 336 pp.

Schwarzenbach, R. P., and W. Giger. 1985. Behavior and Fate of Halogenated Hydrocarbons in Ground Water. In *Ground Water Quality,* C. H. Ward, W. Giger, and P. L. McCarty, eds. John Wiley & Sons. New York, pp. 446-471.

Scrivner, N. C., K. E. Bennett, R. A. Pease, A. Kopatsis, S. J. Sanders, D. M. Clark, and M. Rafal. 1986a. Chemical Fate of Injected Wastes. *Proc. Int. Symp. on Subsurface Inj. Liquid Wastes,* New Orleans, March 3-5.

Scrivner, N. C., K. E. Bennett, R. A. Pease, A. Kopatsis, S. J. Sanders, D. M. Clark, and M. Rafal. 1986b. Chemical Fate of Injected Wastes. *Ground Water Monitoring Review* 6(3):53-58.

Selm, R. F., and B. T. Hulse. 1960. Deep Well Disposal of Industrial Wastes. *Chem Engr. Prog.* 56(5):138-144.

Stone, R. B., P. L. Aamodt, M. R. Engler, and P. Madden. 1975. *Evaluation of Hazardous Wastes Emplacement in Mined Openings.* EPA Report 600/2-75-040, Cincinnati, Ohio, December.

Theis, T. L., D. J. Kirkner, and A. A. Jennings. 1980. *Hydrodynamic and Chemical Modeling of Heavy Metals in*

Ash Pond Leachates. NTIS Report DOE/EV/ 10253-1, March, 32 pp.

Thornton, S. D., and C. J. Radke. 1985. *Dissolution and Condensation Kinetics of Silica in Alkaline Solution.* Paper SPE 13601 pres. SPE 1985 California Regional Meeting, Bakersfield, California, March 27-29.

Thornton, S. D., and P. B. Lorenz. 1987. *Role of Silicate and Aluminate Ions in the Reaction of Sodium Hydroxide with Reservoir Minerals.* Paper SPE 16277 pres. SPE 1987 Int. Symp. on Oilfield Chem., San Antonio, Texas, February 4-6.

U.S. Environmental Protection Agency. 1985. *Report to Congress on Injection of Hazardous Waste.* EPA Report 570/9-85-003 Washington, D.C., August.

Vecchioli, J., G. G. Erlich, E. M. Godsy, and C. A. Pascale. 1984. Alterations in the Chemistry of an Industrial Waste Liquid Injected into Limestone near Pensacola, Florida. In *Hydrogeology of Karstic Terrains, Case Histories.* G. Castany, E. Groba, and E. Romijn, eds. Vol. 1, pp. 217-221.

Veley, C. D. 1969. How Hydrolyzable Metal Ions React with Clays To Control Formation Water Sensitivity. *J. Petr. Tech.,* September:1111-1118.

Warner, D. L. 1966. Deep Well Waste Injection-Reaction with Aquifer Water. *J. Sanitary Engr. Div.,* Proc. Am. Soc. of Civil Engr., August: 45-69.

Warner, D. L. 1977. *An Introduction to the Technology of Subsurface Wastewater Injection.* EPA Report 600/2-77-240, Ada, Oklahoma, December, 187 pp.

Water Well J. 1974. More on Pollution from Wells, Part III. 28(5):100-102.

Wilson, L. G. 1980. *Monitoring in the Vadose Zone: A Review of Technical Elements and Methods.* EPA Report EPA-600/7-80-134, Las Vegas, Nevada, June, 168 pp.

Wilson, J. T., M. J. Noonan, and J. F. McNabb. 1985. Biodegradation of Contaminants in the Subsurface. In *Ground Water Quality,* C. H. Ward, W. Giger, and P. L. McCarty, eds. John Wiley & Sons, New York, pp. 483-492.

Wolbach, C. D., R. R. Whitney, and U. B. Spannagel. 1984. *Design and Development of a Hazardous Waste Reactivity Testing Protocol.* EPA Report 600/2-84-057, Cincinnati, Ohio, February, 143 pp.

ZoBell, C. E., and F. H. Johnson. 1949. The Influence of Hydrostatic Pressure on the Growth and Viability of Terrestrial and Marine Bacteria. *J. Bacteriol.* 57:179-189.

ZoBell, C. E., and C. H. Oppenheimer. 1950. Some Effects of Hydrostatic Pressure on the Multiplication and Morphology of Marine Bacteria. *J. Bacteriol.* 60:771-781.

ZoBell, C. E., and A. B. Cobet. 1962. Growth, Reproduction, and Death Rates of *Escherichia Coli* at Increased Hydrostatic Pressures. *J. Bacteriol.* 84: 1228-1236.

CHAPTER THREE

RESEARCH SUMMARY NO. 2
THE CHEMISTRY OF WASTE FLUID DISPOSAL IN DEEP INJECTION WELLS

3.1 Overview

3.1.1 Origin and Content
Source: The Chemistry of Waste Fluid Disposal in Deep Injection Wells. Second Berkeley Symposium on Topics in Petroleum Engineering, March 9-10, 1988, pp. 79-82. Lawrence Berkeley Laboratory LBL-24337. Prepared for U.S. Department of Energy.

Authors: J. Apps, L. Tsao, and O. Weres. Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

Contents: This paper focuses on chemical aspects of deep-well injection of hazardous wastes. It includes (1) an overview of types of models for predicting fate and of deficiencies in available models, (2) a comparison of the laboratory simulation of the evolution of Gulf Coast brines 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.

3.1.2 Major Conclusions
■ Not much is known about the chemical consequences of injecting dilute toxic waste streams into deep sedimentary formations.

■ Computer simulations of chemical processes currently model only the simplest systems, and laboratory and field studies are required for more realistic predictions. Semiempirical techniques will continue to be necessary for the foreseeable future. Any studies for organic waste disposal must be site-specific, using rock from the proposed injection zone.

■ A computer simulation of the evolution of Gulf Coast brines and experimental studies at 250°C, with a simulated waste stream containing creosol and sodium borate interacting with bentonite clay, illustrates the potential complexities and uncertainties in attempting to

predict quantitatively the fate of waste in the injection formation.

3.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

3.2.1 Overview of Fate-Influencing Processes
Problems arising from deep-well injection may be classified as mechanical, hydrological, or chemical. This paper concentrates on the chemical problems.

The broad scope of chemical processes that must be understood includes (1) the chemical evolution of the ground water in migrating from its source to the injection zone, (2) the interaction of the ground water with the injected waste stream, and (3) the interaction of the injected waste stream with the host rock.

Interaction of the waste stream with the ground water and host rock may have both deleterious and beneficial effects. Deleterious effects include (1) formation of high gas over pressures, (2) hazardous-daughter products resulting from decomposition of constituents in the waste stream, (3) the partition and concentration of hazardous constituents in a more highly mobile form (e.g., vapor phase), and (4) precipitation of reaction products that could seal the injection zone. Beneficial effects would lead to the attenuation of toxic constituents through neutralization, precipitation, decomposition, adsorption, oxidation or reduction, or bacterial decomposition.

Many detailed processes with homogeneous and heterogeneous reactions may be involved in the interaction of a waste stream with ground water and host rock. Homogeneous reaction processes may include complexation, oxidation/reduction, hydrolysis, and polymerization. Heterogeneous reaction processes may include nucleation, colloid formation, precipitation/ dissolution, adsorption, ion exchange, immiscible phase separation (i.e., formation of non-aqueous gas or liquid phases), and bacterial decomposition.

3.2.2 Partition Processes

Adsorption is the only partition process specifically covered by this report. An extensive literature detailing the transport of organic waste compounds in soils provides ample evidence that many organic compounds are effectively adsorbed onto the organophilic surface of organic detritus. Smectite clays also adsorb organic compounds possessing hydrophilic ligands. Models describing adsorption onto natural materials are in preliminary development (see Section 3.5.1).

3.2.3 Transformation Processes

Catalysis is the only transformation process specifically covered by this report. Bentonite clay can serve as a catalyst for several types of reactions involving cresol. A small percentage of cresol will be demethylated to produce phenol. With an acid-washed clay, about 75 wt.% of the cresol reacted to form 1-methoxy-4-methyl benzene, with less than 1% of the initial cresol remaining. See discussion of cresols in Section 3.4.2.

3.2.4 Transport Processes

Transport processes are not specifically discussed in this report.

3.3 Major Environmental Factors Affecting Deep-Well-Injected Waste

3.3.1 Geochemical Characteristics of Deep-Well-Injection Zones

Gulf Coast injection wells are typically between 4,000 and 7,000 ft. deep with temperatures up to 80°C. A typical injection zone is an arenaceous horizon containing up to 70 wt.% detrital quartz, together with 15 wt.% of detrital plagioclase and potash feldspars, with the remainder clay minerals with secondary calcite.* Confining shale horizons typically consist of about 70 wt.% clays with smaller amounts of other detrital minerals and secondary pyrite. A significant although minor amount of organic detritus is present in both shales and sandstones.

3.3.2 Specific Environmental Factors

Brines. Brines in Gulf Coast injection wells typically contain between 30 and 80 g/L (30,000-80,000 mg/L) of a mixture of sodium and calcium chlorides. The salinity is attributed to the dissolution of sodium chloride from evaporites. Table

3-1 shows average concentrations of aqueous species in Gulf Coast brines at 80°C and Table 3-2 lists minerals in saturation with the simulated brines in Table 3-1.

Table 3-1 Comparison of Predicted and Measured Aqueous Species in Gulf Coast Brines, 80°C

| Species | Concentration, Mole $(kg\ H_2O)^{-1}$ | |
	Simulation	7 Aquifers[a]
$Na+$	9.1×10^{-1}	7.8×10^{-1}
K^+	2.5×10^{-2}	8.0×10^{-3}
Mg^{2+}	1.6×10^{-3}	1.2×10^{-2}
Ca^{2+}	4.0×10^{-2}	5.0×10^{-2}
Fe^{2+}	1.6×10^{-7}	
Al^{3+}	3.4×10^{-4}	
CO_32-	6.3×10^{-4}	1.0×10^{-3}
SO_42-	1.6×10^{-7}	$< 1.0 \times 10^{-3}$
S^{2-}	1.0×10^{-6}	
$SiO_2(aq)$	6.3×10^{-4}	
pCO_2	1.6×10^{-2} bar	
pCH_4	1.0×10^{0} bar	
PH_2	3.2×10^{-4} bar	
pH_2S	1.0×10^{-5}	
Eh	-300 mv	
pH	6.8	7.0

[a] Kreitler and Richter

Table 3-2 Minerals Predicted to be in Equilibrium with Gulf Coast Brines at 80°C

| Predicted Minerals | Observed | |
	Primary	Secondary
Calcite		*
Dolomite		*
Hematite	*	?
Kaolinite	*	*
Low Albite		*
Pyrite		*
Pyrrhotite		?
Quartz	*	*
Smectite	*	*

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* The paper states 40% quartz, 15% fedlspar, and 40% clay minerals and calcite. A high percentage of clay minerals was used for geochemical modeling to reflect the fact that the high surface area of clay results in a reactivity that is higher than a simple weight percentage woudl indicate (communication from John Apps, Lawrence Berkeley Laborato Berkeley, California, August 7, 1989.

Low concentrations of magnesium and sulfate ions compared with simulated values suggest that brines in the field are not in homogeneous or heterogeneous equilibrium.

Clays. Clay types commonly found in Gulf Coast deep-well-injection formations include smectite, illite, mixed-layer clays, chlorite, and kaolinite. Most of the clays in both the arenaceous and argillaceous horizons of Gulf Coast deep-well formations are detrital in origin. Smectite clays absorb organic compounds possessing hydrophilic ligands. See Section 3.2.3 for a discussion of the catalytic effects of bentonite clay.

3.4 Geochemical Characteristics and Fate of Hazardous Wastes

3.4.1 Specific Data on Inorganic Wastes
Sodium borate is the only inorganic discussed in this report. This compound (27.1 g/L) catalyzed the condensation of cresol either directly or indirectly by its influence on pH in laboratory-simulated interactions with cresol and bentonite clay.

3.4.2 Specific Data on Organic Wastes Cresols.
Laboratory-simulated interactions between a waste stream of sodium borate and the paracresol isomer with bentonite clay in various concentrations and combinations showed that 1.4 wt.% of cresol was demethylated to produce phenol in 72 hours, and a series of largely unidentifiable condensation products or dimers of cresol were formed during initial experiments. The clay catalyzed the demethylation of cresol. The presence of sodium borate catalyzed the condensation of cresol either directly or indirectly through its influence on pH. With an acid-washed clay, approximately 75 wt.% of the cresol reacted to form 1-methoxy-4-methyl benzene, with less than 1% of the initial cresol remaining. The remainder of the reaction products were methoxybenzene and unidentifiable reaction products.

1-Methoxy-4-methyl benzene. This compound was the primary product of catalytic reactions involving cresol in the presence of acid-washed bentonite clay.

Methoxybenzene. This compound was a minor product of catalytic reactions involving cresol in the presence of acid-washed bentonite clay.

3.5 Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes

3.5.1 Basic Approaches
Because of the chemical complexity of waste streams, aquifer brines, and host rocks, many interactions are possible. Unfortunately the present state of knowledge is quite insufficient to make useful predictions based on computer simulations alone. Laboratory and field experiments must supplement these modeling efforts.

Computer codes used to predict chemical processes may be divided into five broad categories:

■ Models used to reduce and evaluate experimental data.

■ Models used to calculate the thermodynamic properties of phases or species at temperatures and pressures other than standard-state conditions.

■ Models used to determine the distribution of species at equilibrium, given the principal extensive and intensive parameters of the system.

■ Models used to predict the evolution of a chemical system, either as a function of reaction progress or as a function of time. The spatial distribution of reactants or products is not predicted by these models.

■ Models used to predict the chemical evolution of a system in which both chemical reactions and transport proceed simultaneously.

The thermodynamic properties of participating minerals and aqueous species are needed for most types of modeling. Substantial thermodynamic data bases have been compiled, and detailed evaluations have been conducted to ensure that the data are both internally consistent and correct. Serious deficiencies remain.

■ The 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). Either solid-solution models remain to be worked out or appropriate algorithms have not been incorporated into computer cod

- 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 permitting the distribution of species between the adsorbed and aqueous state to be calculated.

- Calcium-sodium chloride brines (which typically occur 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 components in such brines have not been determined. Precise modeling is limited to relatively low salinities, where many parameters are unnecessary, or to chemically simple systems near 25°C.

- Current computer codes usually calculate only the thermodynamically most stable configuration of a system. Modifications can simulate nonequilibrium conditions, but there are limitations to the extent to which codes can be manipulated to simulate processes that are kinetically controlled.

- Little is known about the kinetics of dissolution, precipitation, and oxidation-reduction reactions in the natural environment. Therefore, attempts to simulate the kinetics of the evolution of the more complicated injection-zone chemistry must remain in the developmental stage for some time.

The most sophisticated computer codes are those which combine transport and chemical processes. Few such codes have been developed and successfully tested (see Section 3.5.2, Transport).

The experimental study reported in this paper shows clearly that the reactions observed could not have been anticipated by a priori computer simulations. Furthermore, it will not be easy to simulate the complex reaction paths observed without a more fundamental understanding of the mechanisms involved. Thus, computer simulations of the waste stream reacting with the injection-zone environment will provide only limited insight into the consequences of waste-stream injection.

At present, computer models incorporating kinetics are very limited in their applicability and usefulness for predicting injection-zone conditions. The availability of computer codes for modeling complex kinetic systems will probably precede the availability of suitable data or techniques for correlating theoretical concepts with the reactivity of an injection zone.

Therefore, semi-empirical techniques will continue to be necessary.

3.5.2 Specific Methods and Models

Aqueous- and Solution-Geochemistry Models. Although most available models calculate only the thermodynamically most stable configurations of a system, it is possible to manipulate their operation to simulate metastable conditions. Simple input modifications to include metastable or unstable compounds can produce fairly realistic simulations of nonequilibrium systems.

Where kinetic data are not available, the evolution of a chemical system can be simulated using the reaction-progress variable developed by de Donder and Van Rysselberghe (1936). Helgeson et al. (1970) developed algorithms using this variable. In its simplest form, a reaction-progress code simulates changes in a chemical system in terms of the amount of material reacted rather than as a function of time. Usually, one kilogram of aqueous phase waste is allowed to react with an assemblage of minerals. The aqueous phase is assumed to be always in internal equilibrium and the reactant minerals dissolve in proportion to their initial mole fractions. Product phases are in reversible equilibrium with the aqueous phase.

The paper contains results of a simulation showing the evolution of a typical Gulf Coast brine using reaction-progress variables in the EQ6 code developed by T. J. Wolery and his associates at the Lawrence Livermore National Laboratory. The reaction of a 1 molal sodium-chloride brine (representing dissolution of an evaporite) reacting with a representative detrital mineral assemblage at 80°C was simulated to see whether it would evolve into a sodium-calcium chloride brine and produce the secondary minerals observed in the field. Table 3-1 compares the resulting brine composition, when the reaction progress variable equals 10^{-2}, with average values for Gulf Coast brines; Table 3-2 lists the minerals in saturation with the brine.

With some notable exceptions, results are generally consistent with what is observed in the field. The predicted value for potassium is too high and can be explained by the failure of the simulation to saturate with respect to illite, probably due to erroneous thermodynamic properties for that clay. The low magnesium and sulfate concentrations suggest that the brines in the field are not in equilibrium. Predicted and observed minerals are in good agreement.

Transport Models. White et al. (1984) have developed a groundwater-contamination model that integrates TRUMP (Edwards, 1972), a transport model, with PHREEQE (Parkhurst et al., 1980), a distribution-of-species model. Another model, taking a more fundamental approach, is CHEMTRN (Miller and Benson, 1983).

3.6 Laboratory Procedures And Protocols

Experiments involving a simulated waste stream containing sodium borate and cresol (up to 500 ppm) interacting with bentonite were conducted in 600 mL Parr Minireactors. Initial runs were made at 250°C with 14.3 g/L of cresol and a solution of sodium borate at 27.1 g/L, to obtain measurable product yields in a reasonable time. Even though the waste stream being simulated contained mixed isomers of cresol, the paracresol isomer was chosen because it was expected to be more reactive and a single isomer would make identifying reaction products simpler. Bentonite was used at a concentration of 143 g/L, later decreased to 100 g/L. After closure, the vessel was flushed with helium and pressurized to approximately 16 psig.

At the conclusion of the run and after cooling the vessel, head-space gases were collected over water in a separatory funnel. These gases were analyzed on a Consolidated Engineering Corp. 21-102 mass spectrometer. The vessel was then opened and a spike of perdeuterophenol solution was added to the product solution. After mixing the spiked solution, it was decanted into plastic jars and centrifuged to separate the clay. The supernatant solution was removed and an aliquot was extracted with methylene chloride in a separatory funnel. The methylene-chloride extract was washed once with distilled water and dewatered by filtering through anhydrous sodium sulfate.

The reaction product extract was analyzed by two methods: (1) a gas chromatograph with flame-ionization detector to screen product solutions for further analysis, and (2) a Finnigan 4000 gas chromatograph/mass spectrometer to identify reaction products and determine the absolute quantity of phenol produced. Results of the experiments are discussed in Section 3.4.

3.7 Field Case Studies

No field case studies are included in this report.

3.8 Further Research Needs

3.8.1 General
■ Continue to refine and add to the thermodynamic databases required for modeling.

■ Develop solid-solution models and the capability to model precisely the thermodynamic properties of strong mixed electrolytes for a diverse range of injection-zone conditions.

■ Develop data on thermodynamic properties of water-miscible organic compounds.

■ Develop empirical models describing irreversible adsorption of water-miscible organic compounds on mineral surfaces in an injection zone.

3.8.2 Specific
■ Study further the issue of nonequilibrium in actual brines. The comparison of simulated and actual Gulf Coast brines suggests that the actual brines are not in homogeneous or heterogeneous equilibrium.

■ Conduct field studies to compare results of laboratory experiments and computer modeling reported in the paper. These field studies could involve injecting a simulated waste stream containing variable amounts of sodium borate and cresol in an arenaceous formation. The injected stream could be left in place for an extended period of time, then recovered, and changes in its composition measured. The formation fluids could be continually removed and measured for changes in borate and cresol, allowing the adsorptive-desorptive capacity of the rock, potential decomposition products, and various hydrologic parameters to be determined. The results could be correlated with laboratory studies and conclusions drawn regarding the scaling factors and more fundamental differences in mechanisms between laboratory and field conditions.

References

de Donder, T. H., and P. Van Rysselberghe. 1936. *Thermodynamic Theory of Affinity.* Stanford University Press, 142 pp.

Edwards, A. L. 1972. *TRUMP: A Computer Program for Transient and Steady State Temperature Distributions in Multi-Dimensional Systems.* Lawrence Livermore National Laboratory. Rep. 14754, Rev. 3, Livermore, California.

Helgeson, H. C., T. H. Brown, A. Nigrini, and T. A. Jones. 1970. Calculation of Mass Transfer in Geochemical Processes Involving Aqueous Solutions. *Geochimica et Cosmochimica Acta* 34:569-592.

Kreitler, C. W., and B. C. Richter. 1986. *Hydrochemical Characterization of Saline Aquifers of the Texas Gulf Coast Used for Disposal of Industrial Waste.* Bureau of Economic Geology, University of Texas at Austin, 164 pp.

Miller, C.W., and L.V. Benson. 1983. Simulation of Solute Transport in a Chemically Reactive Heterogeneous System: Model Development and Application. *Water Resources Research*, 19(2):381-391.

Parkhurst, D. L., D. C. Thorstensen, and L. N. Plummer. 1980. *PHREEQE—A Computer Program for Geochemical Calculation.* U.S. Geological Survey Water Resource Investigation 80-96.

U.S. Environmental Protection Agency. 1985. *Report to Congress on the Injection of Hazardous Wastes.* EPA Report 570/9-85-003. Office of Drinking Water, U.S. Environmental Protection Agency, Washington, D.C.

White, A. F., J. M. Delaney, T. N. Narashimhan, and A. Smith. 1984. Groundwater Contamination from an Inactive Uranium Mill Tailings Pile, I., Application of a Chemical Mixing Model. *Water Resources Research* 20:1743-1752.

CHAPTER FOUR

RESEARCH SUMMARY NO. 3
LABORATORY PROTOCOL FOR DETERMINING FATE OF WASTE DISPOSED IN DEEP WELLS

4.1 Overview

4.1.1 Origin and Content

Source: *Laboratory Protocol for Determining Fate of Waste Disposed in Deep Wells.* EPA/600/8-88/008, February 1988. Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. 63 pages. NTIS PB88-166061.

Authors: A. Gene Collins and M. E. Crocker, National Institute for Petroleum and Energy Research, P.O. Box 2128, Bartlesville, Oklahoma 74005.

Contents: Describes laboratory procedures for: (1) core analysis, (2) brine analysis, (3) a dynamic fluid-flow system that simulates the interaction of hazardous organic wastes with injection-zone rock, and (4) a static waste/rock interaction test that simulates longer-term degradation processes.* Protocol testing resulted in some data on the mobility, adsorption, and degradation of phenol and 1,2- dichloro-ethane in simulated subsurface conditions for the Frio sandstones; also presented were some data from earlier adsorption experiments using the Cottage Grove sandstone.

4.1.2 Major Conclusions
■ Laboratory simulation of the interaction between injected hazardous wastes and reservoir rocks can help evaluate the mobility, adsorption, and degradation of organic hazardous wastes in the deep-well environment.

■ Dynamic fluid-flow interactions in the laboratory can be used to evaluate the adsorption and desorption behavior of organic hazardous wastes in reservoir rock at simulated subsurface temperature and pressure conditions. Static waste-reservoir-rock interaction tests can be used to evaluate adsorption behavior and degradation products over longer periods of time (months) under simulated temperatures.

■ Preliminary tests of interactions between simulated phenol-brine and 1,2-dichloroethane-brine solutions and two sandstones (Frio formation in Texas and Cottage Grove sandstone in Oklahoma) indicate the following:

— Adsorption rates of the two compounds are proportional to their concentration in solution and inversely proportional to the temperature. The adsorption process is exothermic, and low isosteric heats of adsorption indicate that Van der Waals, or physical adsorption, is the dominant type of process.

— Adsorption rates for 1,2-dichloroethane were higher in the Cottage Grove sandstone than in the Frio sandstone. The reverse was true for phenol; adsorption rates for phenol on the Cottage Grove sandstones were lower than for the Frio sandstone by a factor of four or five.

— Flushing a Frio core that had attained adsorption equilibrium for phenol with a phenol-free brine resulted in no desorption.

— No phenol degradation products were observed either in effluents generated in the fluid-flow experiments or in

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* Specific laboratory procedures are briefly described in this summary. The original report should be obtained for detailed descriptions. See in particular Appendix B of that report (Experimental Procedures).

static tests where the brine-phenol solution was mixed with crushed Frio rock at 140°F and held for 83 days.

4.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

4.2.1 Overview of Fate-Influencing Processes
Adsorption is a significant process that can affect the migration of injected-waste constituents. Little laboratory data exist on the equilibrium adsorption properties of subsurface formation rocks with respect to organic compounds (Strycker and Collins, 1986).

4.2.2 Partition Processes
Adsorption-desorption. Many organic constituents are hydrophobic, and their movement in groundwater systems is affected by adsorption phenomena, where the solute is transferred from the liquid or solvent phase to the solid phase. Adsorption is a phase-partitioning process and it may be fully or partly reversible (desorption). Many chemical and physical properties of both the solute and the solid phases affect adsorption-desorption, and the physical chemistry is complex.

Adsorption can be categorized into three classes: exchange, physical, and chemical. Exchange occurs from the electrostatic attraction of ions or charged functional groups from the solute phase to the portions of the solid phase that possess charge locations. Physical adsorption occurring between the phases is motivated by Van der Waals forces or electrostatic interaction between atoms and molecules (Miller, 1984). Chemical adsorption (chemisorption) is caused by a reaction between the solute phase and the solid phase. These classes of adsorption rarely act singly. Phase partitioning of a solute- solvent- solid system in which two or all three of the adsorption classes operate probably occurs.

Smith (1968) categorizes the adsorption overall into several physical processes that represent the steps occurring when a molecule is transferred from a solution to an active adsorption site on a solid surface. These steps are: (1) transfer of a molecule from the bulk phase near to the solid surface by molecular or convective diffusion; (2) diffusion of the molecule into the pores of the solid to the site of adsorption; (3) adsorption of the molecule onto the site. Where a chemical reaction takes place, Steps 2 and 3 occur in reverse for the products.

The rate at which adsorption at the site takes place (Step 3) for aqueous solutions is very rapid, especially when it is accompanied by a "loose" bond, which is indicated by a low heat of adsorption. Heats of adsorption that are less than 8 kcal/gmole indicate weak Van der Waals (physical) adsorption. The high rate of adsorption in Step 3 indicates that this step does not influence the overall kinetics of the adsorption process. In physical adsorption, bulk and internal pore diffusion (Steps 1 and 2) are the steps controlling the kinetics. Since diffusion is the controlling mechanism, it is not unusual for organic compounds, where physical adsorption is the dominant process, to exhibit adsorption rate constants that are numerically close.

In general, the rate of adsorption of organic waste compounds is proportional to their concentration in solution and inversely proportional to the temperature. The adsorption process is exothermic for phenol and 1,2-dichloroethane, and low numeric values for the isosteric heats of adsorption (> 8 kcal/gmole) indicate that physical adsorption is the dominant process.

4.2.3 Transformation Processes
None discussed.

4.2.4 Transport Processes
The only transport process covered specifically in this report is solute migration. Possible mechanisms whereby injected hazardous wastes might contaminate aquifers include: (1) a surface spill followed by migration of the waste into ground water; (2) unplugged or incompetently plugged wells that penetrate the geologic zone into which the waste is injected, providing a route whereby the waste can enter an overlying potable aquifer; (3) vertical fracturing of the injection and confining strata caused by excessive injection pressures, whereby a communication channel allows the injected wastes to migrate to a freshwater aquifer; and (4) mechanical failure of the injection system such as corrosion of surface pumps or pipes, or subsurface tubing or casing, which allows the waste to escape and migrate to an aquifer (Collins, 1975).

The U.S. EPA (1985) described four major ways subsurface injection can cause fluids to migrate into underground sources of drinking water (USDWs): (1) faulty well construction; (2) improperly plugged or completed wells in the zone of endangering influence; (3) faulty or fractured confining strata; and (4) lateral displacement.

An injected fluid moving through a porous system spreads into the reservoir fluid being displaced by the simultaneous actions of convective and molecular diffusion. Convective dispersion is influenced by the density and viscosity difference between the two miscible fluids and by local variations of the fluid velocity, pore-size distribution, pore constrictions, and the tortuosity of the flow path.

Molecular diffusion can occur by bulk diffusion and by Knudsen diffusion. Wheeler (1951) suggests that bulk diffusion alone will occur at a pore radius of 10^{-4} cm or greater. The pore-size distributions measured for five sandstones (Donaldson et al., 1975) show that most of the pores have radii greater than this value. Consequently, Knudsen diffusion can be considered negligible.

Other modes of mass transfer that affect dispersion in porous media are eddy diffusion and transverse molecular diffusion. If laminar flow exists (generally the case in sandstone deep-well-injection zones), eddy diffusion is not a contributing factor to dispersion. Transverse diffusion can be neglected if the ratio of the radius to the length of sandstone samples is small and the viscosities of the displaced and injected fluids are equal. Hassinger and von Rosenberg (1968) and Grane and Gardner (1961) provide additional information on transverse dispersion.

4.3 Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes

4.3.1 Geochemical Characteristics of Deep-Well-Injection Zones

Current knowledge of deep subsurface geologic reservoirs was established primarily by petroleum-related sciences. Subsurface reservoirs into which hazardous wastes are injected consist of sedimentary deposits, the same types from which petroleum is generated and produced.

Water Chemistry. Brines found in the Frio formation vary. The salinity (total dissolved solids) can be as low as 16,000 mg/L in some of the geopressured wells and more than 100,000 mg/L in normally pressured wells. The dominant ions are sodium and chloride; alkalis, alkaline earths, and halide ions plus trace elements are present also.

Sandstones. Most deep geologic formations used for disposal of hazardous wastes consist of unconsolidated sands and sandstones, as exemplified by the Frio formation. The minerals in these rock formations serve as sites for the adsorption of numerous organic compounds and thus retard or attenuate the migration of the waste from the injection zone.

The Frio formation is the dominant geologic repository used for hazardous-waste disposal in the Gulf Coast area because of its lithologic characteristics. It is of Oligocene-Miocene age and has produced about 6 billion barrels of oil and 60 trillion cubic feet of gas. Typical subsurface conditions in the Frio formation are 3,000 psi (20.7 MPa) with temperatures up to 140°F (60°C). The core used in the

protocol experiments came from a depth interval of 7,154 to 7,155 ft. Porosity was 36% and permeability was 1.7 darcies. Composition of the core was as follows: quartz (52.0%), feldspar (17.0%), calcite (28.0%), pyrite (trace), kaolinite (3.0%), and illite (trace).

The Cottage Grove sandstone is another formation that is representative of formations into which waste solutions are injected for disposal. The core used in experiments related to the project had 26% porosity and a permeability of 284 millidarcies. Composition of the core was as follows: SiO_2 (75.4%), Al_2O_3 (5.8%), K_2O (5.7%), kaolinite (6.0%), chlorite (1.0%), and illite/mica (6.0%).

Confining Beds. Shale- and/or clay- or silt-dominant formations, which overlie many formations such as the Frio, serve as hydrocarbon traps and also should retard the vertical migration of injected hazardous wastes out of the zone.

4.3.2 Specific Environmental Factors
Temperature. In general, an increase in temperature decreases the rate of adsorption.

Pressure. Pressure affects degree of permeability but should have no effect on adsorption or degradation.

pH. The pH of the flowthrough solutions before reaction with the Frio core was 5.7. After reaction, the solutions were at pH 8.1, indicating that they were probably reacting with minerals such as calcite.

4.4 Chemical Characteristics and Fate of Hazardous Wastes

4.4.1 Chemical Properties of Inorganic Hazardous Wastes
None discussed.

4.4.2 Chemical Properties of Organic Hazardous Wastes
1,2-Dichloroethane. Static adsorption tests of brine solutions containing 1,2-dichloroethane, a halogenated aliphatic hydrocarbon, using Cottage Grove sandstone showed increased rates of adsorption with increased concentrations (about 50 micrograms [µg]/gram [g] of rock at 1,000 ppm to about 340 µg/g at 5,000 ppm at 100°F). Adsorption rates decreased as temperature increased. For example, the rate of 340 µg/g at 100°F declined to about 300 µg/g at 140°F. Similar relationships were found for adsorption onto the Frio sandstone except that the total rate was considerably lower (maximum of about 140 µg/g of Frio sandstone at 100°F vs.

about 340 µg/g of Cottage Grove sandstone). The adsorption process was exothermic, and low isosteric heats of adsorption indicate that Van der Waals (physical) adsorption is the dominant type acting on this waste.

Phenol. Phenol, a monocyclic aromatic, is the predominant organic hazardous waste injected into the Frio formation. Flowthrough experiments with phenol (500 mg/L to 10,000 mg/L) in a simulated sodium-chloride brine (10,170 mg/L) injected through Frio sandstone indicated the following:

- Adsorption increased as concentration increased (from 9 µg/g adsorbed of rock at 500 mg/L phenol to 312 µg/g at 10,000 mg/L and 100°F).

- Adsorption decreased as temperature increased. For example, the rate of 312 µg adsorbed/g of rock at 10,000 mg/L phenol and 100°F decreased to 276 µg/g at 140°F.

- The adsorption process was exothermic, and low isosteric heats of adsorption indicate that Van der Waals (physical) adsorption is the dominant type.

- Flushing a core that had attained adsorption equilibrium for phenol with brine containing no phenol resulted in no desorption.

- No phenol degradation products were observed in effluents generated in the fluid flow experiments. Similarly, no desorption occurred when the brine-phenol solution was mixed with crushed Frio rock at 140°F and held for 83 days.

Static adsorption tests of phenol-brine solution with Cottage Grove sandstone showed similar relationships to those described above for the Frio sandstone except the total rate was considerably lower (maximum of about 80 µg/g of rock at 100°F, and about 50 µg/g at 140°F).

4.5 Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes

4.5.1 Basic Approaches
The fate of wastes injected into subsurface rock can be demonstrated only if the behavior of the waste after injection is known. The interactions of the waste with other reservoir fluids and reservoir-rock constituents such as silicates, carbonates, sulfates, and clays must be determined. Hazardous wastes are complex mixtures, and when these mixtures are combined with other complex mixtures, the numbers of possible interactions increase factorially.

4.5.2 Specific Methods and Models
Adsorption. Adsorption rate constants can be obtained from flowthrough experiments by sampling the effluent at specified time intervals for each concentration level analyzed. After the samples are analyzed by GLC for the specific concentration, the concentrations are then plotted as a function of time.

The Adsorption-Fluid-Flow Method. Waste fluids are injected through a core at temperature and pressure conditions that simulate the deep-well environment. Effluent from the core is sampled periodically to determine when the concentration of the organic hazardous waste is equal to the concentration of the injected fluid. When this equilibrium point is reached, injection stops. Total adsorption is then calculated in µg of waste/g of rock. The equilibrium amount adsorbed is plotted versus the concentration at equilibrium with the rock surface, to obtain the constants for the Freundlich isotherm equation:

$$A_1 = FC^n_{final}$$

where

A_1 = Amount of solute adsorbed by the rock, mg/kg of rock

F = Constant of the Freundlich isotherm (from the intercept with the vertical axis)

C_{final} = Final solution concentration in equilibrium with the solid, mg/L

n = Freundlich isotherm constant (from the slope of the line)

The constants F and n indicate the probable nature of adsorption. The relationships of F to the free-energy changes that occur in adsorption are discussed by Haque and Coshow (1971) and Crisp (1956). When $n = 1$, the intercept F can be used as an indirect measurement of the surface free-energy change. A decrease in the value of F as temperature increases is characteristic of the exothermic nature of adsorption.

Static adsorption curves are developed by plotting the amount of hazardous organic waste adsorbed as a function of time. The adsorption rate constant is calculated using the equation:

$$k = 1/t\ln(C_{final}/C_{final} - C_1)$$

where

k   = Adsorption rate constant, L/hr

t   = time, hours

C_{final} = Final solution concentration in equilibrium with the solid, mg/L

C_1 = Solution concentration at any time, mg/L

If diffusion is suspected as the controlling mechanism for adsorption (i.e., values of k do not change greatly as temperature increases), the coefficients of molecular diffusion for the compound(s) for each temperature can be calculated for verification using the equation developed by Wilke and Chang (1955).

When adsorption experiments are conducted at two temperatures, the isoteric heats of adsorption can be calculated. These values provide information on what type of surface bonding is occurring. Values that are less than 8 kcal/gmole indicate that the most probable mechanism is Van der Waals (physical) bonding.

Desorption experiments can be performed by injecting or pumping brine solutions containing no organic hazardous waste compounds through the core and analyzing the effluents produced for the compounds that were previously adsorbed.

The adsorption-static method evaluates the degree of potential adsorption. In this method, wastes are mixed with crushed samples of reservoir rock and the fluid analyzed at time intervals. This method can be used as a supplement for validating results of flowthrough experiments and can be used to evaluate longer-term interactions.

Reservoir Characterization. Core and reservoir brine samples can be characterized using a variety of methods. The inductively coupled plasma (ICP) spectrometer can be used for elemental analysis of core and brine samples (U.S. EPA, 1979). With ICP, atomic emissions are measured using an optical spectrometer for simultaneous or sequential multi-element determination of trace elements in solution (U.S. EPA, 1979).

Scanning-electron microscopy (SEM) provides visual images and semiquantitative elemental analysis of core samples. Postek et al. (1980) describe procedures for SEM analysis. The method is useful in determining sample morphology, surface mineral composition and type, and location of clays. When the core is compared before and after an experiment, the potential rock-fluid interactions can be more

readily determined and reasons for permeability losses may be indicated.

X-ray-diffraction analysis (XRD) allows further mineral identification and semiquantitative interpretation of mineral abundance (Carroll, 1970). This procedure is particularly valuable for identifying clays in the reservoir rock.

Waste-Reservoir Compatibility. Organic hazardous wastes are usually mixed with an aqueous brine solution before injection into a deep subsurface reservoir. The amount of waste that can be mixed depends on its solubility in the aqueous brine. The information needed to evaluate possible concentration ranges for the injected waste include (1) density (g/mL), (2) boiling point, and (3) solubility in water (g/100 mL). These data can be used to determine ranges of concentrations for use in the adsorption-fluid-flow method described above.

Transport. Dispersion experiments using a tracer must be performed on the assembled injection core system in the adsorption-fluid-flow method to ensure that the core is an integral unit and does not contain channels, bypasses, or other inconsistencies. Two simplifying conditions are set for determining the coefficient of linear dispersion (D) in the method: (1) variations of density and viscosity between the two miscible phases are eliminated by using aqueous-brine solutions so that transverse diffusion does not have to be considered; (2) use of laminar flow eliminates diffusion as a factor. Under these conditions, D is a complex function of molecular diffusion, velocity, and tortuosity. The report provides documentation for a computer code using formulas from Bear (1972) and Satter et al. (1977) that tests multiple values of D until the computed curve matches the experimentally determined effluent-response curve.

4.6 Laboratory Procedures And Protocols

4.6.1 Waste/Reservoir Characterization
The sample reservoir rock and brines were analyzed using an ICP spectrometer, a scanning electron microscope, and X-ray diffraction (see Section 4.5.2). The specific protocols were summarized in Appendix B of the report and can be found in U.S. EPA (1979), Postek et al. (1980), and Caroll (1970), respectively.

The porosity of the core was determined in a 7-step procedure:

1. Determine dimensions of the core.

2. Mount the core in the flowthrough-test-cell apparatus (see Section 4.6.3).

3. Determine dry weight of core and fittings.

4. Saturate core with brine.

5. Determine saturated core weight.

6. Determine weight and volume of brine reservoir.

7. Calculate porosity and pore volume.

Dispersion experiments using a tracer were carried out as described in Section 4.5.2 (Transport).

Wastes (phenol and 1,2-dichloroethane) were reagent-grade chemicals in a stock solution containing 10.17 g/L sodium chloride in Milli-Q water. Waste/brine solutions of 500, 5,000, and 10,000 ppm solutions of phenol and 500, 2,500, and 5,000 ppm solutions of 1,2-dichloroethane were created for the experiments. The lowest concentration for each chemical was selected based on a series of tests run with a gas-liquid chromatograph using a hydrogen-flame-ionization detector, which identified each chemical's lower detection limit. The highest concentrations were selected based on solubility limits or on the fact that single organic components of injected wastes do not usually exceed 10,000 ppm. Data on density, boiling point, solubility in water, and concentration ranges for these wastes were obtained from the literature.

4.6.2 Static Interaction Tests
This static test method was used to determine the adsorption and desorption rates and degradation potentials of the organic wastes. It was also used to evaluate the core dimensions and adsorption potentials for the fluid-flowthrough tests.

Two series of tests were run, each of which consisted of one blank sample plus the experimental samples. A commercially available Paar bomb unit was used in the analysis.

In the first series, consolidated Frio core rock was crushed and sized for passing through a No. 20 (μ 841) mesh sieve. One gram of this crushed core material was then mixed with each waste sample, which was prepared as discussed above, sealed into the Paar bomb unit and placed in an oven at the test temperature. The individual samples were evaluated for adsorption at 2-, 4-, 6-, or 24-hour intervals using a gas chromatograph. The results were then compared with the chromatograph of the hazardous-waste standard. Finally, the blanks were analyzed to validate the test's integrity.

In the second test series, all procedures were the same except that the samples were placed in glass vials in a 1:1

rock-to-liquid ratio, shaken, and the amount of adsorption determined by comparing the waste concentrations at each sample time with the initial test concentration.

Static degradation tests were also run using crushed Frio rock mixed with a brine/phenol solution sealed in a unit heated to 140°F for 83 days. The fluid was then analyzed for degradation products.

4.6.3 Dynamic Flowthrough Tests
The dynamic flowthrough system was designed to estimate adsorption, desorption, and degradation potentials of organic wastes under conditions simulating the temperatures, pressures, overburden pressures, and linear-flow rates found in subsurface injection systems.

General Apparatus. The flowthrough system resembled a high-pressure liquid chromatograph except that the chromatographic column is replaced by a core sample (Donaldson et al., 1980). Figure 4-1 presents a diagram of the system. The heart of this system is the test cell, which is machined from 321 stainless-steel tubing stock (2.5-in. ID and 3-in. OD). It was tested to 10,000 psi (68.9 MPa), twice the normal operating pressure. The flow lines were made from stainless-steel tubing and the connections were 316 stainless-steel Swagelok fittings, allowing reactive materials (such as brines and corrosives) to be analyzed.

A 5,000-psi hydraulic pump was used to simulate overburden pressure, and a heating mantle around the cell simulated reservoir temperatures. Dead volume in the system was minimized using capillary tubing where possible. Total system volume was 3.86 mL.

The sample-collection system included an automatic fraction collector, as well as a UV spectrophotometer/ refractometer for onstream analysis. This arrangement allowed the researchers to choose the most suitable method of detection. Brine fractions, for example, cannot be analyzed using UV but must be collected for analysis by another method.

Pressure Simulations. The core was placed in the high-pressure cell and the cell then filled with fluid, which can be pressurized using the overburden pump. The pressure applied to the outside of the core, which was separated from the overburden fluid by a rubber Hassler sleeve, simulated the overburden pressure on an aquifer system and prevented the injected fluid from leaking when the injection pressure was increased.

The experimental fluids were injected using a high-pressure, constant-rate pump, and the internal pressure of the system was adjusted using a pressure control valve.

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Figure 4-1 Schematic of fluid flow apparatus.
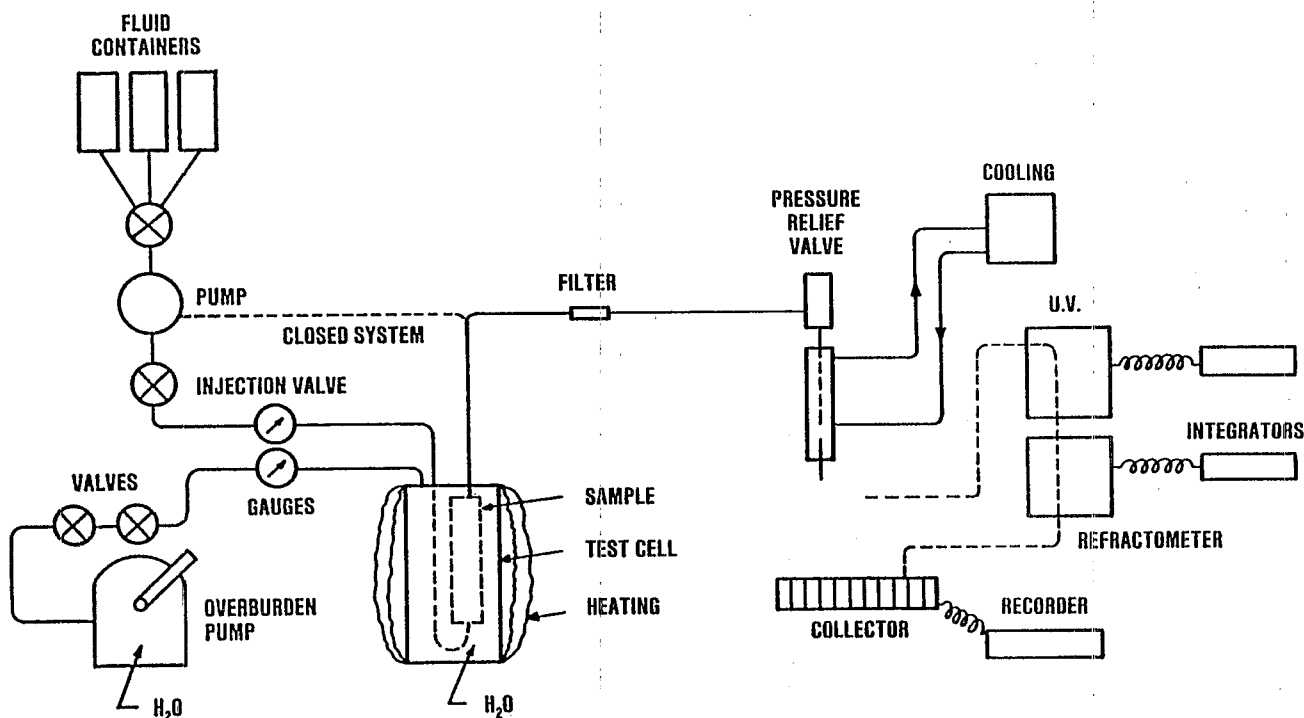
Temperature Simulations. The heating mantle allowed the core to be heated to reservoir temperatures.

Linear-Flow-Rate Simulations. The high-pressure, constant-rate pump (a Waters HPLC pump with a 6,000 psi pressure and reservoir-flow rate) provided the needed 1 ft/day linear flow rate found in subsurface waste-injection systems. To simulate these conditions, experimenters must ensure that the pump can operate at this rate with negligible pulsation at pressures approaching 3,675 psi. The pump must also have an inlet manifold capable of switching between fluids with no mixing or disruption (i.e., it must have zero dead volume).

Fluid-Flow-System Operation. Dynamic flow experiments were performed using 500, 5,000, and 10,000 ppm phenol solutions. The overburden pressure was simulated at 3,400-3,500 psi; the internal (injection) pressure was 2,900-3,000 psi; the pump pressure was 2,900 psi; the injection rate was 0.3 mL/min., and the temperature was set at either 100°F or 140°F.

The core was mounted in the cell, the constant-rate pump primed, and the overburden pressure applied around the core. The flowing pressure of the system, controlled by the

spring setting of the pressure-control valve, was set to the desired pressure, and the initial solution was pumped through the core. Simultaneously, the cell temperature was gradually increased to the desired level. When the predetermined temperature and pressure settings reached equilibrium, the sample was injected into the core using the injection valve and the sample collector and recorder were activated.

Desorption Experiments. Brine containing no phenol was flushed through the core and effluents were analyzed for the presence of phenol and degradation products.

4.6.4 Quality Assurance/Quality Control Procedures

Waste Selection, Handling, and Analysis. Wastes were purchased as pure, reagent-grade chemicals and solutions stored at 40°F to preserve sample integrity.

Gas chromatography was performed in accordance with procedures established by the EPA Environmental Monitoring and Support Laboratory.

To evaluate the waste samples, ASTM Method D2580-83, *Phenols in Water by Gas Liquid Chromatography,* and

ASTM Method 2908-74, *Measuring Volatile Organic Matter in Water by Aqueous-Injection Chromatography,* were used as guidelines. These methods incorporated other methods and guidelines:

- ASTM D1129, *Definition of Terms Relating to Water* (ASTM, 1987a)

- ASTM D1193, *Specification for Reagent Water* (ASTM, 1987a)

- ASTM E200, *Methods for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis* (ASTM, 1987a)

- ASTM E260, *Recommended Practices for General Gas Chromatograph Procedures* (ASTM, 1987b)

- ASTM E355, *Recommended Practices for Gas Chromatography Terms and Relationships* (ASTM, 1987b)

- Section III of the *1987 Annual Book of ASTM Standards-Saline and Brackish Waters, Seawaters, and Brines* (ASTM, 1987a)

- *Properties of Reservoir Rocks: Core Analysis* (Monicard, 1980)

- *API Recommended Practices for Analysis of Oil-Field Waters* (API, 1968)

Instrument Maintenance. To ensure proper operation of the instruments, a detailed preventive-maintenance schedule was followed.

Corrective Action. Laboratory personnel were responsible for noting the need for corrective actions when temperatures, pressures, resolution, or fluid loss varied to an unexpected degree. The managers of the project were responsible for noting major problems and defining corrective procedures.

Documentation. All aspects of each individual experiment and analytical test were monitored and logged. Each sample tested was assigned a unique number to establish a chain of custody for future reference.

Data Evaluation. Where practical, standard analytical procedures were used to expedite comparison of results from other experiments.

4.7 Case Studies

No case studies were reported.

4.8 Further Research Needs

No research needs were noted.

References

American Petroleum Institute (API). 1968. *API Recommended Practices for Analysis of Oil-Field Waters.* API R.P. 45, Second Edition, API, Washington, D.C.

American Society for Testing and Materials (ASTM). 1987a. *1987 Annual Book of ASTM* Standards. *Water and Environmental Technology,* Vol. 11.01 and 11.02 (Water). ASTM, Philadelphia, Penn.

American Society for Testing and Materials (ASTM). 1987b. *1987 Annual Book of ASTM Standards,* Vol. 14.01, ASTM, Philadelphia, Penn.

Bear, J. 1972. *Dynamics of Fluids in Porous Media,* Chapter 10, American Elsevier Publishing Co., New York.

Carroll, D. 1970. *Clay Minerals: A Guide to Their X-Ray Identification.* USGS Special Paper No. 126.

Collins, A. G. 1975. *Geochemistry of Oilfield Waters.* Elsevier Scientific Publishing Co., New York, p. 434.

Crisp, D. J. 1956. The Adsorption of Alcohols and Phenols from Nonpolar Solvents onto Alumina. *J. Colloid Sci.* 11:356-376.

Donaldson, E. C., M. E. Crocker, and F. S. Manning. 1975. *Adsorption of Organic Compounds on Cottage Grove Sandstone.* ERDA/BERC/RI-75/4.

Donaldson, E. C., R. F. Kendall, E. A. Pavelka, and M. E. Crocker. 1980. *Equipment and Procedures for Fluid Flow and Wettability Tests of Geologic Materials.* U.S. Department of Energy Report DOE/BETC/IC-79/5.

Grane, F. E., and G. H. F. Gardner. 1961. Measurements of Transverse Dispersion in Granular Media. *J. Chem. and Eng. Data* 6(2):283-287.

Haque, R., and W. R. Coshow. 1971. Adsorption of Isocil and Bromacil from Aqueous Solution onto Some Mineral Surfaces. *Environmental Sci. & Tech.* 5(2):139-141.

Hassinger, R. C., and D. U. von Rosenberg. 1968. A Mathematical and Experimental Examination of Transverse Dispersion Coefficients. *Soc. Pet. Eng. J.* 8(2):195-204.

Miller, C. T. 1984. *Modeling of Sorption and Desorption Phenomena for Hydrophobic Organic Contaminants in Saturated Soil Environments.* PhD dissertation, Univ. of Michigan, p. 402.

Monicard, R. P. 1980. *Properties of Reservoir Rocks: Core Analysis.* Gulf Publishing Co., Houston, Texas.

Postek, M. T., K. Howard, A. Johnson, and K. L. McMichael. 1980. *Scanning Electron Microscopy.* Ladd Research Industries, Inc.

Satter, A., Y. M. Shum, W. T. Adams, and L. A. Davis. 1977. *Chemical Transport in Porous Media.* Presented at the 52nd Annual Technical Conference of Society of Petroleum Engineers, Denver, Colorado, Oct. 9-12, SPE Paper 6847.

Smith, J. M. 1968. Kinetics of Adsorption. In *Adsorption from Aqueous Solution.* ACS Advances in Chemistry Series 79, pp.8-22.

Strycker, A., and A. G. Collins. 1986. *Injection of Hazardous Waste in Deep Wells: State-of-the-Art Report.* Dept. of Energy Report No. NIPER-230. (Note: Chapter One of the Research Summaries document is the summary of an updated version of this report.)

U.S. Environmental Protection Agency. 1979. *Methods for Chemical Analysis of Water and Wastes.* U.S. EPA Environmental Monitoring and Support Laboratory, Cincinnati, Ohio, EPA Report 600/4-79-020.

U.S. Environmental Protection Agency. 1985. *Report to Congress on Injection of Hazardous Waste.* EPA Report 570/9-85-003.

Wheeler, A. 1951. *Advances in Catalysis and Related Subjects.* Academic Press, New York Vol. III, pp. 249-327.

Wilke, C. R., and P. Chang. 1955. Correlation of Diffusion Coefficients in Dilute Solutions. *AIChE J.* 1(2):264-270.

CHAPTER FIVE

RESEARCH SUMMARY NO. 4
GEOCHEMICAL INTERACTIONS OF HAZARDOUS WASTES
WITH GEOLOGICAL FORMATIONS IN DEEP-WELL SYSTEMS*

5.1 Overview

5.1.1 Origin and Content

Source: *Geochemical Interactions of Hazardous Wastes with Geological Formations in Deep-Well Systems.* Prepared for the U.S. Environmental Protection Agency and the Illinois Hazardous Waste Research and Information Center. HWRIC Project Number 86015, November 1988. Available from HWRIC, 1808 Woodfield Drive, Savoy, Illinois 61874. 61 p.

Authors: W. R. Roy, S. C. Mravik, I. G. Krapac, D. R. Dickerson, and R. A. Griffin, Illinois State Geological Survey, 615 E. Peabody Drive, Champaign, Illinois 61820.

Contents: This report 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 upper Midwest (Mt. Simon sandstone, Potosi dolomite, and Proviso siltstone); and (3) a comparison of the empirical data with predictions using two solution-geochemistry models (WATEQ2 and SOLMNEQF).

5.1.2 Major Conclusions

■ Batch-type-interaction studies of hazardous waste and reservoir brines and rocks performed to assess geochemical interactions in deep-well systems should be conducted in a range of temperatures and pressure simulating subsurface conditions. Both gaseous and aqueous samples should be collected and analyzed.

■ Thermodynamic models of dissolution-precipitation of mineral phases (such as WATEQ2 and SOLMNEQF) can predict some solution equilibria of waste-brine-rock interactions but have too many limitations to predict all interactions. Consequently, empirical, laboratory-based investigations are needed to assess the chemical interactions among injected wastes, injection formations, and associated formation waters.

■ The acidic waste was neutralized when it reacted with the dolomite and siltstone through carbonate dissolution, generating dissolved carbonate species and carbon dioxide. The waste was partially neutralized by the sandstone through dissolution of clay minerals and ion exchange augmented by the dissolution of a minor amount of calcareous material.

■ At temperatures and pressures lower than those simulating temperatures and pressures at a depth of 3,000 ft, the alkaline waste was hazardous, whereas it was not hazardous under the proper depth-simulating conditions. The silica solid phases of the Mt. Simon sandstone and Proviso siltstone dissolved in the alkaline waste.

5.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

5.2.1 Overview of Fate-Influencing Processes

The geochemical interactions among liquid wastes, formation waters, and formations have not been well researched

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*   Version 3.1 of this report was used to prepare this summary. Changes in the reference section have been incorporated into this summary. A slightly revised version of this report was published in 1989 by the Illinois State Geological Survey as Environmental Geology Note 130.

**   A detailed description of laboratory products can be found in Appendix B of the full report.

(Brower et al., 1988; Warner, 1965; van Everdingen and Freeze, 1971; Gordon and Bloom, 1984; LaMoreaux and Smith, 1985; Sullivan et al., 1986).

A chemically incompatible waste-formation system is one in which precipitates or gases evolve during injection. Chemical precipitates can accumulate in the void spaces that make up the formation and reduce its porosity. The reduced porosity will lead to a reduction in injection efficiency, buildup of pressures, and possibly complete well failure. The accumulation of gaseous components, formed as reaction products, can also plug formation voids, reduce the permeability of the receiving formation, and create pressures in the formation leading to blowouts.

Liquid wastes injected into chemically incompatible formations (including in-situ brines) may cause the confining strata to deteriorate and wastes to migrate out of the injection zone (Gordon and Bloom, 1984).

5.2.2 Partition Processes

Adsorption-desorption. Butanol, n-hexylamine, and phenol were adsorbed on Cottage Grove sandstone in laboratory tests at elevated temperatures and pressures (Donaldson and Johansen, 1973). The presence of organic compounds adsorbed on solid surfaces can retard the rate of calcite crystallization (Skirrow, 1975). Rapid calcium-carbonate precipitation from sea water does not occur until much of the dissolved organic matter is removed (Skirrow, 1975). The major organic compound in the alkaline waste, hexachlorocyclopentadiene, can be adsorbed by clay minerals (Chou and Griffin, 1983). Consequently, the organic solutes in the alkaline waste may have retarded the development of calcite equilibrium.

Precipitation-dissolution. The amount of limestone that dissolved during laboratory tests with mixed acidic organic wastes increased with pressure (Goolsby, 1972). Adding hydrochloric acid (HCl) to a ferric-chloride waste solution mixed with dolomite resulted in ferric-hydroxide precipitation; adding acetic or citric acid in lieu of the HCl resulted in no iron precipitation (Hower et al., 1972).

In this study, calcium dissolution increased somewhat at higher temperature and pressure in the acidic-siltstone system, and more so in the acidic-dolomite system. Magnesium showed relatively greater dissolution with increased temperature and pressure in the acid-dolomite system. Other studies have demonstrated that calcite is more soluble when Mg^{2+} is present in the solution. Mg^{2+} derived from the dissolution of dolomite can form $Mg-CO_3$ complexes, which reduce the activity of CO_3^{2-} in solution, inducing further calcite dissolution (Hassett and Jurinak, 1971; Berner, 1975). Silica dissolution increased substan-tially as temperature and pressure increased in the acid-St. Peter sandstone system. The lack of thermal response in the St. Peter sandstone indicated that ion-exchange mechanisms, not just dissolution, contributed to the appearance of aluminum in the solution. Mixing of the connate brine, which contained 117 mg/L magnesium, with the alkaline waste resulted in the Mg^{2+} disappearing from solution, apparently due to brucite ($Mg[OH]_2$) precipitation. In an unrelated study, Mehnert et al. (1988) found that brucite precipitated near the injection zone of the Velsicol facility at Marshall, Illinois.

In each alkaline-rock system an increase in temperature and pressure was associated with lower quantities of calcium in solution. The reverse was true for sulfates. The solubility of calcite decreased with temperature and increased with pressure, although temperature had more effect on solubility than did pressure. The sulfate equilibria of the alkaline-rock system could not be resolved using computer models.

Immiscible Phase Separation. In this study under ambient conditions, carbon dioxide gas was generated in acid-rock systems. The relative amount of carbon dioxide was reduced by an order of magnitude at the higher temperatures and pressures, presumably due to the greater gas pressure exerted on the liquid, preventing degassing. A portion of the dissolved carbon dioxide converted to carbonates, depending on the pH of the solution.

A major problem that can occur when acidic wastes are injected into carbonate formations is **well blowout**, where gaseous CO_2 escapes to the surface. The Cabot Corporation initially injected a 32% HCl solution and in 1975 their well erupted. The amount of CO_2 generated far exceeded its solubility in the reservoir fluids at that HCl concentration. Since the 1975 incident, the Cabot Corporation reduced the HCl concentration to avoid this problem. The dilute nature of the sample used in this project (0.09% HCl) reflected this concern. No further problems with blowout have been reported, nor would they be expected based on the laboratory results presented in this study.

5.2.3 Transformation Processes

Neutralization. Carbonate dissolution is the main contributor to neutralization of acidic wastes. Neutralization may also be facilitated by dissolution of aluminosilicate solid phases in the Mt. Simon sandstone, but dissolution decreased as temperature and pressure increased. The neutralization of HCl by a base is an exothermic reaction. At low HCl percentages (<1%), the temperature increase is negligible. However, thermochemical calculations indicate that temperature increases can become significant (10°C) when the amount of HCl is greater than about 8% (Panagiotopoulos and Reid, 1986).

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The dominant mechanism of HCl-waste neutralization in Mt. Simon sandstone was the dissolution of clay minerals and ion exchange augmented by the dissolution of a minor amount of calcareous material. After 15 days of contact, the waste was rendered nonhazardous by the pH criterion but remained acidic. The extent of reaction progressed slightly with an increase in temperature.

The injection of waste acids, particularly inorganic acids in carbonate formations, has been widely practiced for years. The chemical interactions in such systems have been discussed by Kamath and Salazar (1986). The practice has the obvious attraction of neutralizing a hazardous waste via acid-base chemistry, and the process may increase the capacity of the formation to receive injected wastes.

Oxidation-Reduction. See discussion of measuring oxidation-reduction potential (Eh) in Section 5.6.1, Waste/Reservoir Characterization.

5.2.4 Transport Processes
Not discussed.

5.3 Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes

5.3.1 Geochemical Characteristics of Deep-Well-Injection Zones
General Data. Sandstones and carbonates are the two major types of injection materials in Illinois as well as in the United States (Warner and Lehr, 1977). Injection zones in Illinois range in depth from approximately 1,550 to 5,540 ft. Subsurface geologic formations have been used in Illinois for waste disposal for about 20 years. Currently, nine Class I injection wells are operating, including two standby wells, at seven industrial sites. The following describes some of the geochemical characteristics of the injection zones used in Illinois.

Water Chemistry. A connate-formation brine sample was collected from the injection zone (observation well at about 2,400 ft in Devonian limestone) at the Velsicol site. The brine was very reduced and tended to oxidize quickly when removed from the pressure canister. Total dissolved solids measured about 22,000 mg/L with a pH of 9.07. Brine data from other sources indicate a range of about 12,000 to 28,100 mg/L (Meents et al., 1952, Illinois State Geological Survey files, 1977-1985).

Carbonates. The Cambrian-age Potosi dolomite is used for deep-well injection in Illinois. It is a finely crystalline, pure

to slightly argillaceous dolomite that ranges in thickness from 100 to 300 ft. The sample used was 95% dolomite with approximately 5% quartz. Alkaline waste from the Velsicol pesticide plant at Marshall, Illinois, is injected into a Devonian limestone.

Sandstones. The Cambrian-age Mt. Simon sandstone is also used for deep-well injection in Illinois. It ranges from less than 500 ft to approximately 2,600 ft in thickness. The formation consists of fine- to coarse-grained, partly pebbly, friable sandstone. The bulk sample was approximately 90% quartz, 6% potassium feldspar, and less than 5% clay. The clays were composed of about 75% illite, 25% expandable clays, and a trace of chlorite.

Confining Beds. The Proviso siltstone member (Eau Claire formation) overlies the Mt. Simon sandstone. The Eau Claire formation is used as the upper confining layer at two deep-well-injection facilities in Illinois (Brower et al., 1988). The siltstone is approximately 150 to 300 ft thick and is predominantly a dolomitic, sandy, feldspathic, slightly glauconitic siltstone (Willman et al., 1975). The Proviso sample was composed of approximately 50% quartz, 25% potassium feldspar, 15% dolomite, and 10% clay. The clays were composed of approximately 87% illite, 7% chlorite, and 6% expandable clays.

The New Albany shale (upper) and Maquoketa shale (lower) serve as confining units for injected wastes at the Velsicol pesticide plant at Marshall, Illinois.

5.3.2 Specific Environmental Factors
pH. The pH of the Velsicol alkaline waste did not react strongly with the sandstone, siltstone, or dolomite, nor did it appear to correlate with formation type, time, or temperature and pressure.

Eh. Reducing conditions (-154 mV) existed in brines from Devonian limestone (at about 3,200 ft). The Eh of the Proviso siltstone-acidic waste system rapidly decreased during the first 3 days (from +800 to +300 mV at ambient temperature and pressure). More-reducing conditions were generally associated with an increase in temperature and pressure (around +100 mV at 55°C and 11.7 MPa). In the Proviso siltstone-alkaline waste system, Eh showed little change at ambient temperature and pressure, but dropped significantly at 55°C and 11.7 MPa (from +600 to around +200 mV). See also discussion on measuring redox potential in Section 5.6.1, Waste/Reservoir Characterization.

Salinity. See the discussion of ion concentration in Section 5.5, Aqueous and Solution Geochemistry.

Reservoir matrix (clays, iron oxides). The dissolution of feldspars and clay minerals is characteristically a very slow reaction.

Temperature. Temperatures of 40°C simulate an approximate depth of 1,500 ft, and 55°C, an approximate depth of 3,000 ft. At a depth of 3,000 ft temperatures range from 50° to 100°C (Roedder, 1959; Bayazeed and Donaldson, 1973).

Time. Some chemical reactions require considerably longer to go to completion than others (Ostroff, 1965). The time required to establish dolomite equilibrium in neutralized acidic wastes is not known. Quartz dissolution-precipitation at temperatures less than 50°C is extremely slow (Stumm and Morgan, 1981). Fifteen days was not long enough for silica dissolution in the the Proviso siltstone to reach equilibrium, even though the system appeared to be stable at ambient temperatures.

Pressure. Estimates vary, but injected liquids at a depth of 3,000 ft are subjected to hydrostatic pressure exceeding 10 MPa (Roedder, 1959; Bayazeed and Donaldson, 1973). A pressure of 6 MPa (871 psig) simulates the pressure at approximately 1,500 ft, and 11.7 MPa (1,697 psig) a depth of about 3,000 ft. A few investigators have conducted laboratory experiments at elevated pressures and temperatures to simulate subsurface conditions. Goolsby (1972) found that the amount of limestone that dissolved in laboratory tests with an acidic, mixed organic waste increased with pressure with a concomitant decrease in solution pH. Higher temperature and pressure tended to increase the dissolution of calcium in the acidic waste-rock interactions.

5.4 Geochemical Characteristics and Fate of Hazardous Wastes

5.4.1 Chemical Properties of Inorganic Hazardous Wastes

This report discusses the chemical properties of extremely acid/alkaline wastes. Laboratory compatibility studies include Goolsby (1972) and Bayazeed and Donaldson (1973).

In this study, an acidic inorganic liquid waste was collected from the Cabot Corporation plant near Tuscola, Illinois. The waste liquid is a byproduct of the production of a high-purity, amorphous silica and contains 0.09% HCl (Bergonson, 1988).

An alkaline liquid waste was collected from the Velsicol Chemical Corporation at Marshall, Illinois. The brine-like solution (200,000 mg/L) was the caustic process water from pesticide manufacturing. It did not react strongly with the three core samples except for the dissolution of silica. The pH did not appear to correlate with formation type, temperature, or pressure.

5.4.2 Chemical Properties of Organic Hazardous Wastes

The Velsicol alkaline waste contained numerous organic compounds. Volatile organic hazardous wastes detected in the solution included six halogenated aliphatic hydrocarbons (chloroform, 1,1-dichloroethane, carbon tetrachloride, trichloroethene, bromoform, and tetrachloro-ethene) and monocyclic aromatics (benzene, toluene, ethylbenzene, and o-xylene). Interactions of these materials with reservoir rock were not evaluated.

Phenol. Phenol was adsorbed on Cottage Grove sandstone at elevated temperatures and pressures in static laboratory tests (Donaldson and Johansen, 1973).

Butanol. Butanol was adsorbed on Cottage Grove sandstone at elevated temperatures and pressures in static laboratory tests (Donaldson and Johansen, 1973).

n-Hexylamine. n-Hexylamine was adsorbed on Cottage Grove sandstone at elevated temperatures and pressures in static laboratory tests (Donaldson and Johansen, 1973).

5.4.3 Mixtures of Hazardous Wastes

Laboratory experiments on interaction of acidic wastes containing adiponitrile, hexamethylenediamine, alcohols, ketones, and esters with limestone under pressure have been conducted by Goolsby (1972).

5.5 Methods And Models For Predicting The Geochemical Fate Of Deep-Well-Injected Wastes

5.5.1 Basic Approaches

Accurate thermodynamic data are lacking for many heterogeneous solid wastes and chemical interactions. Kinetic data for many reactions under elevated temperature and pressure are unknown. Because of the lack of data, the application of thermodynamic models to predict the fate of injected wastes is tenuous (Sullivan et al., 1986). Brower et al. (1988) concluded that laboratory compatibility studies on

chemical interactions have better predictive value than equilibrium models.

To avoid using laboratory studies to determine the possible chemical interactions of specific waste-formation systems, some investigators have attempted to use computer-assisted transport and chemical (thermodynamically based) models to assess the fate and distribution of chemical constituents in injection scenarios. Scrivner et al. (1986) concluded that the chemical fate of injected wastes can be determined by "standard chemical engineering techniques" and that the concentrations of hazardous constituents are typically reduced by reactions within the waste or injection environment. Scrivner and his co-workers at E.I. Du Pont de Nemours and Company have used computer simulations to model the fate of injected hazardous wastes. The models considered reaction rates and the equilibrium constants for the dominant reactions. The Du Pont model has not been validated, and was not publicly available at the time this summarized research report was published.

5.5.2 Specific Methods and Models

Waste-Reservoir Compatibility. Very few studies of chemical compatibility have been conducted. Some of these studies consisted of mixing a sample of the liquid waste with a synthetic formation-water sample for 4 to 6 hours at room temperature and pressure. Since the mixture remained free of precipitates, the waste was considered compatible with the formation fluid (Warner, 1965). Sufficient time is necessary to allow chemical reactions to go to completion (Ostroff, 1965), and past studies have tended to ignore the effects of formation temperatures and pressures on chemical reactions (see, for example, Headlee, 1950; Bayazeed and Donaldson, 1971; and Barnes, 1972). Studies involving elevated temperatures and pressures include Goolsby (1972) (static, limestone and acidic mixed organic waste); Hower et al. (1972) (static, dolomite and ferric chloride mixed with several acids); and Donaldson and Johansen (1973) (static, Cottage Grove sandstone with various organic compounds: butanol, n-hexylamine, and phenol). Studies involving flowthrough experiments at ambient temperatures with simulated acid wastes from steel processing and Mt. Simon sandstone were performed by Bayazeed and Donaldson (1973).

The change in calcium concentrations in the alkaline waste-rock systems with increased temperature and pressure suggests that fate or compatibility-type demonstrations conducted under ambient conditions may not generate data that simulate subsurface conditions. The Proviso siltstone appeared to be stable at ambient conditions, but dissolution of silica occurred at elevated temperatures and pressures, and apparently the system had not reached equilibrium after 15 days.

Aqueous and Solution Geochemistry. In some cases, solution equilibria could be modeled using the thermodynamic principles of dissolution-precipitation of mineral phases. In other cases, empirical, laboratory-based investigations are needed to assess the interactions among injected wastes, injection formations, and associated formation waters.

The thermodynamic model WATEQ2 (Truesdell and Jones, 1974; Plummer et al., 1976; Ball and Jenne, 1979) was used to help understand the geochemical interactions between the liquid hazardous wastes and the core samples. This computer program is based on the equilibrium-constant approach that predicts the distribution of aqueous species based on the input chemical data. The program simultaneously solves several nonlinear equations by successive approximation using the continued-fraction approach.

WATEQ2 has a temperature range of applicability of 0°C to 100°C. Equilibrium constants are calculated at a given temperature using empirical regression depending on the availability of data for a specific solid phase, or they are interpolated using a Van't Hoff equation.

The equilibrium constants for calcite dissolution at 6 MPa and 11.7 MPa pressure were calculated from changes in the partial molar volume of the reaction, using the method given in Skirrow (1975). Dolomite equilibria could not be corrected for pressure effects because of a lack of reliable data.

The chemical data were also treated by the thermodynamic model SOLMNEQF (Kharaka and Barnes, 1973). SOLMNEQF is similar to WATEQ2 in structure and database, although fewer solid phases are considered. Like WATEQ2, SOLMNEQF calculates equilibrium constants as a function of temperature using a Van't Hoff equation, but it also corrects for pressure over a range of 1 to 1,000 atmospheres (atm) (101.3 MPa). Pressure-corrected equilibrium constants of solid phases are approximated using the coefficient of expansion, isothermal compressibility, and molar volume of the mineral phase. The effects of pressure on ionic species are not considered. As with all thermodynamic models, the results must be interpreted cautiously owing to discrepancies in reported values for equilibrium constants, heterogeneous redox equilibria, and kinetically inhibited reactions. Both models were used in this study for the sake of comparison.

The only equilibrium relationship indicated by WATEQ2 and SOLMNEQF was the hydrolysis of chalcedony, a fibrous form of silica. Chalcedony occurs in sedimentary rocks, possibly forming from the dissolution of clay minerals (Jenne, 1988). At higher temperatures and pressures, the increased dissolution of silica was due to the increased

solubility of chalcedony. The waste-brine system was also equilibrated with chalcedony. It appears that the amount of silica in solution in this system could be estimated using equilibrium constants for the hydrolysis of chalcedony. Therefore, this approach could be used in the modeling to predict the dissolution of chalcedony in similar deep-well scenarios.

The Potosi acidic system was neutralized by the dissolution of dolomite, but dolomite equilibrium was not attained at any temperature; the solution was supersaturated with respect to a dolomitic-carbonate phase. The time required to establish dolomite equilibrium is not known.

Nordstrom and Ball (1984) concluded that ion-association models (such as WATEQ2 and SOLMNEQF) cannot be used to predict mineral solubilities or solute activities at ionic strengths exceeding 0.6 mole/L. The methods and concepts used by these programs, such as estimating activity coefficients, were based on solutions with much lower ionic strengths than those of the alkaline waste-rock systems (about 4.6 mole/L). Consequently, for some reactions, the ionic strength of waste sample was beyond the range where reliable data for ion associations and hydrolytic reactions are available. Although these ion-association models have limitations when applied to concentrated solutions, they were used in this study to help explain observed trends.

The inability to determine very low solution concentrations (such as those of magnesium) is a limitation in using equilibrium models coupled with laboratory studies to predict chemical interactions.

Thermodynamics and Kinetics. Heats of reaction determined under ambient conditions provide an indicator of chemical reactivity. Such measurements represent the summing of many exothermic and endothermic reactions and must be interpreted cautiously.

As with all thermodynamic models, the results must be interpreted cautiously because of discrepancies in reported values for equilibrium constants, heterogeneous redox equilibria, and kinetically inhibited reactions. Both models were used in this study for the sake of comparison.

5.6 Laboratory Procedures And Protocols

5.6.1 Waste/Reservoir Characterization
General Characterization. The brine sample from Velsicol was stored under nitrogen in the field at 345 Pa in a stainless-steel pressure canister to minimize oxidation and degassing. Solution concentrations of chloride, fluoride,

nitrate, sulfate, and iron (Fe^{+3}) were determined using an ion chromatograph. Solution concentrations of metals and other cations were determined using an inductively coupled argon-plasma (ICAP) emission spectrophotometer. Samples of the alkaline liquid were analyzed by gas chromatography/mass spectroscopy (GC/MS). Volatile organic compounds were determined by direct GC injection. Gas samples were characterized with a gas chroma-tograph. The pH and electrical conductivity of the solutions were measured by electrode (American Public Health Association, 1985). Mineralogical composition of the three core samples was determined by x-ray diffraction using procedures discussed in Russell and Rimmer (1979).

Heats of reaction between the liquid wastes and the disaggregated core sample were determined with a Parr 1451 solution calorimeter (see Ramette [1984] for details on procedures and theory of operation).

Measurement of Eh. The oxidation-reduction potential (Eh) of a solution is usually measured using a platinum electrode or a saturated calomel electrode. In this study, Eh electrode measurements were made using procedures described by the American Public Health Association (1985) and the Eh reference solution described by ZoBell (1946) and Wood (1976). Such measurements are difficult to duplicate, and readings of a sample solution with two identical electrodes may vary by as much as 50 mV depending on the stability of the solution, the electrode, and the skill of the analyst (Nordstrom et al., 1979). Some investigators (summarized by Nordstrom et al., 1979) have found good agreement between measured Eh and a dominant redox couple, while others regard Eh measurements as only a qualitative indication of redox potential.

In this study, ion chromatography (IC) was applied to determine the concentrations of Fe^{2+} and Fe^{3+} to derive Eh values for comparison with the electrode-based observations. As an alternative method, ferrous ion was determined by titrating the solutions with dichromate using a combination platinum electrode (Skoog and West, 1976). The IC-based Eh values showed poor agreement with the electrode-based observations, and the investigators concluded that ion chromatography is unlikely to yield reliable iron-couple data without considerably more research. Consequently, the redox potentials reported in the study should be considered *qualitative* values.

When a redox electrode is immersed in a solution, the observed reading may reflect the summation of different individual redox couples, and this combined potential may differ greatly from that of any known potential (Bohn et al., 1979). Lindberg and Runnells (1984), in an analysis of more than 600 groundwater samples from diverse geographic

areas, concluded that aqueous oxidation-reduction reactions in natural groundwater systems are generally not at equilibrium. Multiple redox couples present in individual samples yielded computed Eh values spanning as much as 1,000 mV. Thus, the potential of a platinum electrode in a redox mixture may be a poorly defined average of the potential of redox couples present. Furthermore, the point at which the electrode has equilibrated with a solution is not always certain; often the reading may slowly drift rather than stabilizing on a value. The contribution of each couple to the observed measurement is an unknown function of its concentration. For example, nitrate stabilizes potentials at 200 to 400 mV and prevents the formation of Fe^{2+} in soils (Ponnamperuma, 1972).

5.6.2 Static Interaction Tests
Batch pressure reaction vessels were operated in temperature-controlled water baths to represent subsurface temperature-pressure regimes. Vessels could not be pressurized to exceed 11.7 MPa without risking failure of the rupture disks.

5.6.3 Dynamic (Flowthrough) Tests
These tests were not used.

5.6.4 Quality Assurance/Quality Control Procedures
Quality-control standards obtained from the U.S. EPA were used to verify results at the time of analysis.

5.7 Case Studies

This study presents the results of laboratory waste-reservoir interaction tests of acidic, inorganic waste from the Cabot Corporation near Tuscola, Illinois, and alkaline liquid waste from the Velsicol Chemical Corporation in Marshall, Illinois. See Section 5.4.1 for additional information on the chemical properties of the wastes.

5.8 Further Research Needs

No further research needs were discussed.

References

American Public Health Association. 1985. *Standard Methods for the Examination of Water and Wastewater,* 16th ed. American Public Health Association, Washington, DC, 1,268 pp.

Ball, J. W., and E. A. Jenne. 1979. WATEQ2—A Chemical Model for Trace and Major Element Speciation and Mineral Equilibria of Natural Waters. In *Chemical Modeling in Aqueous Systems.* American Chemical Society Symposium Series 93, pp. 815-836.

Barnes, I. 1972. Water-Mineral Reactions Related to Potential Fluid-Injection Problems. In *Underground Waste Management and Environmental Implications.* T.D. Cook, ed. American Association of Petroleum Geologists, Memoir 18, pp. 294-297.

Bayazeed, A. F., and E. C. Donaldson. 1971. *Deep-Well Disposal of Steel Pickling Acid.* Paper No. SPE 3615, presented at the 46th Annual Meeting of the Society of Petroleum Engineers of AIME, New Orleans, Louisiana, Oct. 3-6.

Bayazeed, A. F., and E. C. Donaldson. 1973. *Subsurface Disposal of Pickle Liquor.* U.S. Bureau of Mines, Report of Investigations 7804, 31 pp.

Bergonson, R. 1988. Personal communication. Cabot Corporation, Tuscola, Illinois.

Berner, R. A. 1975. The Role of Magnesium in the Crystal Growth of Calcite and Aragonite from Sea Water. *Geochimica et Cosmochimica Acta* 39:489-504.

Bohn, H. L., B. L. McNeal, and G. A. O'Connor. 1979. *Soil Chemistry.* John Wiley & Sons, New York, 329 pp.

Brower, R. D., I. G. Krapac, B. R. Hensel, A. P. Visocky, G. R. Peyton, J. S. Nealon, and M. Guthrie. 1988. *Evaluation of Current Underground Injection of Industrial Waste in Illinois.* Final Report HWRIC RR008, Hazardous Waste Research and Information Center, Savoy, Illinois.

Chou, S. F. J., and R. A. Griffin. 1983. *Soil, Clay, and Caustic Soda Effects on Solubility, Sorption, and Mobility of Hexachlorocyclopentadiene.* Environmental Geology Notes 104, Illinois State Geological Survey, Champaign, Illinois, 54 pp.

Donaldson, E. C., and R. T. Johansen. 1973. History of a Two-Well Industrial-Waste Disposal System. In *Second International Symposium on Underground Waste Management and Artificial Recharge,* Vol. 1, pp. 603-621.

Goolsby, D. A. 1972. Geochemical Effects and Movement of Injected Industrial Waste in a Limestone Aquifer. In *Underground Waste Management and Environmental Implications,* T. D. Cook, ed. American Association of Petroleum Geologists, Memoir 18, pp. 355-368.

Gordon, W., and J. Bloom. 1984. *Deeper Problems: Limits to Underground Injection as a Hazardous Waste Disposal Method.* Natural Resources Defense Council Inc., New York, New York.

Hassett, J. J., and J. J. Jurinak. 1971. Effect of Mg^{2+} Ion on the Solubility of Solid Carbonates. *Soil Science Society of America Proceedings* 35:403-408.

Headlee, A. J. W. 1950. Interactions Between Interstitial and Injected Water. In *Secondary Recovery of Oil in the United States.* American Petroleum Institute, New York, New York. pp. 59-64.

Hower, W. F., R. M. Lasater, and R. G. Mihram. 1972. Compatibility of Injection Fluids with Reservoir Components. In *Underground Waste Management and Environmental Implications.* T. D. Cook, ed. American Association of Petroleum Geologists, Memoir 18, pp. 287-293.

Jenne, E. A. 1988. Personal communication. Battelle Pacific Northwest Laboratories, Richland, Washington.

Kamath, K., and M. Salazar. 1986. The Role of the Critical Temperature of Carbon Dioxide on the Behavior of Wells Injecting Hydrochloric Acid into Carbonate Formations. In *International Symposium of Subsurface Injection of Liquid Wastes.* Underground Injection Practices Council, New Orleans, Louisiana, March 3-5.

Kharaka, Y. K., and I. Barnes. 1973. *SOLMENQ: Solution-Mineral Equilibrium Computations.* U.S. Geological Survey. National Technical Information Service, PB 215 899, 81 pp.

LaMoreaux, P. E., and J. Y. Smith. 1985. *Waste Injection Present Status and Viability.* Environmental Institute for Waste Management Studies, University of Alabama, Open File Report, 23 pp.

Lindberg, R. D., and D. D. Runnells. 1984. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. *Science* 225:925-927.

Meents, W. F., A. H. Bell, O. W. Rees, and W. G. Tilbury. 1952. *Illinois Oil-Field Brines.* Illinois State Geological Survey, Illinois Petroleum No. 66, 38 pp.

Mehnert, E., C. R. Gendron, and R. D. Brower. 1988. *Investigation of the Hydraulic Effects of Deep-Well Injection of Industrial Wastes.* Final Report, Hazardous Waste Research and Information Center, Savoy, Illinois (in review).

Nordstrom, D. K., and J. W. Ball. 1984. Chemical Models, Computer Programs and Metal Complexation in Natural Waters. In *Complexation of Trace Metals in Natural Waters,* C. J. M. Kramer and J. C. Duinker, eds. Martinus Nijhoff/Dr. W. Junk, The Hague, Netherlands, pp. 149-165.

Nordstrom, D. K., E. A. Jenne, and J. W. Ball. 1979. Redox Equilibria of Iron in Acid Mine Waters. In *Chemical Modeling in Aqueous Systems,* E. A. Jenne, ed. American Chemical Society Symposium Series 93, pp. 41-79.

Ostroff, A. G. 1965. *Introduction to Oil Field Water Technology.* Prentice-Hall, Inc., Englewood Cliffs, New Jersey.

Panagiotopoulos, A. Z., and R. C. Reid. 1986. Deep-Well Injection of Aqueous Hydrochloric Acid. In *International Symposium on Subsurface Injection of Liquid Wastes.* Underground Injection Practices Council, New Orleans, Louisiana, March 3-5.

Plummer, L. N., B. F. Jones, and A. H. Truesdell. 1976. *WATEQF—A FORTRAN IV Version of WATEQ, A Computer Program for Calculating Chemical Equilibrium of Natural Waters.* U.S. Geological Survey, Water Resources Investigations 76-13, 61 pp.

Ponnamperuma, F. N. 1972. The Chemistry of Submerged Soils. *Advances in Agronomy* 24:29-96.

Ramette, R. W. 1984. Solution Calorimetry in the Advanced Laboratory. *Journal of Chemical Education* 61:76-77.

Roedder, E. 1959. *Problems in the Disposal of Acid Aluminum Nitrate High-Level Radioactive Waste Solutions by Injection into Deep-Lying Permeable Formations.* U.S. Geological Survey Bulletin 1088, 65 pp.

Russell, S. J., and S. M. Rimmer. 1979. Analysis of Mineral Matter in Coal, Coal Gasification Ash, and Liquefaction Residues by Scanning Electron Microscopy and X-Ray Diffraction. In *Analytical Methods for Coal and Coal Products,* C. Karr, ed. Academic Press, New York, Vol. 3, pp. 133-162.

Scrivner, N. C., K. E. Bennett, R. A. Pease, A. Kopatsis, S. J. Sanders, D. M. Clark, and M. Rafal. 1986. Chemical Fate of Injected Wastes. In *International Symposium on Subsurface Injection of Liquid Wastes.* Underground Injection Practices Council, New Orleans, Louisiana, March 3-5.

Skirrow, G. 1975. The Dissolved Gases —Carbon Dioxide. In *Chemical Oceanography.* J. P. Riley and G. Skirrow, eds. Academic Press Inc., London, Vol. 2, Chap. 9, pp. 1-192.

Skoog, D. A., and D. M. West. 1976. *Fundamentals of Analytical Chemistry*, 3rd ed. Holt, Rinehart, and Winston, New York, 804 pp.

Stumm, W., and J. J. Morgan. 1981. *Aquatic Chemistry.* John Wiley & Sons, New York, 780 pp.

Sullivan, P., M. Essington, R. Poulsen, J. Bowen, J. McKay, and R. Donovan. 1986. *Modeling the Geochemistry of Hazardous Waste Injection.* Western Research Institute, Laramie, Wyoming, 90 pp.

Truesdell, A. H., and B. F. Jones. 1974. WATEQ, a Computer Program for Calculating Chemical Equilibria of Natural Waters. *U.S. Geological Survey Journal of Research* 2:233-248.

U.S. Environmental Protection Agency. 1980. Hazardous Waste Management: Rules and Regulations. *Federal Register* 45:33110-33112.

U.S. Environmental Protection Agency. 1987. Underground Injection Control Program; Proposed Rule. *Federal Register* 52:32446-32476.

U.S. Environmental Protection Agency. 1988. Underground Injection Control Program: Final Rule. *Federal Register* 53:28118-28157.

Van Everdingen, R. O., and R. A. Freeze. 1971. *Subsurface Disposal of Waste in Canada.* Department of the Environment, Inland Waters Branch, Technical Bulletin No. 49, Ottawa, Ontario, 64 pp.

Warner, D. L. 1965. *Deep-Well Injection of Liquid Waste: A Review of Existing Knowledge and an Evaluation of Research Needs.* U.S. Department of Health, Education, and Welfare, Public Health Service Publication No. 999-WP-21, 55 p.

Warner, D. L., and J. H. Lehr. 1977. *An Introduction to the Technology of Subsurface Waste Water Injection.* U.S. Environmental Protection Agency, EPA Report 600/2-77-240, 319 pp.

Willman, H. B., E. Atherton, T. C. Buschbach, C. Collinson, J. C. Frye, M. E. Hopkins, J. A. Lineback, and J. A. Simon. 1975. *Handbook of Illinois Stratigraphy.* Bulletin 95, Illinois State Geological Survey, Urbana, Illinois, 261 pp.

Wood, W. W. 1976. *Guidelines for Collection and Field Analysis of Ground-Water Samples for Selected Unstable Constituents.* U.S. Geological Survey, Techniques of Water-Resources Investigations, Chap. D-2, 24 pp.

ZoBell, C. E. 1946. Studies on Redox Potential of Marine Sediments. *American Association of Petroleum Geologists Bulletin* 30:477-513.

CHAPTER SIX

RESEACH SUMMARY NO. 5
CURRENT GEOCHEMICAL MODELS TO PREDICT THE FATE OF HAZARDOUS
WASTES IN THE INJECTION ZONES OF DEEP DISPOSAL WELLS

6.1 Overview

6.1.1 Origin and Content
Source: *Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of Deep Disposal Wells.* Draft Report. January 1988. Lawrence Berkeley Laboratory Report LBL-26007. Draft Report Prepared for U.S. Environmental Protection Agency. 118 pages. *

Authors: John A. Apps, Earth Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.

Contents: This report 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) a 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) modeling of nonequilibrium systems; (6) the availability of geochemical-modeling computer codes; (7) criteria affecting the satisfactory chemical modeling of waste injection; and (8) conclusions and recommendations.

6.1.2 Major Conclusions
■ The geochemical modeling of the fate of hazardous wastes in saline aquifers contained in deep sedimentary formations is in a preliminary state of development. Geochemical modeling has not been adequately tested

in the field or the laboratory to show that it can be used to make quantitative predictions under all conditions.

■ Many diverse mechanisms affect the fate of hazardous constituents in deep aquifers. No single computer code is currently capable of modeling all processes. Available codes must be selected by how they perform on a particular application.

■ The state of the art in many areas of geochemical research is embryonic. For example, activity coefficients of ions in strongly mixed electrolytes (i.e., brines), the thermodynamic properties of clays, and the thermodynamics of adsorption have yet to be accurately determined. Thermodynamic data for many minerals and organic aqueous species are unavailable. Therefore, much preparatory research must be done before suitable simulations can be conducted. Existing thermodynamic databases used with geochemical modeling codes will require close scrutiny before they are used.

■ Although the literature describing the adsorption of inorganic and organic species on clays is substantial, integrated compilations of data are not available for practical applications. Additionally, suitable adsorption or ion-exchange models that can be used for the diverse range of conditions expected in deep-well environments are also not available.

■ Information on the kinetics of both heterogeneous and homogeneous reactions relevant to the fate of hazard-

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* The report was undergoing peer review at the time this summary was prepared and had several minor errors in the text and references section. The author was consulted where questions arose, and corrections were incorporated into this summary.
** This part of the report is not summarized here because it deals with regulatory rather than technical matters.
*** Except for simple equations, mathematical discussions in the report are not reproduced here.

ous compounds is fragmentary and often inadequate. Careful evaluation of the literature and experiments will often be required.

- A substantial number of computer codes are available to evaluate the distribution of chemical species in solutions. Computer codes that model mass transfer or mass transport with simultaneous chemical reactions are currently limited in availability and/or scope. Codes should be selected with caution to ensure aptness.

- There are two types of distribution-of-species codes— the equilibrium-constant codes and the Gibbs free-energy-minimization code. Both types are mathematically equivalent, but in principle the latter is more flexible and easier to use. Most available codes are equilibrium- constant codes; additional effort is required to modify these types for use in deep-well injection studies.

- Chemical-transport codes fall into two categories—the "one-step" or the "two-step" codes. For the one-step codes, highly nonlinear computationally intensive equations must be calculated. The two-step codes have had problems with drift, but tend to be more flexible in a diverse range of problems.

- Some geochemical codes have been verified, but few have been used to test the validity of the underlying models. There is an urgent need to conduct additional field- validation studies under any conditions, especially those in deep disposal wells.

6.2 Processes Affecting the Geochemical Fate of Deep-Well-Injected Wastes

6.2.1 Overview of Fate-Influencing Processes
Many waste streams contain organic constituents, which may be partly or completely miscible in water. These streams adsorb on minerals and can hydrolyze, decarboxylate, or be destroyed through bacterial action. The fate of those containing toxic heavy metals (such as cadmium, hexavalent chromium, mercury, nickel, and lead) must be considered in light of potential interactions between the host rock and the waste stream and the presence of complexing agents.

Immobilizing Reactions. The mechanisms that can lead to immobilization of hazardous constituents in the waste stream in the injection zone are precipitation/co-precipitation, ion exchange, or adsorption. Total immobilization is impossible because all precipitates have a finite solubility. Also, all ion-exchange and adsorption processes must have finite, though sometimes very small, reversible-exchange or adsorption coefficients. The immobilization of wastes may be further complicated by (1) metastability and the slow kinetics of heterogeneous processes, and (2) waste streams with more than one hazardous constituent. To obtain an injection-well permit based on geochemical immobilization of wastes, an operator must show that the hazardous waste will be immobilized for the next 10,000 years (i.e., the concentration in solution decreases well below regulatory standards or three orders of magnitude below current detection limits). In reality, many hazardous constituents, particularly water-miscible organic species, are not immobilized effectively.

The effects of immobilization or decomposition may be enhanced by viewing the injection zone as a reactor in which constituents added to the waste stream can react beneficially with the hazardous constituents. Examples of such innovative techniques include (1) wet combustion (Smith and Raptis, 1986) and (2) addition of a fixation agent such as tetramethyl ammonium ion to a waste stream to enhance sorption of organic wastes on smectite clays (Barrer and MacLeod, 1955). Much research is needed to demonstrate that these techniques are both effective and reliable; the added cost of such research and treatment procedures may exceed the benefits of the enhanced containment potential.

Reactions for Which Kinetics May Be Important. Many reactions in an injection zone proceed rapidly enough that a local, reversible equilibrium may be assumed with reasonable confidence. Most homogeneous reactions in the aqueous phase (with the exception of some oxidation-reduction reactions), surface-adsorption reactions, and ion-exchange reactions are of this type. At the other end of the spectrum, some reaction rates are so slow that equilibrium is not attained even after 10,000 years. In this case, hydrologic arguments alone must be used to demonstrate containment. Several categories of chemical reactions proceed sufficiently slowly that local equilibrium cannot be assumed, yet substantial progress toward equilibrium is achieved within the 10,000-year time frame. Types of reactions that may require analysis using a kinetic equation include:

- Heterogeneous precipitation of secondary minerals or solid phases from solution

- Oxidation/reduction reactions in the aqueous phase

- Hydrolysis, decarboxylation, dechlorination, etc., of organic compounds

- Bacterial destruction of nitrogen compounds, hydrocarbons, and halogenated hydrocarbons

For predictive modeling, the range of magnitudes for the rate constants $k_i(s^{-1})$ of chemical reactions that fall between the two reaction rate extremes must be determined.

The actual attenuation of a species in solution to nonhazardous levels, whether through adsorption, precipitation, or decomposition, depends on the following factors:

- Rate constant

- Initial concentration of the species and other participating species

- Substrate area or nucleation sites if a heterogeneous reaction is involved

- Concentration levels below which the chemical is no longer considered hazardous

Figure 6-1   Plot of first-order decomposition rate constant vs. time for given attenuation ratios, $C_{i,t}/C_{i,0}$
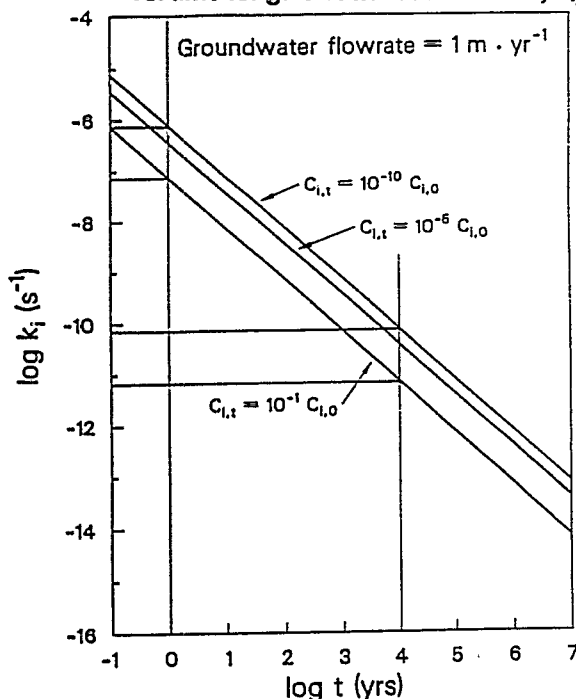

Figure 6-1 is a graph of the simple case in which removal of the hazardous constituent is a first-order equation with respect to time for various attenuations in concentration, from 10^{-1} to 10^{-10}. For reaction half-lives greater than 1 year, rate constants greater than $10^{-6}s^{-1}$ will not be of concern, because the hazardous constituent will be immobilized or destroyed near the injection well (although formation of pore-blocking precipitates might adversely affect well operations). At the other extreme, rate constants less than $10^{-11}s^{-1}$ will not result in significant attenuation in 10,000 years. Consequently, for "irreversible" first-order reactions of interest, the rate constant generally falls between 10^{-11} and $10^{-6}s^{-1}$.

6.2.2 Partition Processes

Three groups of partition processes are discussed in this report:

- Adsorption-desorption

- Precipitation-dissolution

- Immiscible phase separation

These mechanisms are discussed in the sections below.

Adsorption-desorption. One of the most important mechanisms by which small amounts of hazardous constituents can be removed from a waste stream is adsorption. Adsorption is a process in which chemical species in solution attach to the surface of a solid substrate. The process should be thermodynamically reversible, but many adsorption experiments have demonstrated apparent irreversibility.* Some researchers consider adsorption an irreversible phenomenon (Van Genuchten et al., 1974). The meaning of adsorption is further confused, since manganese oxide, clay interlayer, and zeolite-ion exchange are often defined as adsorption mechanisms. Thus, parallel treatments have been developed for ion exchange and adsorption, which are essentially the same phenomenon. For further information, see the discussion of Reservoir Matrix (Section 6.3.2) and Adsorption (Section 6.5.2.3).

Precipitation-dissolution. Any waste stream can react with the host rock or ground water to produce undesirable side reactions; separate gas phases can form or pore-clogging solids can precipitate. Several conditions contribute to

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* Editor's note: Rao and Davidson (1980) have suggested three major causes of apparent irreversibility in adsorption-desorption experiments: (1) artifacts created by some aspect of the experimental method, (2) failure to establish complete equilibrium during the adsorption phase, and (3) chemical and/or microbial transformations during the experiment.

precipitation. For example, even before injection begins, waste streams can be supersaturated with either benign or hazardous constituents; precipitation in the zone near the well bore could seriously decrease injection rates unless pumping pressure is increased. Increases in pumping pressure can lead in turn to hydrofracturing and escape of the injected waste outside the injection zone. Neutralization of exceedingly acid or alkaline wastes involves substantial hydrolysis and dissolution of host-rock minerals, which may also lead to precipitation.

During the late 1950s, investigators focused on slow, surface-controlled dissolution reactions involving the oxidation of sulfides in abandoned coal and nonferrous-metals mines and the waste and spoils heaps from such operations. Also, at this time, geochemists conducted the first tentative studies on the dissolution kinetics of silicates (Garrels and Howard, 1957). Studies of the hydrometallurgical treatment of ores to recover metals concentrated on many matters identical to present concerns (Burkin 1966, 1983). New techniques for characterizing and observing surfaces, such as ESCA, SIMS, and SEM, were introduced and provided an added incentive to interpret correctly the dissolution or precipitation mechanisms involved in hazardous-waste injection.

Except for carbonate dissolution by strong acids, most heterogeneous reactions involving dissolution or precipitation of solid phases occur slowly (in relation to the 10,000-year-containment standard) at injection-zone temperatures. Unfortunately, information on the kinetics of precipitation or dissolution of relevant phases is sparse. For example, a review paper on this subject by Lasaga (1981a) summarized investigations of the kinetics of only 14 minerals, and studies of only a few more minerals have been completed since that time. Geochemical research has tended to address specific issues, such as:

- Feldspar weathering (Wollast, 1967; Helgeson, 1974; Weare et al., 1976; Petrovich, 1976; Petrovich et al., 1976; Berner and Holdren, 1977, 1979; Holdren and Berner, 1979; Fleer, 1982; Helgeson et al., 1984)

- Quartz-dissolution kinetics (Apps et al., 1975; Rimstidt and Barnes, 1980; Bird and Boon, 1984; Bird et al., 1986)

- Carbonates (Sjoberg, 1976; Plummer and Wigley, 1976; Plummer et al., 1978)

- Sulfates such as gypsum and anhydrite

Dissolution or precipitation studies of other minerals are uncommon (Lasaga, 1981b, 1984).

Only during the last decade have researchers attempted to understand mineral dissolution and precipitation kinetics in multicomponent heterogeneous systems (Dibble and Tiller, 1981; Lasaga, 1981a,b,c; Petrovich, 1981a,b; Aargaard and Helgeson, 1982; Helgeson and Murphy, 1983; Helgeson et al., 1984). Absolute-rate theory or transition-state theory (Glasstone et al., 1941) is often used to interpret heterogeneous reactions. The general theory proposed by Aargaard and Helgeson (1982) is complicated, yet does not quantify actual dissolution or precipitation mechanisms, which must be determined by experiment. Unfortunately, incongruent dissolution or precipitation and secondary nucleation effects, as well as mechanisms in which H^+, OH^-, or other dissolved species catalyze reactions, may complicate the interpretation of experiments.

When a solution is grossly undersaturated or supersaturated with a given mineral, precipitation-dissolution rates are a function of the surface area of the mineral (or, more accurately, the growth of dissolution sites on the surface of the mineral) and whether the rate is zero-order (independent of the concentrations of reactants in solution). Wood and Walther (1983) evaluated dissolution rates of a number of rock-forming aluminosilicates, quartz, and corundum, and found that reaction rates were consistent with the equation:

$$\log k = \sim 2,900/T - 6.85$$

when all data were normalized to the number of gram-atoms of oxygen per square centimeter (cm^2) of mineral surface.

Wood and Walther (1983) proposed that zero-order dissolution kinetics of aluminosilicate minerals might be determined by a simple linear equation when their surfaces are normalized to the number of gram-atoms of oxygen per cm^2. Unfortunately, more recent studies (Murphy and Helgeson, 1984) have questioned the validity of this simple model. When gross supersaturation occurs, the thermodynamically most stable phase does not necessarily precipitate. In fact, the nucleating and precipitating phases are functions of the degree of supersaturation, the surface tension of the precipitating phase (Sohnel, 1982), and the growth mechanism (Stranski and Totomanow, 1933; Gutzow and Toschev, 1968).

As equilibrium is approached, back reactions, which depend on the activities of the species in solution, begin to retard the overall rate. The participating species and the associated rate laws cannot be identified readily except by direct experimentation. Original investigations may be necessary, however, to clarify the kinetics of reactions unless literature describing the kinetics for the phase of interest is available.

For example, Petrovich (1986) has developed a generalized scheme for explaining the kinetics of aluminosilicate precipitation and dissolution.

Immiscible Phase Separation. Most deep aquifers contain such carbonates as calcite, dolomite, ankerite, or siderite; thus, substantial quantities of carbon dioxide may be generated and form a separate CO_2-rich phase.

6.2.3 Transformation Processes

The two transformation processes discussed in this report are:

■ Hydrolysis

■ Thermal degradation

Hydrolysis. Mabey and Mill (1978) reviewed hydrolysis rates of organic compounds. Their results indicate that hydrolysis involves the participation of either H^+, OH^-, or water. The overall rate is the sum of the three mechanisms:

$$K_L = k_B[OH^-] + k_a[H^+] + k_N$$

The (pseudo) first-order hydrolysis constants for different organics vary widely, from 10^{-2} to $10^{-13}s^{-s}$. The region of concern covers a broad range of constants, as indicated in Section 6.2.1 (i.e., 10^{-6} to $10^{-11}s^{-1}$).

Thermal Degradation. Smith and Raptis (1986) suggested using the injection zone as a reactor for wet combustion.

6.2.4 Transport Processes

Transport processes were not addressed specifically.

6.3 Major Environmental Factors Affecting Deep-Well-Injection Geochemical Processes

6.3.1 Geochemical Characteristics of Deep-Well-Injection Zones

General Data. Most deep-well-injection facilities are operated by the chemical industry, and nearly two-thirds of the injected-waste volume originates from manufacturers of organic chemicals. Another 25% of the volume originates from petroleum-refining and petrochemical industries. The balance is generated by the metals, minerals, and aerospace industries, and commercial facilities receiving wastes from many industrial sources. Most large plants have onsite injection wells (U.S. EPA, 1985).

It is difficult to generalize about waste-stream compositions because of their diversity. Most are relatively dilute, i.e., greater than 90% of the stream by weight is water. Waste streams can be either exceedingly acid or alkaline, can contain organic constituents, which can be partly or completely miscible in water, or can contain a variety of toxic heavy metals. Table 6-1 summarizes the most likely range of chemical characteristics of injected fluid.

Table 6-1   Variations in Chemical Parameters for Injected Fluid

Parameters	Unit	Range
TDS	$mg.kg^{-1}$	1,000—300,000
pH	$mol.kg^{-1}$	2—12.5
EH	mV	-1,000—+1,500
Organic	wt%	0—5 or more
Inorganic	molal	0—30
Heavy metals, e.g., Cd, Cr^{6+}, Hg, Ni, Pb	ppm	0—500

Class I wells are located where deep sedimentary basins exist. Most are concentrated along the Gulf Coast of Texas, Louisiana, Arkansas, and Mississippi and in states overlying the Illinois Basin, i.e., Illinois, Indiana, Ohio, and Michigan (U.S. EPA, 1985). Approximately two-thirds of the wells are located in Texas and Louisiana, which receive 90% of the injected wastes. Injection sites are also concentrated in Texas north of the Oachita uplift and in Oklahoma and Kansas. A relatively small number of wells islocated in California and Florida. Table 6-2 summarizes the range of environmental and reservoir conditions most likely to be encountered in a typical Class I zone.

Water Chemistry. Table 6-2 presents the most likely concentration ranges of major ions in solution.

Lithology. The injection zones of Class I wells are normally arenaceous (sands and sandstones) aquifers, confined by argillaceous (clay and shale) horizons that can be tens to hundreds of feet thick. Occasionally, the injection zone is limestone, a beneficial choice for the disposal of acid wastes provided precautions are taken.

Table 6-2 Chemical Parameter Variation in the Injection Zone Environment

Parameter	Unit	Range
T	°C	20-50
P	bar	50-300
Formation Fluid		
TDS	$mg.kg^{-1}$	10,000-350,000
pH	$mol.kg^{-1}$	5.0-8.5
Eh	mV	0.0-500
Na	$mg.kg^{-1}$	5,000-70,000
K		1-250
Mg		1-2,400
Ca		20-36,000
Al		0.1-1.0
SiO_2		5-50
HCO_3-(alkalinity)		10-6,000
SO_4^{2-}		1-3,000
F^-		?
Cl^-		5,000-150,000
Mineral Assemblage		
Quartz	wt%	30-85
Plagioclase		3-10
K Feldspar		3-10
Carbonate, e.g.,		
Calcite		0-15
Dolomite		0-15
Siderite		0-5
Clays		
Smectites		0-10
Illite		0-10
Chlorite		0-10
Mixed-layer clays		0-10

6.3.2 Specific Environmental Factors

pH/Eh. The pH range in the deep-well environment generally ranges between 5.0 and 8.5, and typical Eh from about 0 to -500 mV. See Table 6-2.

Salinity. The maximum salinity range likely to be found for total dissolved solids (TDS) is from 10,000 to 350,000 mg/kg. See Table 6-2.

Reservoir Matrix. Table 6-2 shows the breakdown of mineral assemblage. In particular, exchange sites on clays, and perhaps zeolites, affect adsorption reactions. Many cations can be readily exchanged on natural clays and zeolites, thereby making them very effective scavengers for certain heavy metals and some organic species. Because smectites, illites, and kaolinite make up a substantial portion of clays in typical sedimentary injection zones, the cation-exchange properties of such clays are of particular interest. Aargaard and Helgeson (1983) used the site-mixing theory (see Section 6.5.2.1) to investigate the assumed ideal mixing of atoms on sites in montmorillonites, illites, and mixed-layer clays.

Kent et al. (1988) classified minerals into four categories that have distinctly different properties when adsorption phenomena are considered:

■ **Simple oxides**, such as silica (SiO_2) or corundum (Al_2O_3), with crystal lattices that are electrically neutral, i.e., they possess no residual charge except on surface sites resulting from the discontinuity caused by the surface itself.

■ **Multiple-surface-site minerals**, such as silicates, aluminosilicates, and complex oxides, which also have no residual charge except on surface sites, but the presence of more than one type of atom in the crystal lattice means that at least two different types of adsorption sites exist at the surface. Among these are feldspars, which commonly occur as detrital or secondary minerals in deep aquifers. For example, potash feldspar, $KAlSi_3O_8$, would expose both SiOH and AlOH surface groups.

■ **Fixed-charge minerals**, which have a permanent negative charge due to the presence of substitutions in the lattice that are compensated by electrostatically bound exchangeable cations. Clays, zeolites, and manganese oxides fall into this category. Clays, with their large surface areas and cation-exchange capacity, are important adsorbents in the deep-well environment, and they are expected to dominate the total adsorption capacity of the injection zone. Zeolites and manganese oxides are normally less important. Deep sedimentary aquifers, unless contaminated by ash-falls, are unlikely to contain zeolites, and manganese oxides are present in minor amounts or have been replaced by manganese-containing carbonates. Both mineral types can be artificially created in an injection zone, however, depending on the composition of the waste stream.

■ **Salt-type minerals**, such as calcite ($CaCO_3$) and gypsum ($CaSO_4.H_2O$), which are formed from ionically bonded anions and cations. Consequently, the surface area of these minerals is arranged in a grid of negatively and positively charged sites corresponding to sections through the ionic lattices of the solid. Carbonates are frequently an important constituent of saline-aquifer host rocks. Therefore, the ion-exchange mechanisms

discussed in Section 6.5.2.3, for example, could be effective in removing heavy metals.

The adsorption properties of organic matter must also be considered because the specific surface area of organic detritus could be quite large and could significantly contribute to the total adsorption capacity of the sedimentary rock contained in the injection zone (Sposito, 1984; Karickhoff, 1984). Kerogen, often a major constituent of shales, can have a wide variety of nitrogen, oxygen, or sulfur (NOS) functional groups attached to its surface, such as $-SO_3H$, $-NH_2$, $-COOH$, $-OH$, as well as saturated hydrocarbons and aromatic rings. NOS functional groups, in particular, can be reactive adsorbents.

Temperature. The maximum temperature range likely to be found in injection zones is 20°C to 150°C. See Table 6-2.

Pressure. The most likely pressure range in injection zones is 50 to 300 bars. Higher pumping pressures required as a result of precipitation reactions caused by waste-reservoir interactions could exceed EPA-mandated limits and lead to hydrofracturing and bypassing of the zone by the injected fluid.

6.4 Geochemical Characteristics and Fate of Hazardous Wastes

6.4.1 Geochemical Characteristics and Fate of Inorganic Hazardous Wastes
The chemical characteristics and fate of inorganic hazardous wastes were not specifically discussed.

6.4.2 Geochemical Characteristics and Fate of Organic Hazardous Wastes
The chemical characteristics and fate of organic hazardous wastes were not specifically discussed.

6.5 Methods and Models for Predicting the Geochemical Fate of Deep-Well-Injected Wastes

6.5.1 Basic Approaches
Geochemical modeling uses information previously acquired through theory, experiment, and testing to predict the geochemical evolution of a system. It must be coordinated with hydrologic modeling, laboratory studies, and field tests, all of which are essential in the no-migration petition process. Most geochemical modeling performed has not been relevant to hazardous-waste injection. Therefore,

whether modeling can convincingly demonstrate how a particular injection scenario will perform is largely unproved.

Geochemical modeling of deep-well injection of hazardous wastes requires an understanding of physicochemical phenomena that have been studied as components of many disciplines, including soil chemistry; clay chemistry and mineralogy; aqueous geochemistry; boiler-water chemistry; hydrometallurgy; the physical chemistry of strong electrolytes; process chemistry; engineering; physical organic chemistry; and environmental chemistry. Scientists are rarely required to integrate so many fields to address a technological problem of such complexity. Each subdiscipline has its own specialized literature, so it is difficult to determine whether even state-of-the-art techniques are sufficiently well developed that practical answers can be found for chemical problems relating to hazardous-waste disposal.

The geochemistry of injected waste is modeled to provide answers to such questions as:

■ What type of compounds and what amount will precipitate or be adsorbed from a solution of a given composition?

■ What will be the saturation concentration of a hazardous constituent after precipitation?

■ What will be the effect of the dissolved constituents of a hazardous waste on the saturation concentration?

■ How will the concentration of a hazardous waste in solution be affected by reactions of the waste stream with ground water or host rocks?

■ Are there unforeseen chemical consequences of injecting a waste stream?

■ How fast will a given substance precipitate or be adsorbed from solution?

A number of computer codes, discussed below, have been developed to try to answer these questions.

6.5.1.1 Geochemical Computer Codes
Existing geochemical modeling codes can often provide answers to the questions listed above if thermodynamic data relating to the participating species and phases are available (see Thermodynamic Data Bases in Section 6.5.1.3). However, no available computer code can solve all the problems of predicting waste migration in subsurface aquifers. For all but extremely simple systems, waste

migration must still be predicted using several techniques, and computer codes only facilitate the calculations.

Computer codes may be used to:

- Reduce and evaluate experimental data.

- Calculate thermodynamic properties of phases or species at temperatures and pressures other than those at standard-state conditions using **equations of state** algorithms (see discussion in this subsection).

- Determine the distribution of species at equilibrium, given the principal extensive and intensive parameters of the systems (distribution codes—see Aqueous and Geochemistry Models, Section 6.5.2.4.

- Predict the evolution of a chemical system, either as a function of the reaction progress (the amount of material reacted) or as a function of time (mass-transfer codes). Such codes do not account for the spatial distribution of reactants to products (see Aqueous and Geochemistry Models, Section 6.5.2.4).

- Predict the chemical evolution of a system in which the chemical reactions and chemical transport proceed simultaneously (chemical-transport codes)—see Transport Models, Section 6.5.2.5.

Equations of State. An equation of state relates the measurable physical and compositional properties of a phase with its thermodynamic properties as a function of parameters such as pressure and temperature. An equation is usually valid only over a specified range of temperatures, pressures, or compositions. Outside this range it may prove seriously defective. The principal equations of state relevant to deep-well injections can be subdivided into four categories:

- Pure and multicomponent solids (see Reservoir Characterization, Section 6.5.2.1).

- Pure and multicomponent fluids (see Waste-Reservoir Interactions, Section 6.5.2.2).

- Component behavior in liquid aqueous systems (see Aqueous and Solution Geochemistry, Section 6.5.2.4).

- Systems involving interfacial phenomena (see Adsorption, Section 6.5.2.3).

Development of Computer Codes. To model geochemical transport, the researcher must create a mathematical model of the physical and chemical environment in which hazardous waste transport occurs. To simulate the behavior of the system in response to various perturbations over time, the system must be represented numerically. This process usually involves writing algorithms representing the evolution of the system over time in coded form as a set of instructions to a computer, which performs the calculations.

Errors can occur at all stages of the modeling and simulations process. To help reduce error:

- The physical and chemical conditions and processes must be correctly identified to create a realistic mathematical model.

- Even if the physical and chemical conditions are correctly identified, they must be represented in the correct mathematical form.

The mathematical model must be represented by algorithms acceptable for digital computation and the correct boundary conditions identified.

- The algorithms must be correctly coded for use by a digital computer.

- In conducting a computer simulation, the correct initial conditions and parameter values must be identified and chosen.

- Laboratory or field data must be correctly measured and/or analyzed.

- A predictive simulation must be made over a time period for which the model assumptions and parameters are valid.

6.5.1.2 Model Verification, Calibration, and Validation

An important aspect of quality assurance in geochemical modeling is the verification, calibration, and validation of computer codes.

Verification. In verification, the code is tested to ensure that it yields a correct or nearly correct answer with specified input data. Models are verified by comparing the numerical with the analytical solutions, by back-calculating a result to ensure that it is consistent with the algorithm and input data used, or by directly comparing the results with the results of another code capable of solving the same problem. In most cases, verifying geochemical codes is relatively straightforward.

Several verification studies of geochemical models have been conducted. In these studies, the output of one code was compared with another and the same problem was

initially proposed for solution. These studies include one by Nordstrom et al. (1979) on 14 distribution-of-species codes, a comparison of EQ3/6 with PHREEQE (Intera Environmental Consultants, 1983), and a study by Kincaid and Morrey (1984). Verification studies involving chemical-transport codes include those by Miller and Benson (1983), Cederberg et al. (1985), and Liu and Narasimhan (1989b).

Calibration. Calibration of transport or chemical-transport codes is performed when some but not all of the parameters used have been assigned correct initial values. Correct values are estimated by comparing the computer simulation with observed field data and then adjusting the unknown parameters until a good fit is obtained. The simulation might be tested against several sets of field data to obtain a range of values for the parameters in question. The calibration process typically is used when certain parameters cannot be measured directly, either in the laboratory or in the field.

Validation. Codes are validated by testing the model on which the code is based. For simple distribution-of-species problems, validation attempts often reveal serious discrepancies between the real and simulated environments. The discrepancies can be traced to three sources: (1) use of an inappropriate model for the problem; (2) errors in the thermodynamic or kinetic data, or other parameter values; or (3) misinterpretation of laboratory or field data.

In many cases, all three types of errors are present but the principal contributor is usually not readily apparent. Thus when undertaking validation studies, the investigator must ensure that the chemical system under scrutiny is completely and unambiguously characterized.

Validation studies using chemical-transport codes have typically been restricted to simple or partial systems in which only qualitative validation was achieved. For example, the results of a simulation correlated well with the gross features of the system's chemical response, but quantitative agreement was lacking or unavailable. The best quantitative agreement between simulation and laboratory or field observation has been demonstrated by Valocchi et al. (1981), Miller and Benson (1983), and Cederberg et al. (1985), all using the same data from the Palo Alto Baylands project. In this study, simple reversible ion-exchange processes on alluvium were assumed, resulting in a good agreement with the response of a sedimentary aquifer to injected fluid of a different composition from the preexisting ground water. Grove and Wood (1979) studied a slightly more complex system involving the dissolution of gypsum as well as ion exchange. The results were compared with data obtained from a laboratory experiment and a shallow test aquifer at Lubbock, Texas; field observations agreed reasonably well.

In general, the work developing and verifying computer codes for geochemical modeling has exceeded validation efforts. Because validation studies are lacking, the reliability of thermodynamic data and the understanding of geochemical processes occurring in the field are questionable. Even if predicted mineral stabilities correlate with those observed, the simulation may still be only a very rough approximation.

Validation of more elaborate geochemical codes, such as those simulating reaction progress, is even less secure. These codes may help calibrate the evolution of a chemical system during advective transport in groundwater systems. Consequently, their use should probably be expanded provided that problems related to thermodynamic data can be resolved. These problems are discussed below.

6.5.1.3 Thermodynamic Data Bases
To model a geochemical problem, researchers must often use experimental data to derive thermodynamic data. Suggested steps are to:

■ Derive reference-state properties of a phase (heat of formation, free energy, entropy, heat capacity, and specific volume) or the corresponding partial molal properties for an aqueous species at the reference 25°C and one atmosphere pressure.

■ Use equations of state to predict the properties at the conditions required for the simulation (see Section 6.5.1.1).

Differences between temperatures and pressures in the injection zone and those in the reference state lead to small but significant changes in the thermodynamic properties of participating species, which for precise work must be corrected.

Thermodynamic data can be retrieved through a variety of techniques:

■ The heat capacity, heat content, and heats of reactions in which the phase or species participates, and the specific volume of a phase or species as a function of temperature and pressure, can be directly measured to derive the values of entropy and heat of formation and their functional dependence on pressure and temperature.

■ The thermodynamic properties of a phase or species can be computed indirectly from phase equilibria, solubility (miscibility), electrochemical or spectrometric data or phase relations and groundwater compositions observed in the field.

Robinson et al. (1982) details these techniques. Often these techniques are combined, resulting in the need to reconcile the results from different sources of information and reach "best value" consensus for a particular thermodynamic parameter. Although best values have been agreed on for a number of minerals and species, they may not be available for those present in the injection zone; in this case, the available data must be critically evaluated to choose a best value.

Because the thermodynamic properties of chemicals are important to industry and the sciences, many compilations have been published over the years:

- JANAF (Joint Army, Navy, and Air Forces) (Chase et al., 1978)

- *Thermal Constants of Compounds* (Glushko, 1965)

- Robie et al. (1978) (restricted to geochemistry)

- Naumov et al. (1971) (restricted to geochemistry)

These compilations refer to original source material, and the published data have been carefully scrutinized. Even so, the information in these sources may have to be reconciled with more recent material or may require an independent reevaluation in response to specialized needs. In particular, recent geochemical studies have focused on statistical and linear programming methods to ensure internal consistency of thermodynamic data sets.

In the following sections, the availability, reliability, and suitability of reference-state thermodynamic data are discussed in relationship to the need to model minerals, aqueous species, adsorbed species, and other phases.

Availability, Reliability, and Suitability of Thermodynamic Data. *Minerals.*

In recent years, internally consistent thermodynamic data for mineral phases have been compiled and evaluated, using information derived both from calorimetric and phase-equilibrium measurements. Some partial or comprehensive compilations include those by Helgeson et al. (1978), Perkins et al. (1979), Hemley et al. (1980), Haas et al. (1981), Robinson et al. (1982), Chatterjee et al. (1984), Halbach and Chatterjee (1982, 1984), Wood and Holloway (1984), Berman et al., (1985) and Berman (1988). These compilations serve to highlight the inconsistencies between the independent sets of experimental data and underline the need to resolve inconsistencies.

The thermodynamic properties of minerals are typically estimated using cycles (Robinson et al., 1982) or paths for constructing internally consistent thermodynamic data sets,

which can be linked to reference phases whose properties have universal acceptance. Helgeson et al. (1978) used the traditional method in which various data sets are compared and judged for correctness and/or quality. The data are refined statistically or subjectively to obtain "best values" for the thermodynamic parameters, usually starting with a reference standard such as corundum or quartz, and progressing from the well established mineral thermodynamic properties to those less well characterized. Using this approach allows the investigator to start from a secure base and concentrate on evaluating specific subsets of experimental data; however, errors may be propagated rather than distributed.

Inconsistencies in earlier thermodynamic-data compilations are beginning to be mitigated. New techniques use internally consistent functions to analyze related thermodynamic parameters and analyze large numbers of data sets simultaneously to find those which are consistent. These techniques include a multiple-regression approach in which functions for molar volume and heat capacity are fitted to the data and appropriate integration constants to compute the associated entropy, enthalpy, and Gibbs free energy (Haas, 1985). This technique was described first by Haas and Fisher (1976) and used by them in several compilations (Haas et al., 1981; Robinson et al., 1982).

A technique suggested by Gordon (1973) and employed by Halbach and Chatterjee (1982, 1984), Chatterjee et al. (1984), Berman et al. (1985), and Berman (1988) uses linear-programming methods, which compare all data sets simultaneously. Haas (1985) lists the relative advantages of the two methods. Regardless of the approach, the investigator must ensure that the maximum number of independent checks are available to verify the selected thermodynamic parameters. Additionally, combinations of data sets in which one or more inconsistencies are detected must be tested to determine why they are present. If inconsistencies are overlooked, these data can become a major source of error.

Data sets typically used to compute the thermodynamic properties of minerals are the currently available calorimetric and phase-equilibrium data. Solubility data, with the exception of those for quartz and such readily soluble salts as the carbonates and sulfates, are typically unavailable. This deficiency is serious because mineral thermodynamic databases are often used extensively to predict mineral solubilities in groundwater systems despite not having been adequately verified through independent tests.

When independent thermodynamic databases such as those developed by Helgeson et al. (1978) and Berman et al. (1985) are compared, major inconsistencies often ap-

pear. The researchers either interpreted the same data in different ways or used different techniques to estimate thermodynamic parameters for minerals when no experimental data were available.

Often the minerals under consideration have been inadequately characterized, usually when researchers interpret laboratory phase-equilibrium studies that exhibit relatively short equilibrium times or that have been performed at relatively low temperatures. In such situations, fine crystallite size, site disorder, metastable polymorphs, or unknown contaminants can drastically affect the perceived equilibrium state without the investigators' being aware. Occasionally, the experimental setup can produce erroneous results—for example, phase-equilibria data obtained using a uniaxial press when a vapor phase participated in the reaction (see Delany and Helgeson [1978] regarding the work of Kennedy [1959]).

Despite these difficulties, increasingly reliable and more comprehensive thermodynamic databases for minerals are becoming available. Thermodynamic data for many mineral phases relevant to host-rock/groundwater interactions, however, remain either poorly determined or totally lacking. Data are particularly scarce for solid solutions such as clays, and satisfactory models to describe the thermodynamics of solid solutions are formative (see Section 6.5.2.1). Furthermore, researchers modeling the thermodynamics of rock-water interactions usually overlook the fact that clays are finely crystalline, and consequently their surface free energy contributes significantly to their thermodynamic stability (Stumm and Morgan, 1970).

Many other detrital minerals and alteration products (feldspars, pyroxenes, amphiboles, zeolites, carbonates, and sulfates) are also solid solutions, and the thermodynamic properties of some of the end members remain in doubt, e.g., anorthite (Chatterjee et al., 1984; Berman, 1988).

Aqueous Species. As with other data bases, thermodynamic databases for aqueous species are either uncritical compilations or contain data that have been selected as best values through critical review. During a critical review, incomplete or questionable data may be augmented, rejected, or accepted using correspondence plots (Criss and Cobble, 1964; Helgeson and Kirkham, 1976; Helgeson et al., 1981; Tanger and Helgeson, 1988; and Shock and Helgeson, 1988, 1989). Data at different temperatures can be reconciled using such techniques as those adopted by Cobble et al. (1982) and Phillips and Silvester (1984) or using more elaborate models such as the HKF equation of state (Tanger and Helgeson, 1988; Shock and Helgeson, 1988).

Many techniques are used both to identify the species and to determine the thermodynamic properties of complexes present in the aqueous phase. Among these are the titration techniques developed by Sillen et al. (1960). The user should be fully aware of the techniques, assumptions, and models used in the critical review. Critically reviewed data should be in the standard state and not in an uncorrected form at the ionic strength of a supporting electrolyte such as a noncomplexing perchlorate.

Despite their lack of review, uncritical compilations, such as by Sillen and Martell (1964), may be very comprehensive and contain a wealth of information. They serve to assess both the level of knowledge regarding a particular complex and the level of agreement among different investigators and are important sources of information on which to base a critical review.

The thermodynamic properties of organic molecules in the aqueous phase are of particular interest when evaluating the injection of hazardous wastes. Calculating such properties usually requires some knowledge of hydration reactions. From solubility studies, the Gibbs free energy of such a reaction can be computed, which, when combined with that of the pure substance in its gaseous, liquid, or solid state, will yield the Gibbs free energy of the molecular species in solution. The thermodynamic properties of hydration have already been compiled (Cabani et al., 1981; Abraham, 1982, 1984). Shock and Helgeson (1989) have recently compiled an extensive listing of thermodynamic properties of aqueous organic species for use with the HKF equation of state and embodied in the SUPCRT code. Literature search and evaluation will be required for species not included in these references; additional sources of solubility or miscibility data for specific organic compounds might be found in the Chemfate data base compiled by Syracuse Research Corporation (1986) or in the Arizona data base compiled by Yalkowsky et al (1987).

Adsorbed Species. The thermodynamics of adsorbed species are limited primarily to reference temperature and pressure values (25°C and 1 atm pressure). Compilations based on the triple-layer model have been summarized (Kent et al., 1988), but as noted in Section 6.5.2.3, most such data pertain only to oxide substrates. Properties are usually given as dissociation constants.

Organic and organometallic species adsorb on clays through a variety of mechanisms (see MacEwan and Wilson, 1984; Laszlo, 1987). A vast body of literature describing adsorption on clays and organophilic substrates exists in uncompiled form. Many studies have been conducted using specially cleaned and characterized clays whose adsorption properties bear little relation to those found in

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situ. Information is available in the form of various adsorption isotherms, exchange constants, and K_d or K_p values (Karickhoff, 1984). This type of information and the procedures for presenting adsorption data in a usable form should be surveyed. Since such a survey is currently unavailable, investigators wishing to model adsorption must do their own literature survey, data evaluation, and derivation of thermodynamic data.

Other Phases. Waste streams may contain substantial concentrations of dissolved salts that do not occur naturally or that exceed naturally occurring concentrations. Thus, unusual phases never observed to occur naturally can possibly precipitate, substantially affecting the evolution of the waste stream in the injection zone and markedly affecting the behavior of coexisting hazardous constituents.

The thermodynamic properties of these unusual phases are not as easily characterized as those covered in the preceding three sections. These phases, as well as those which can develop from other types of interactions, include kerogens, colloids, micelles, organic liquids, amorphous gels, adsorbed surface phases, and slimes of ill-defined composition or structure. Such substances may play a dominant role in mobilizing or containing hazardous-waste constituents through coprecipitation or adsorption. Geochemical models generally fail to account for such materials, except in specialized applications. The computer code RELAX (Weres et al., 1986) is an example of a model designed to determine the partitioning of liquid hydrocarbons between aqueous, oil, and gaseous phases for a specified bulk composition, temperature, and pressure. Additional literature search and calculation of thermodynamic data for such phases may be required.

Calculating Thermodynamic Data. Typically, specialists calculate thermodynamic data by writing computer codes. Furthermore, the sources of thermodynamic data for modeling purposes is so diverse that computer codes must often be used opportunistically rather than systematically. One particular code, SUPCRT, includes the revised HKF equation of state (Tanger and Helgeson, 1988) for computing the partial-molal properties and molecular species and is particularly valuable for extracting thermodynamic properties of solid phases from phase equilibrium and solubility data. Another, PHAS20, is used by the USGS (Haas, 1974; Haas and Fisher, 1976).

Using systematic procedures (see Shock and Helgeson, 1988, 1989), partial-molal properties of ions or molecular species from raw data can be calculated for insertion into the SUPCRT data base. SUPCRT can then be used to calculate the dissolution reaction constants at any specified pressure and temperature from 1 to 5.5 kbar and between 0° and 800°C. Such information is necessary for all distribution-of-species codes using the equilibrium-constant approach (see Section 6.5.2.4). The author recommends using SUPCRT as a tool for computing equilibrium constants whenever temperatures in an injection zone differ significantly from 25°C. In this way, data treatment can be standardized more readily and dissociation constants and solubility products extrapolated to higher temperatures with greater accuracy than by other methods, such as the Criss and Cobble approach (Criss and Cobble, 1964; Cobble et al., 1982). If fluid is injected at temperatures greater than 200°C or if wet combustion in the injection zone is being considered (see Smith and Raptis, 1986),*then use of the modified HKF model and the SUPCRT code is almost mandatory.

6.5.2 Specific Methods and Models

6.5.2.1 Reservoir Characterization
Injection-zone host rocks are composed of a wide variety of heterogeneous components. The most important equation of state for solids is the Gibbs free-energy equation. The phase distribution (minerals) in this system at thermodynamic equilibrium can be predicted provided the thermodynamic properties of the individual phases can be specified. The free energy of a phase at a certain temperature and pressure determines whether it will be stable or unstable. If the free energy is negative, chemical reactions occur spontaneously; if it is positive, energy must be added to the system for changes to occur.

The fundamental properties of the solid phase are (1) the **specific volume**, (2) the **heat capacity** as a function of temperature, and (3) the **heat of formation** (the energy required or given off when a compound is formed from its elements, also called the **enthalpy of formation**). The **entropy** (degree of randomness) of a phase may be computed from low-temperature heat-capacity measurements. If the heat of formation and entropy of a phase are known, the Gibbs free energy can be calculated. (These properties are always calculated at a reference temperature and pres-

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*   Editors's note: The process described by Smith and Raptis (1986) does not involve geochemical interactions with the reservoir rock or fluids. The injected wastewater returns to the surface for additional treatment or disposal when combustion is completed. Consequently, no migration occurs in the injection zone.

sure so that values for different substances can be compared.)

Equations of state incorporating certain model assumptions must be applied to calculate the thermodynamic properties of phases at conditions other than the reference temperature and pressure. Such equations have been developed by Delany and Helgeson (1978), Helgeson et al. (1978), Robinson et al. (1982), Berman et al. (1985), and Berman (1988). Two simplifying assumptions are used to predict entropy, heat of formation, and free energy to pressures and temperatures at or above those necessary for deep-well-injection calculations: (1) the heat capacity of a mineral can be represented by the Maier-Kelley equation (Maier and Kelley, 1932), which describes heat capacity as a function of temperature with the use of three empirical coefficients, and (2) the molal volume of a mineral is independent of pressure and temperature (i.e., compressibility and thermal expansivity are of minor importance).

The thermodynamic properties of many pure minerals have been determined, but natural systems are composed primarily of minerals that are multicomponent solid solutions (i.e., different cations substitute for each other in the crystal lattice structure). Equations of state for these minerals must incorporate the effects of solid solutions.

Wood and Frazer (1977) and Helgeson and Aargaard (1985) reviewed the literature on predicting the behavior of mineral solid solutions. Currently there are two general approaches to such modeling. The first considers that the solid solution is made up of components representing the end members (Bourcier, 1985). The second uses the site-mixing model approach (Helgeson and Aargaard, 1985). In the second approach, individual structural sites in the crystal lattice of a solid solution are considered to be those in which ionic substitution or ordering can occur. Helgeson and Aargaard (1985) derived the general thermodynamic relations for site mixing. Aargaard and Helgeson (1983) used site-mixing theory to investigate the assumed ideal mixing of atoms on sites in montmorillonites, illites, and mixed-layer clays.

6.5.2.2 Waste-Reservoir Interactions
The thermodynamic parameters used to predict reactions among minerals and water for the range of conditions expected in the deep-well environment can be obtained using the computer code SUPCRT (Kirkham et al., 1978).

The aqueous phase possesses a significantly varying heat capacity, thermal expansivity, and compressibility, even beyond the range of temperatures and pressures expected in an injection well. This variability must be accommodated with a carefully calibrated equation of state. One equation

frequently used in geochemical evaluations comes from Keenan et al. (1969). It is well suited to modeling the properties of pure water under injection-well conditions and has been adapted for use with aqueous electrolytes by Helgeson and Kirkham (1974a) in the SUPCRT code.

If a CO_2-rich or organic phase partitions in the subsurface environment, it will be necessary to calculate its stability in relationship to the aqueous phase and the manner in which hazardous constituents partition between the two phases. Unlike solid phases, polar and nonpolar liquids and dense fluids possess significantly varying molal volumes, heat capacities, and derivative properties, i.e., compressibility and thermal expansion as a function of pressure and temperature. Therefore, complex equations of state are sometimes required to describe their thermodynamic properties. Prausnitz (1969) reviewed equations of state to describe the behavior of CO_2-rich phases. For more recent developments, the literature must be reviewed.

An equation of state for an aqueous solution is necessary to establish thermodynamic relations between solid-phase assemblages and the aqueous phase. This might, for example, involve combining an aqueous-electrolyte model (see Section 6.5.2.4, Aqueous and Solution Geochemistry) and a solid-solution model (see Section 6.5.2.1, Reservoir Characterization).

6.5.2.3 Adsorption
In order of increasing sophistication, adsorption of a given species can be measured as follows:

■ The distribution coefficient (K_d) can be measured either in a reaction vessel containing a disaggregated or comminuted (crushed or ground) mass of sorbent in suspension, or by flowing a waste stream through an intact core of porous injection-zone rock under simulated downhole conditions and examining the degree of retardation.

■ Adsorption of a species on injection-zone rock can be measured under simulated subsurface conditions as a function of concentration. Such experiments establish whether reversible adsorption occurs, over what range of concentrations, and whether the adsorption follows a linear (i.e., Langmuir) or logarithmic (i.e., Freundlich) isotherm.

■ For ion exchange, Scrivner et al. (1986) have successfully applied regular solution theory described by Garrels and Christ (1965) with a mixing rule by Hildebrand et al. (1970) to analyze binary and ternary ion-exchange data on illites. When exchange data are available for specific metals or organic compounds of interest, this

approach could be used to predict hazardous waste uptake on clays (and zeolites if present).

- Experimental data can be collected over a wide range of parameter values, and triple-layer or related theory can be used to calculate surface-adsorption constants for the hazardous species adsorbing on a variety of natural substrates.

These approaches range from the naive but practical (measuring the K_d) to the sophisticated but impractical (triple-layer models). The first approach is the one most likely to be used to evaluate the adsorptivity of an injection zone and its ability to retard the transport of hazardous waste constituents. Much research would be needed to characterize the adsorption process in terms of fundamental thermodynamic parameters and would not necessarily be successful in predicting the behavior of a hazardous waste constituent during transport.

Use and Abuse of the Distribution Coefficient K_d. Adsorption of metal ions or organic compounds on soil is well known, and soil scientists have developed an empirical method for quantifying the process using the distribution coefficient, K_d. The term is defined as the distribution of a given species between solution and solid, expressed as a ratio of mass of adsorbent per unit mass of solid.

The inherent weaknesses in using a K_d value to characterize adsorption of a species have long been recognized (Apps et al., 1977). One problem is that the method used to measure it (see Section 6.6.2) is severely limited to the specific conditions under which the test was performed. Any deviation from experimental conditions is very likely to cause changes in the K_d value, sometimes by orders of magnitude. Table 6-3, adapted from Apps et al. (1977), lists some variables that would affect K_d.

A more specific problem with applying K_d measures to underground injection zones is that it is difficult to compare a dispersed solid such as a soil with a coherent rock. Clearly, crushing and grinding the rock will lead to a much larger specific surface area than that present in the injection zone. Furthermore, the newly exposed surfaces will not be representative of injection-zone material, and may adsorb differently from those normally in contact with the ground water. A final problem is that the adsorption experiment may be completed within a few days, whereas the hazardous waste stream may be in contact with the host rock for tens of thousands of years, allowing slower reactions to proceed. These slower reactions may eventually completely dominate any short-term adsorption reactions reflected in the K_d term.

In spite of these problems, K_d measurements are used frequently by hydrologic modelers because of their simplicity. The K_d values can be used to calculate a **retardation** factor, which in turn can be used in a one-dimensional differential equation to describe solute transport (Javandal et al., 1984). By assuming that the conditions postulated in the model are identical to those in the K_d measurement experiment and that the adsorption reaction is locally reversible, the modeler may be able to estimate the degree of retardation expected for a given adsorbent.

The adsorption capacity and potential retardation in the injection zone can be estimated by measuring adsorption of a hazardous constituent in a core from the injection zone under simulated downhole conditions using core-flowthrough experiments. The results will probably be conservative because the test will be of short duration; more long-term processes involving diffusion into micropores or solid-state ion exchange will not be observed. Also, the injected formation will probably be relatively permeable and therefore will contain minor concentrations of such adsorbents as smectites, which are more likely to be found in the adjacent confining zone. If such an experiment is properly designed, a K_d value that can be incorporated into transport models can be calculated.

Langmuir and Freundlich Isotherms. The use of K_d measurements assumes that no complicating factors, such as supersaturation with respect to a solid phase or the complexation of variable degrees of adsorbent in solution, will affect adsorption. If side reactions or extensive mixing and dilution of the waste stream occur in the injection zone, experiments should be conducted over a range of adsorbent concentrations to determine an adsorption isotherm. As with K_d, such measurements may be taken using cores or disaggregated material. The difference is that separate measurements are made at different concentrations (see Section 6.6.2).

The Langmuir and Freundlich equations are both well-accepted representations of adsorption behavior. The Langmuir adsorption isotherm is measured by assuming that the surface of the adsorbing substrate is covered by a monolayer of solvent and adsorbent molecules in competition with each other. This formulation predicts a linear change in adsorption in response to increased concentrations and was applied originally to gas adsorption on a metal surface (Langmuir, 1918). The linear isotherm response is observed widely in the adsorption of trace concentrations of compounds on soils and other heterogeneous substrates (Chiou et al., 1983; Schellenberg et al., 1984). Kincaid and Morrey (1984) show that the Langmuir adsorption equation is valid only at extremely low concentrations of adsorbing solute and at fixed pH. Karickhoff (1984) has developed a

Table 6-3 Factors Influencing K_d for an Adsorbent, Based on Conditions Expected in a Subsurface Injection Zone

Parameters	Principal Effect	Injection-Zone Conditions	Potential Effect on K_d
1a. Major Components	Solution Chemistry Ionic strength Activity coefficients Complexing	Determined by host-rock chemistry and other factors including leaching chemistry of waste product..	Unpredictable— probably 10^{-3} to 10^{+3}
b. Minor Components	Complexing	As above	As above
c. Ph	Complexing Chemical potential	5.0-8.5 Buffering of hetero- and homogeneous equilibria keep pH within narrow limits	10^{-5} to 10^{+5}
d. Eh	Chemical potential	Variable, over a narrower range, usually reducing	Up to 10^{10} or even more
2. Hazardous constituent concentration and speciation	Supersaturation Polymerization Metastable equilibrium	Very variable concentration Could range from 10,000 ppm to 0 near the isoelectric point (-10^6)	Difficult to estimate but could be very large for inorganic amphoteric species
3. Flow rate	Metastable equilbrium transport mechanisms Changes in apparent surface area contacted	10^{-3} to 10^{-7} cm/sec	Slow flow rates could lead to different rate-controlling transport mechanisms, (e.g., ionic or molecular diffusion) and to different thermodynamic controls (0 to 10^6)
4. Permeability	Flow rate (see above)	10^{-3} to 10^{-8} darcys	Same as above
5. Surface Area	Adsorption	$\sim 10^{-2}$ cm^2/g fractures, microfractures intergranular pores	$\sim 10^3$
6. Temperature	Complexing Solubility Adsorption	10° to 150°C	Up to 10^3

simplified approximate linear-adsorption-isotherm equation that is essentially a form of Henry's Law constant. It appears to be valid for natural sediments, as long as the concentration of hydrophobic adsorbent is less than 10^{-5} M, or less than one-half its solubility in water.

The Langmuir adsorption equation inherently assumes that the surface activity coefficients of the adsorbing species are unity, i.e., adsorption behavior is ideal. Experience has shown that the equilibrium constant in the Langmuir equation varies with the fraction of surface occupied, suggesting that this assumption is not valid. Adamson (1982) points out that if this variation is attributed entirely to a variation in the heat of adsorption, then observed adsorbence changes logarithmically.

This logarithmic adsorption isotherm is named after Freundlich (1926), who first used it extensively in many applications. The Freundlich equation has two empirical constants: the intercept and the slope. Because the constant for the slope represents a number of parameters that cannot easily be derived independently, the Freundlich isotherm equation remains a purely empirical formulation, albeit with some theoretical basis. If the adsorption process does not show reversibility, then the implicit assumption that the Freundlich isotherm is an approximation of a thermodynamic process is incorrect and has no theoretical basis. Van Genuchten et al. (1974) suggest that it would be preferable to use kinetic rate equations to describe adsorption (e.g., Lapidus and Amundson, 1952; Lindstrom et al., 1971; Oddson et al., 1970).

Each Freundlich isotherm must be measured keeping all but the adsorbent concentration parameter (pH, Eh, temperature, and solution composition) constant. Kincaid and Morrey (1984) found that the Freundlich isotherm operates over a far wider range of solute concentrations at a given pH than the Langmuir isotherm, and thus the former has been used successfully to measure adsorption of a variety of metal ions on clays as part of the Civilian Radioactive Waste Management Project of the U.S. Department of Energy (1987) and in the adsorption of organic species on clays and soils (Means et al., 1982; Sheindorf et al., 1982).

Triple-Layer Adsorption Models. More complex adsorption models are required to model host-rock or groundwater interaction with the injected waste stream when substantial changes in pH, EH, ionic strength, or ionic concentrations are expected. Unfortunately, complex models require that more parameters be measured and the model conditions defined more rigorously.

One of the most sophisticated model developments for describing adsorption phenomena in aqueous solutions is known as the triple-layer model (TLM). This model describes the surface of a mineral in terms of a site-binding model, developed by Yates et al. (1974), combined with a surface-binding model, by Davis and Leckie (1978). It has been refined, developed, and tested over a number of years by faculty and research staff at Stanford University (Davis and Leckie, 1978, 1980; Kent et al., 1988) and is also referred to as the Stanford General Model for Adsorption (SGMA).

TLM separates the aqueous interface with the adsorbent surface into three layers: surface, inner diffuse, and outer diffuse. Each layer has an associated electrical potential, charge density, capacitance, and dielectric constant. Protons (hydrogen ions) are assumed to bind at the surface plane whereas electrolyte ions 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 surface sites may either react with other ions in solution(s) or dissociate, according to a series of reactions, each reaction being identified with an associated equilibrium constant (Kent et al., 1988). Experimental terms relate the concentrations of the ions at their respective surface planes to those in the bulk solution. The sum of charges in the three layers is assumed to be zero (i.e., the triple layer is electronically neutral).

Of the four groups of minerals discussed in Section 6.3.2 (simple oxides, multiple-surface-site minerals, fixed-charge minerals, and salt-type minerals), simple oxides have been the only group successfully modeled using TLM. Oxide substrates have been studied extensively and their adsorption behavior modeled over a range of environmental conditions. Unfortunately, simple oxide surfaces (represented by one adsorption site) are not the only surfaces a waste stream can encounter in an injection zone, and adsorption capacity due to the presence of simple oxides may represent only a small fraction of the total capacity of the zone.

TLMs representing two or more sites have not yet been developed because data sets adequate to characterize the adsorption properties of aluminosilicates do not exist (Kent et al., 1988). To characterize the surface chemical properties of fixed-charge minerals, both ion-exchange and adsorption reactions must be measured. Although significant achievements have been made in this area, a data base that would allow clay-mineral adsorption to be predicted over a wide range of clay compositions and environmental conditions does not exist. Similar problems apply to zeolite and manganese oxide; further, the latter group is sensitive to the oxidation state of the system.

The surface charge and potential of salt-type minerals are controlled by the relative abundance of the constituent ions

in the associated solution and only indirectly by the pH. Adsorption on salts has not been investigated with any thoroughness, and potential adsorption mechanisms are speculative. Anionic adsorption, as well as cationic or anionic exchange, appears to be possible (Kent et al., 1988). Carbonates are often important constituents of saline-aquifer host rocks. Therefore, cationic adsorption on such minerals could be important in removing heavy metals from the injection zone.

The TLM formulation assumes that adsorbent properties are experimentally characterized as a suspension or slurry in the aqueous phase. However, with varying suspension concentrations, particle interference can take place, which modifies the apparent surface properties of the adsorbent. Still greater effects may be observed in the properties of two adsorbents when mixed. Ideally, the adsorption properties of an aggregate of different adsorbents would be additive, obeying what is called the linear adsorptivity model (LAM). However, experimental studies reported by Honeyman (1984) and unpublished studies conducted by Myer (personal communication) of ORNL reveal that major nonlinear adsorption effects are sometimes observed with mixtures and that LAM may represent the exception rather than the rule.

Any sophisticated adsorption model requires a corresponding electrolyte model that accurately replicates the thermodynamic properties of the solute species. Conventional models using a single parameter extension of the Debye-Huckel equation for individual ion-activity coefficients, as in MINEQL (Westall et al., 1976), are limited to an ionic strength of 0.1 molal for accurate modeling (about 5,800 mg/L for NaCl solutions), or 0.5 molal (about 29,900 mg/L) for less precise interpretations. Any treatment of brines with higher ionic strength would require an entirely different formulation of the adsorption model, using, for example, the Pitzer interaction model (Pitzer, 1973; Pitzer and Kim, 1974).

Any further developments of TLM must be designed such that the solubility product with respect to any solid phase involving the participating components in solution is not exceeded. Researchers can use an appropriate distribution-of-species computer code such as EQ3 (Wolery, 1983) to ensure that the solubility product is not exceeded. However, the effectiveness of the code in identifying super-saturating phases depends on the availability of thermodynamic data for them.

For all its sophistication, TLM is of limited value in demonstrating the containment of hazardous-waste constituents in an injection zone for the following reasons:

■ Site-binding constants have been determined for only a limited range of simple oxides with only one type of surface site.

■ Extensive fundamental studies of common clays and other minerals found in the typical injection-zone host rock would be required. The successful outcome of such studies is uncertain.

■ No satisfactory model has been developed that would permit predictions of adsorption properties of mixtures of adsorbents based on the properties of individual adsorbents.

■ No satisfactory means of measuring and interpreting the adsorptive properties of intact host rock in relation to TLM has been developed.

■ The present TLM is restricted in its application to coexisting electrolytes with ionic strengths much less than unity.

For those situations where none of these problems applies, the SGMA model has been incorporated into several codes, including MINEQL (Westall et al., 1976) and the MINTEQ code, which combines MINEQL with WATEQ (Felmy et al., 1984; Krupka and Morrey, 1985). Otherwise, less-sophisticated models using the Langmuir or Freundlich isotherms, or even the distribution coefficient K_d, would be required.

6.5.2.4 Aqueous and Solution Geochemistry
Two types of codes are used to model aqueous and solution geochemistry: **distribution-of-species** codes, which represent the thermodynamics of a static system, and **reaction-progress codes**, which examine the consequences of an evolving system in which various phases in a system react with one another. Each code uses **equations of state**, which establish the thermodynamic relationships between the solid- and aqueous-phase assemblages. Equations of state are discussed below; discussions of the two types of code follow.

Equations of State. There are a number of approaches for developing equations of state. These approaches can be divided into two basic types: an approach that calculates the partial molal properties of the standard state, and an approach that uses an aqueous electrolyte model. The HKF equation represents the first approach and the Debye-Huckel and its B-dot extension, the Davies equation, and the Pitzer model represent the second.

HKF Equation of State. The HKF equation of state (named after its principal authors, Helgeson, Kirkham, and Flowers, 1981) predicts the standard-state, partial-molal, ther-

modynamic properties of ionic and molecular species in aqueous solution over a range of temperatures and pressures suitable for modeling deep-well conditions. The equation has been under development for 15 years (Helgeson and Kirkham, 1974a,b, 1976; Helgeson et al., 1981), and Tanger and Helgeson (1988) have eliminated some serious deficiencies in earlier versions.

The HKF equation estimates entropy and Gibbs free energy as well as the standard-state properties over a range of pressures and temperatures, provided that (1) the partial-molal volume, the partial-molal heat capacity, and the partial-molal heat of formation of an ionic species at the reference temperature and pressure (298.15°K and 1 bar) are known and (2) a series of model parameters are evaluated for that particular species. Shock and Helgeson (1988) provide guidelines and summarize the values and the model parameters for a large number of common inorganic ionic species at reference temperatures and pressures. Shock and Helgeson (1989) also provide similar data for many water-miscible, low-carbon-number organic species. A modified HKF equation of state is incorporated into a revised version of the SUPCRT code, which is currently undergoing prerelease testing and evaluation. (Documentation for an earlier version is given in Kirkham et al. [1978]).

The HKF equation is highly rated because of its general precision and its versatility for modeling injection-zone conditions. However, simpler equations of state may be used instead. One simplification assumes that the heat capacity of a reaction is constant over the range of pressure and temperature under consideration. This simplification was popularized by Criss and Cobble (1964). In general, assuming constant heat capacity of reaction is a reasonable approximation for extrapolating from 25°C to 200°C provided the total pressure of the system remains less than 300 bars and precise predictions are not required (Cobble et al., 1982).

Aqueous-Electrolyte Models. Aqueous-electrolyte models can be used to relate the measured concentrations of dissolved constituents and waste and reservoir fluids to the thermodynamic properties of the dissolved species using distribution-of-species codes (discussed later). General reviews of the theory and development of these models can be found in textbooks by Lewis and Randall (1961) and Robinson and Stokes (1959) and a paper by Pitzer (1977). Aqueous-electrolyte models provide important means for relating the measured concentrations of dissolved constituents and waste and reservoir fluids to the thermodynamic properties of the dissolved species.

Aqueous-electrolyte models use the concept of the **activity coefficient**, which determines the concentration of a sub-

stance in solution. This coefficient varies depending on the nature and total concentration of dissolved constituents, temperature, and whether the species is charged or neutral. The **Debye-Huckel equation** (Debye and Huckel, 1923; Debye 1923, 1924) can be used to predict the activity coefficient of species in dilute solutions less than 0.1 molal but is too imprecise for solutions with concentrations of dissolved constituents in the molal range, as is typical of most waste streams and saline ground water.

Several methods have been used to extend the range of applicability of the Debye-Huckel equation. Most important are (1) the Debye-Huckel B-dot extension, (2) the Davies equation, and (3) the Pitzer interaction model. Several other extensions of the Debye-Huckel equation have also been formulated to compute activity coefficients in high-ionic-strength, mixed electrolytes. Zemaitis et al. (1986) extensively review and compare various equations for computing the individual ion activity coefficients or mean activity coefficients of salts in single and multicomponent strong electrolytes.

The **B-dot extension** adjusts the Debye-Huckel equation (Guggenheim, 1935; Guggenheim and Turgeon, 1955) using empirical data, and its value has been demonstrated by Pitzer and Brewer in Lewis and Randall (1961). The B-dot parameter is adjustable and normally set so that the activity coefficient best reflects that measured in NaCl solutions. Because NaCl is usually the dominant salt in deep ground waters, this setting is appropriate for many situations. Hazardous waste streams with significant concentrations of dissolved salts other than NaCl, however, would require an empirical adjustment of B-dot for each composition, which is inconvenient. Furthermore, the B-dot extension becomes unreliable at ionic strengths greater than about 0.5 molal, considerably less than the ionic strength of many deep saline aquifers and waste streams. The B-dot extension is used in several distribution-of-species computer codes, e.g., EQ3/6 (Wolery, 1983), PATH (Helgeson et al., 1969), FASTPATH (Schlitt and Jackson (1981), and PHREEQE (Parkhurst et al., 1980).

The **Davies equation** (Davies, 1962) is another empirical extension of the Debye-Huckel equation that gives fairly good estimates to about 0.5 molal. It suffers, however, from the same disadvantages as the B-dot parameter extension. It has been incorporated in the GEOCHEM (Sposito and Mattigod, 1980), MINTEQ (Felmy et al., 1984), MINEQL (Westall et al., 1976), and PHREEQE (Parkhurst et al., 1980) distribution-of-species codes and will be an option for the latest version of EQ3/6.

The **Pitzer interaction model** (Pitzer, 1977) uses a more complex equation that contains several empirical coeffi-

cients for application to a variety of solutions. It also contains three parameters that reflect electrostatic interactions between ions of like and opposing charges specific to each ionic interaction and unchanging with variations in the bulk composition of the electrolyte. Pitzer and Mayorga (1973) have obtained interaction parameters by fitting osmotic coefficients for about 200 electrolytes. To determine interactions among three or more unlike ions, osmotic-coefficient data must be fitted to data on mixed electrolytes with the binary-interaction parameters fixed, resulting in somewhat more complicated expressions for activity coefficients (Pitzer and Kim, 1974).

The Pitzer interaction equations can model multicomponent electrolytes to very high ionic strengths accurately—often to saturation limits. Several studies have validated the Pitzer interaction model by simulating brine-salt equilibria in natural evaporite systems (Eugster et al., 1980; Harvie and Weare, 1980; Harvie et al., 1982, 1984; Felmy and Weare, 1986).

The Pitzer equation has several disadvantages:

■ Data are lacking on the interaction parameters and their temperature dependence for many important electrolytes and minor components.

■ It is premised on electrostatic interactions between ionic species, thereby eliminating the need to account explicitly for ion-pair formation. Consequently, it cannot account for strong, covalently bonded complexation. If covalent bonding of aqueous complexes occurs, some hybrid model must be formulated.

Despite these limitations, the Pitzer interaction model is very promising.

Distribution-of-Species Codes. All equations of state require information on how the concentrations of various elements or constituents measured analytically in solution are distributed among the ionic or molecular species in solution. This information is developed using distribution-of-species codes. These codes also determine which species represent the most stable configuration for the system, i.e., the minimum Gibbs free energy of the system at a given temperature and pressure. Two approaches have evolved: the equilibrium-constant approach and the Gibbs free energy minimization method. As pointed out by Zeleznik and Gordon (1968), the methods have a common origin and their content is the same. Thus, the choice of method becomes one of convenience and traditional use.

Most distribution-of-species codes use the equilibrium-constant approach, primarily because equilibrium constants relating to aqueous species can be determined directly and

are better-known than the underlying thermodynamic properties of the participating species (Nordstrom et al., 1979). Almost all codes employ the equilibrium-constant approach, including:

■ EQUILIB (Shannon et al., 1977; Morrey, 1981; Morrey and Shannon, 1981)

■ EQ3/EQ6 (Wolery, 1983; Wolery et al., 1985)

■ GEOCHEM and REDEQL (Morel and Morgan, 1972; McDuff and Morel, 1978; Sposito and Mattigod, 1980)

■ MINEQL (Westall et al., 1976; James and Parks, 1976)

■ MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985)

■ PHREEQE (Parkhurst et al., 1980; Plummer and Parkhurst, 1985)

■ WATEQ and related codes (Truesdell and Jones, 1973, 1974; Plummer et al., 1976; Ball et al., 1981; Krupka and Jenne, 1982)

When complex multicomponent systems are evaluated, however, several serious disadvantages are apparent:

■ The measured equilibrium constants are rarely measured at a standard temperature and pressure and must always be corrected to standard-state conditions for subsequent modeling purposes.

■ The temperature and pressure at which a system is to be modeled usually differ from the temperature and pressure at which the equilibrium constant was measured. The equilibrium constant must be recalculated either using some equation of state or interpolating between corrected experimental values.

■ The chemical reactions needed to define the equilibrium constants are usually arbitrary and their choice often has no effect on the final results. Therefore, code writers have developed little uniformity in their use. Further, the reactions connote a mechanistic interpretation that often has no basis in reality.

■ Most equilibrium constants, especially those for solid phases, are not obtained by direct measurement. Thus, they must be calculated from Gibbs free-energy-of-specification data after the reaction equation has been specified.

- Because equilibrium constants are usually computed from the Gibbs free-energy data, the equilibrium constants of all reactions in which a species participates must be recalculated whenever the thermodynamic properties of that species change.

- Equilibrium constants must be calculated for a range of pressures and temperatures and stored in a database. The pressure and temperature ranges covered may not be appropriate for the user.

The Gibbs free-energy-minimization approach could be more convenient than the equilibrium-constant method. Once thermodynamic data for a given mineral or aqueous species were stored in a data base, the Gibbs free-energy minimization method could be used to calculate the standard-state Gibbs free energies of the participating species at a given pressure and temperature for entry into a distribution-of-species code. The distribution-of-species code could thereby be made more flexible, and refinements in the thermodynamic properties of participating species could be easily incorporated. Unfortunately, no such method exists, although it appears that one such as this eventually will become available.

The equilibrium-constant method solves a set of nonlinear mass-action equations and linear mass-balance equations and can calculate the charge balance constraint. The mass-action equations for aqueous species and solids are usually written as dissociation or dissolution equations, each breaking down into its "basis" species. These species are usually the simple charged ionic species of an element, such as Na^+, Mg^{+2}, Al^{+3}, Cl^-, or commonly occurring, simple molecular or ionic species such as $SiO_2(aq)$, SO_4-, CO_3-, or NO_3-.

The Debye-Huckel equation, or some empirical or semi-empirical extension, is always used to calculate the activity coefficient of charged species. For neutral species, the activity coefficients are often determined by empirically correlating the activity of carbon dioxide in a solution of corresponding ionic strength. To calculate the activity of water, various equations are used (see, for example, Wolery, 1983, p. 22). Ideally, the Gibbs-Duhem relationship between the solvent and solute species is used, but this is not done often.

For solutions with many components and many species and complexes in solution, the number of linear and nonlinear equations can often exceed 100. The mathematical technique used to solve the set of linear mass-balance and nonlinear mass-action equations incorporates algorithms for calculating the activity coefficient, converts the nonlinear equation to an infinite sequence of linear equations, and then solves the equations iteratively.

Zeleznik and Gordon (1968) and Van Zeggeren and Story (1970) reviewed the various methods for solving these equations. The Newton-Raphson method is most often used in such schemes. Various techniques are used to ensure rapid convergence. Although not essential, the system should be electrically neutral. Chemical analyses always contain some analytical error, usually less than 5% by weight of the total charge. This error can be eliminated by "balancing" on a predominant species in solution, such as Cl^- or Na^+. A species should be chosen such that the addition or subtraction of a small quantity of the balancing element does not significantly affect the thermodynamic properties of the system.

Not all iterative methods will converge for all types of problems. Some codes may hang-up or crash, and problems without solution can be specified. It is helpful if the code writer has incorporated diagnostic statements to identify potential problems. Wolery (1983) has made particular efforts in this direction with the EQ3/6 code.

Most codes require data from a typical chemical analysis (i.e., the concentrations of various elements or species). Other inputs such as alkalinity, pH, Eh, temperature, and solution density may also be required, as well as specification of the aqueous species needed to balance the charge and ensure electrical neutrality. Some codes allow other features: for example, a solution with a particular mineral can be modeled. The partial pressure of a gas phase can be controlled, and the oxidation state can be specified in terms of various redox pairs (e.g., $H_2S(aq)/SO_4-$, $CH_4(aq)/CO_2(aq)$, NH_4+/NO_3-, etc.). The actual codes that allow temperature of the sample to be specified, rather than an approximate temperature, are particularly valuable.

The output of a distribution-of-species computer code can include the distribution of the species (usually listed in order of abundance), specifying the concentrations, activities, and logarithms of activities. The code can also show the relative abundance of species containing a particular element, calculate saturation indices with respect to minerals and gases, or even conduct a mass-transfer calculation to show what and how much material must precipitate to prevent supersaturation in solution. Three codes—the latest version of EQ3/6 (Jackson and Wolery, 1985), TRANSCHEM (Scrivner et al., 1986), and PHREEQE (Crowe and Longstaffe, 1987)—incorporate the Pitzer interaction-parameter electrolyte model, which is required when highly saline waste streams or ground waters are modeled.

The choice of distribution-of-species code depends on its use. The following comparative reviews may be useful in selecting an appropriate code: Nordstrom et al. (1979), Jenne (1981), Kincaid and Morrey (1984), Carnahan

(1987b), and Mangold and Tsang (1987). Intera (1983) assessed computer codes specifically for radioactive-waste containment.

Reaction Progress and Kinetics. Distribution-of-species codes represent a static system, reaction-progress codes a dynamic system. The original concept of reaction progress was developed by deDonder (1920) and deDonder and Van Rysselbeurghe (1936) and subsequently adopted by Helgeson et al. (1969). The essential modeling premise made by Helgeson et al. (1969) is that 1 kg of water and the dissolved species are allowed to react with a defined quantity and number of solid or gaseous phases. Progress of the chemical reaction is monitored as a function of the amount of material that reacts and usually is expressed in terms of gram-moles of the normalized stoichiometry of the reactant assemblage. In its simplest form, the model assumes the following:

■ The aqueous phase is always in internal equilibrium.

■ Product phases are in reversible equilibrium with the aqueous phase.

■ The system is isothermal.

■ The reactant phases always dissolve in proportion to their initial stoichiometric ratios.

These assumptions are reasonable approximations of natural hydrothermal environments where time spans are relatively long and higher temperatures promote rapid equilibration with product or secondary minerals. They break down, however, when applied to problems involving relatively slow reactions such as those which occur during deep-well disposal of hazardous wastes at relatively low temperatures. Such systems are rarely in equilibrium. For example, natural low-temperature systems, such as brines in Gulf Coast sediments, may not be in internal equilibrium even though the brines may be millions of years old (Apps et al., 1988; Shock, 1988). Lindberg and Runnels (1984) have questioned whether redox pairs can predict system EH, since coexisting aqueous redox species are often not in equilibrium and yield different Eh values. These researchers estimate that homogeneous equilibrium with respect to Eh in ground waters may be achieved only after thousands of years. Other investigators (Palciauskas and Domenico, 1976; James and Rubin, 1979) have also questioned whether adsorption or ion-exchange reactions reach local equilibrium. Attempts to model chemical transport systems that assume local equilibrium with respect to adsorption have demonstrated that kinetic factors must play a role (Van Genuchten et al., 1974; Vallette-Silver et al., 1981).

Helgeson et al. (1969) also applied the reaction-progress variable in monitoring geochemical reactions so as to avoid the explicit use of chemical kinetics, because so little is known about the dissolution and precipitation kinetics of minerals in aqueous solution (see discussion of precipitation-dissolution, Section 6.2.2). No unifying method that quantitatively predicts mineral-dissolution kinetics is currently available.

Few computer codes have been written to simulate reaction progress. The best-known and documented are EQ3/6 (Wolery, 1983) and PHREEQE (Parkhurst et al., 1980). Others cited in the literature include SOLVEQ (Reed, 1982) and the now obsolete PATH1 (Helgeson et al., 1969). Several codes such as REDEQL (Morel and Morgan, 1972; McDuff and Morel, 1973) and MINEQL (Westall et al., 1976) contain options for reaction-progress simulations, but these codes are very limited in scope compared with EQ3/6 and PHREEQE.

Two greatly improved codes based on PATH1 principles were written during the 1970s—FASTPATH (Schlitt and Jackson, 1981) and one developed by C. Herick at Los Alamos National Laboratory—but they are now obsolete and not available to the general user. EQ3/6 is currently the most versatile code, and it has quality-assurance documentation (Wolery, 1986), but a revised version of PHREEQE is to be released soon.

The assumptions inherent in computer codes such as PATH1 (Helgeson et al., 1969), EQ3/6 (Wolery, 1983), and PHREEQE (Parkhurst et al., 1980) are generally not valid for predicting the fate of hazardous wastes in the injection zones of deep wells when reaction rates are slow in relationship to groundwater movement (i.e., if local homogeneous or heterogeneous reversibility within about a meter of the point of injection is not attained). If the assumptions implicit in the model are good approximations (i.e., acid or alkaline neutralization or system reduction), reaction-progress codes are convenient and permit powerful simulations of reaction chemistry.

Reaction-progress codes can incorporate the net enthalpy "generated" by the simulated chemical reactions. For simple adiabatic systems, reaction-progress codes could monitor the resulting temperature excursion as a function of reaction progress. This feature may be useful where participating reactions are strongly endothermic or exothermic, as in the case of wet combustion.

Despite their lack of applicability for systems in which reactions are slow compared with groundwater movement, reaction-progress simulations have sometimes provided insights into the processes occurring in natural hydrochemical

systems. Thus Plummer et al. (1983) reconciled the evolution of ground water with the mineralogy of the limestone and dolomite aquifer between Polk City and Wachula, Florida, using the reaction-transport code PHREEQE. Apps et al. (1988) simulated the evolution of Gulf Coast brines using EQ3/6, which was consistent with many but not all field observations. Solomon (1986) has demonstrated that EQ3/6 simulations of the evolution of ground waters in basalts correspond well to observations in the Grande Ronde formation in Washington. Kerrisk (1983) has simulated the evolution of groundwater chemistry and mineral formation at Rainier Mesa, Nevada.

Reaction-progress codes have also been used to interpret laboratory studies (Knauss et al., 1984). Apart from these examples, few other reaction-progress simulations have been rigorously correlated with field or laboratory observations, and to the author's knowledge none has been applied to the analysis of a hazardous-waste plume.

Reaction-progress codes for geochemical simulations are readily modified to incorporate chemical kinetics. Aargaard and Helgeson (1982) use the term **reaction velocity** (the change in material reacted over a specified period of time) to relate reaction progress with the kinetics of the process. The EQ6 code can simulate reaction kinetics (Delany et al., 1986), and can be used to simulate the evolution of systems where several heterogeneous reactions compete (Helgeson amd Murphy, 1983).

6.5.2.5 Transport
Currently, two approaches are available for modeling chemical transport. In the first, 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 (one-step approach). In the second, two linked but separate subroutines are used (two-step approach).

The one-step approach solves for mass, momentum, and energy balances for the fluid at each time step. Then the chemistry is reequilibrated through a distribution-of-species code. This type of approach has been applied for a number of years and includes studies by Lai and Jurinak (1971), Rubin and James (1973), Valocchi et al. (1981), Jennings et al. (1982), Miller and Benson (1983), Noorishad and Carnahan (1985), Carnahan (1986), Noorishad et al. (1987), Willis and Rubin (1987), Merino et al. (1986) and Carnahan (1987a). In most early studies, relatively primitive isothermal systems were investigated. These systems usually involved simple ion-exchange formulations, sometimes including complexation; system pH was assumed constant. Under such conditions, even the ion-activity coefficients changed little and could be ignored without major error.

Many reactions controlling groundwater composition are slow in relation to groundwater movement, and chemical kinetics must be introduced into the transport models. Therefore, the conditions of local reversibility, or instantaneous local equilibrium as assumed in early simulations involving ion exchange or adsorption (e.g., Rubin and James, 1973; Valocchi et al., 1981; Jennings et al., 1982), cannot be used in many realistic simulations. A recent development is the application of CHEMTRANS (Noorishad et al., 1987). This code can simulate in one dimension both homogeneous aqueous-phase and heterogeneous temperature-dependent reaction kinetics. It has been applied to a variety of simple problems involving both reversible and irreversible dissolution, oxidation/reduction, and carbon-isotope fractionation in ground water. If the kinetic and thermodynamic parameters are known for a particular problem, it is relatively easy to modify the code to simulate a problem in which heterogeneous and homogeneous reactions and equilibria play a part. This code is, however, difficult to use and computationally intensive, and has not been tested with complex multicomponent systems.

In addition to the approaches discussed above, the Freundlich isotherm can be substituted into a differential equation to describe solute transport. Often desorption experiments do not indicate that the Freundlich adsorption process is reversible, and it therefore is necessary to incorporate separate expressions for adsorption and desorption in transport equations (e.g., see Van Genuchten et al., 1974). In general, substituting chemical reactions into transport equations results in equations that are very non-linear and difficult to solve numerically, and entail extended execution times.

The second approach appears to have been used first by Grove and Wood (1979) and subsequently adopted by the following researchers:

■   Reardon (1981)

■   Walsh et al. (1982) used a distribution-of-species code developed by Morel and Morgan (1972)

■   Cederberg et al. (1985) incorporated the distribution-of-species code MICROQL (Westall, 1976) into a transport code TRANQL (Cederberg, 1985)

■   Theis et al. (1983); Kirkner et al. (1984, 1985)

■   EPRI (Electric Power Research Institute) combined the transport code SATURN (Huyakorn et al., 1983) with

MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985) to produce FASTCHEM

- Narasimhan et al. (1986) united TRUMP (Edwards, 1972), a three-dimensional-transport model, with PHREEQE (Parkhurst et al., 1980) to produce DYNAMIX. Liu (1988) developed refinements, and the most recent version of DYNAMIX (Liu and Narasimhan, 1989b) can handle the thermodynamics of hydrolysis, aqueous complexation, redox reactions, precipitation-dissolution, and the kinetics of mineral dissolution. It can model systems in three dimensions and accommodate large arrays of both solid and aqueous species. An earlier version successfully modeled the behavior of groundwater contamination from an abandoned uranium-mill-tailings dam (White et al., 1984)

The few cases in which the one-step and two-step approaches have been compared by modeling identical problems indicate that they give comparable results, with the two-step approach requiring less computer time. Cederberg et al. (1985) modeled the one-dimensional Palo Alto Baylands groundwater transport with ion-exchange reactions using TRANQL and compared the results with the earlier one-step analysis by Valocchi et al. (1981). The results were the same but execution times were faster in the two-step analysis. Liu and Narasimhan (1989a) compared DYNAMIX with THCC (Carnahan, 1986), a model similar to CHEMTRNS (Noorishad et al., 1987). In this study, the one-dimensional transport of uranium in the presence of redox reactions was simulated in a hypothetical 3-meter column. Local equilibrium was assumed, and no kinetically controlled reactions were included. The resulting outputs from both simulations were similar.

Which of the two type codes is more useful for modeling transport in underground-injection environments has not been established. If more computationally efficient algorithms are developed to solve a one-step code, the differences in execution times between the two may not be of concern. Although the methods have been shown to yield similar results, the fundamental differences in method may lead to extremely different results for certain problems. For example, a two-step code may have difficulty maintaining mass balance when rapid precipitation and dissolution occur. Drift with respect to the mass balance of elements present in the system can occur when the method uses linearized ordinary differential equations that approximate nonlinear differential equations. Codes should thus be selected for aptness.

6.6 Laboratory Procedures and Protocols

6.6.1 Waste-Reservoir Characterization
Laboratory procedures for waste-reservoir characterization were not specifically discussed.

6.6.2 Static and Flowthrough-Interaction Tests
Static and flowthrough tests are often used to determine the K_d or adsorption isotherms of a substance. The experimental procedure for determining K_d usually involves agitating a suspension of a known particulate mass of soil or other solid in a solution of defined volume and known concentration of adsorbent. After a specified time, the concentration of the adsorbent in solution is measured, and the amount adsorbed is calculated by comparing the initial and final concentrations in the solution. Similar procedures are used for determining Langmuir or Freundlich adsorption isotherms except that experiments are repeated at various concentrations.

Flowthrough tests approximate adsorption characteristics of injection-well reservoirs more closely than batch-type tests. A suitable core material must be selected, however, and the core should be installed in the measuring apparatus such that the injected fluid is not bypassed.

If a flowthrough system is too costly or suitable core material is not available, rock wafers can be used. Using a rock wafer, the researcher allows the hazardous-waste solution to permeate a saturated wafer and measures the concentration of the adsorbent as a function of time. The total surface area exposed may be insufficient to obtain quantitative measurements, however, and the process of shaping or disaggregating the sample will also introduce major uncertainties.

Researchers must characterize very carefully the material under study when performing laboratory studies to support more sophisticated adsorption models, such as the triple-layer model. The specific surface area must be measured, usually by the BET method. The surface-site density and number of site types must also be measured. As with simpler adsorption experiments, the exposed surfaces must be representative of the undisturbed material and should not be disaggregated. The use of undisturbed material can present problems in some cases, however, because it is difficult to conduct adsorption experiments with consolidated materials like sandstone or shale.

Even if the surface area and the density of material can be properly characterized, a lengthy series of experiments would be required to analyze adsorption characteristics completely. To compute the appropriate binding constants, the adsorption capacity of the material must be examined over a wide range of pH, ionic strengths, and coexisting solution compositions, including variations in the total concentration of adsorbates.

6.6.3 Quality-Assurance/Quality-Control Procedures

EPA regulations require a quality-assurance and quality-control plan that covers all aspects of a no-migration demonstration. Only the EQ3/6 code (Wolery, 1986) supports the kind of stringent quality-assurance documentation acceptable to EPA because such documentation is expensive to produce. One benefit of quality-assurance documentation is the traceability of sources of information from which the computer code or its associated thermodynamic database is derived. This traceability facilitates checking the source material and judging the reliability of the package for an application.

If the petitioner must derive original thermodynamic and kinetic data to conduct the simulations for submission to EPA, then all such derivations should be completely documented, and all experimental data should be obtained using analytical methods and procedures acceptable to EPA. All standards should be calibrated and referenced to National Bureau of Standards (NBS) guidelines or other acceptable standards. Deviations from acceptable procedures must be fully documented and include demonstrations that alternative procedures yield results the same as or better than those accepted by EPA.

6.7 Case Studies

No case studies were discussed.

6.8 Further Research Needs

The following areas need to be developed to advance the state of the art of geochemical modeling:

■ Accurate determination of activity coefficients of ions in strong mixed electrolytes (brines).

■ Better data on and understanding of the thermodynamic properties of clays, and thermodynamic data for minerals and organic aqueous species for which none are currently available.

■ An integrated compilation of data in the extensive literature describing the adsorption of inorganic and organic species of clays.

■ Adsorption or ion-exchange models that can be used for the diverse range of conditions expected in deep-well injection.

■ More field validation studies of geochemical codes.

References

Aagaard, P., and H. C. Helgeson. 1982. Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions, I. Theoretical Considerations. *American Journal of Science* 282:237-285.

Aagaard, P., and H. C. Helgeson. 1983. Activity/Composition Relations Among Silicates and Aqueous Solutions, II. Chemical and Thermodynamic Consequences of Ideal Mixing of Atoms Among Energetically Equivalent Sites in Montmorillonites, Illites, and Mixing Layer Clays. *Clays and Clay Minerals* 31:307-317.

Abraham, H. H. 1982. Free Energies, Enthalpies, and Entropies of Solutions of Gaseous Nonpolar Non-electrolytes in Water and Nonaqueous Solvents. The Hydrophobic Effect. *Journal of the American Chemical Society* 104:2085-2094.

Abraham, H. H. 1984. Thermodynamic of Solution of Homologous Series of Solute in Water. *Journal of the Chemical Society, Faraday Society Transactions* 80:153-181.

Adamson, A. W. 1982. *Physical Chemistry of Surfaces*, 4th ed. John Wiley and Sons, New York, 664 pp.

Apps, J., L. Tsao, and O. Weres. 1988. The Chemistry of Waste Fluid Disposal in Deep Injection Wells. Second Berkeley Symposium on Topics in Petroleum Engineering. LBL-24337. Lawrence Berkeley Laboratory, Berkeley, California, pp. 79-82.

Apps, J. A., J. Lucas, A. K. Mathur, and L. Tsao. 1977. *Theoretical and Experimental Evaluation of Waste Transport in Selected Rocks*. 1977 Annual Report of LBL Contract No. H5901AK, Lawrence Berkeley Laboratory LBL-7022, 139 pp.

Apps, J. A., E. L. Madsen, and R. L. Hinkins. 1975. *The Kinetics of Quartz Dissolution and Precipitation*. Annual

Report, Lawrence Berkeley Laboratory, Energy and Environment Division. LBL-5259, pp. 12-15.

Ball, J. W., E. A. Jenne, and M. W. Cantrell. 1981. *WATEQ3—A Geochemical Model with Uranium Added.* U.S. Geological Survey, Open-File Report 81-1183, Menlo Park, California, 84 pp.

Barrer, R. M., and D. M. MacLeod. 1955. Activation of Montmorillonite by Ion Exchange and Sorption Complexes of Tetra-Alkyl Ammonium Montmorillonites. *Faraday Society Transactions* 51:1290-1300.

Berman, R., T. H. Brown, and H. J. Greenwood. 1985. *An Internally Consistent Data-Base of the Thermodynamic Properties of the System $Na_2O-K_2O-CaO-MgO-FeO-F_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$.* Atomic Energy Canada Ltd., Technical Report 377, 62 pp.

Berman, R. G. 1988. Internally-Consistent Thermodynamic Data for Minerals in the System $Na_2O-K_2O-CaO-MgO-FeO-Fe_2O_3-Al_2O_3-SiO_2-TiO_2-H_2O-CO_2$. *Journal of Petrology* 29:445-522.

Berner, R. A., and G. R. Holdren, Jr. 1977. Mechanism of Feldspar Weathering. Some Observational Evidence. *Geology* 5:369-372.

Berner, R. A., and G. R. Holdren, Jr. 1979. Mechanism of Feldspar Weathering. II. Observations of Feldspars from Soils. *Geochimica et Cosmochimica Acta* 43:1173-1186.

Bird, G., and J. Boon. 1984. *Silica Transport During Steam Injection into Oil Sands: I. Dissolution and Precipitation Kinetics of Quartz—New Results and Review of Existing Data.* Oil Sands Research Department, Alberta Research Council, Edmonton, Alberta, Canada. File No. 1545-1-18, 22 pp.

Bird, G., J. Boon, and T. Stone. 1986. Silica Transport During Steam Injection into Oil Sands. Part I, Dissolution and Precipitation Kinetics of Quartz—New Results and Review of Existing Data. *Chemical Geology* 54:69-80.

Bourcier, W. L. 1985. *Improvements in the Solid Solution Modeling Capabilities of the EQ3/6 Geochemical Code.* Lawrence Livermore National Laboratory Report UCID-20587, 8 pp.

Burkin, A. R. 1966. *The Chemistry of Hydrometallurgical Processes.* Van Nostrand, New Jersey, 157 pp.

Burkin, A. R. 1983. Hydrometallurgy, 1952-1982, a Quiet Revolution. *Chemistry and Industry* October 17, pp. 690.

Cabani, S., P. Gianni, V. Mollica, and L. Lepori. 1981. Group Contributions to the Thermodynamic Properties of Non-Ionic Organic Solutes in Dilute Aqueous Solutions. *Journal of Solution Chemistry* 10:563-595.

Carnahan, C. L. 1986. *Simulation of Uranium Transport with Variable Temperature and Oxidation Potential: The Computer Program THCC.* Report 21639, Lawrence Berkeley Laboratory.

Carnahan, C. L. 1987a. Simulation of Chemically Reactive Solute Transport Under Conditions of Changing Temperature. In *Coupled Processes Associated with Nuclear Waste Repositories.* C. F. Tsang, ed. Academic Press, Orlando, Florida, pp. 249-257.

Carnahan, C. L. 1987b. *Effects of Coupled Thermal Hydrological and Chemical Processes on Nuclide Transport.* Paper presented at GEOVAL-87, a symposium on verification and validation of geosphere performance assessment models, Swedish Nuclear Power Inspectorate (SKI), Stockholm, April 7-9, 14 pp.

Cederberg, G. A. 1985. *TRANQL: A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems.* PhD dissertation, Stanford University.

Cederberg, G. A., R. L. Street, and J. O. Leckie. 1985. A Groundwater Mass Transport and Equilibrium Chemistry Model for Multicomponent Systems. *Water Resources Research* 21:1095-1104.

Chase, M. W., J. L. Curnutt, R. A. McDonald, and A. N. Syverud. 1978. JANAF Thermochemical Tables, 1978 Supplement. *Journal of Physical and Chemical Reference Data* 7(3):793-940.

Chatterjee, N. D., W. Johannes, and H. Leistner. 1984. The System $CaO-Al_2O_3-SiO_2-H_2O$: New Phase Equilibria Data, Some Calculated Phase Relations, and Their Petrological Applications. *Mineralogy and Petrology* 88:1-13.

Chiou, C. T., P. E. Porter, and D. W. Schmedding. 1983. Partition Equilibria of Nonionic Organic Compounds Between Soil Organic Matter and Water. *Environmental Science and Technology* 17:227-231

Cobble, J. W., R. C. Murray, P. J. Turner, and K. Chen. 1982. *High-Temperature Thermodynamic Data for Species in Aqueous Solutions.* Electric Power Research Institute Report NP-2400, San Diego State University, San Diego, California, 180 pp.

Criss, C. M., and J. W. Cobble. 1964. The Thermodynamic Properties of High Temperature Aqueous Solutions. V, The Calculation of Ionic Heat Capacities up to 200°C Entropies and Heat Capacities above 200°C. *Journal of the American Chemical Society* 86:5390-5393.

Crowe, A.S., and F.J. Longstaffe. 1987. Extension of Geochemical Modeling Techniques to Brines: Coupling of the Pitzer Equations to PHREEQE. In *Solving Groundwater Problems With Models.* Conference on Solving Groundwater Problems with Models, Denver, Colorado. National Water Well Association, Dublin, Ohio pp. 110-129.

Davies, C. W. 1962. *Ion Association,* Butterworths, London.

Davis, J. A., and J. O. Leckie. 1978. Surface Ionization and Complexation at the Oxide/Water Interface. II, Surface Properties of Amorphous Iron Oxyhydroxide and Adsorption of Metal Ions. *Journal of Colloid and Interface Science* 67:90-107.

Davis, J. A., and J. O. Leckie. 1980. Surface Ionization and Complexation of the Oxide/Water Interface. III, Adsorption of Ions. *Journal of Colloid and Interface Science* 74:32-49.

Debye, P. 1923. Kinetische Theorie der Gesetze des Osmotischen Drucksber Starken Elektolyten. *Physikalische Zeitschrift* 24:334-338.

Debye, P. 1924. Osmotische Zustandsgleichung und Aktivit Verdnnter Starker Electrolyte. *Physikalische Zeitschrift* 25:97-107.

Debye, P., and E. Huckel. 1923. Zur Theorie der Electrolyte. I: Gefrierpunktsernie-drigung und Verwandte Erscheinungen. *Physikalische Zeitschrift* 24:334-338.

deDonder, Th. 1920. *Lecons de Thermodynamique et de Chimie-Physique.* Gauthier-Villars, Paris.

deDonder, Th., and P. Van Rysselberghe. 1936. *The Thermodynamic Theory of Affinity.* Stanford University Press.

Delany, J. M., and H. C. Helgeson. 1978. Calculation of the Thermodynamic Consequences of Dehydration in Subducting Oceanic Crust to 100 kb and 800°C. *American Journal of Science* 278:638-686.

Delany J. M., I. Puigdomenech, and T. J. Wolery. 1986. *Precipitation Kinetics Option for the EQ6 Geochemical Reaction Path Code.* Lawrence Livermore National Laboratory Report UCRL-53642, 44 pp.

Dibble, W.E., Jr., and W. A. Tiller. 1981. Non-Equilibrium Water/Rock Interactions. I, Model for Interface-Controlled Reactions. *Geochimica et Cosmochimica Acta* 45:70-92.

Edwards, A. L. 1972. *TRUMP: A Computer Program for Transient and Steady State Temperature Distributions in Multi-Dimensional Systems.* Rep. 14754, Rev. 3, Lawrence Livermore National Laboratory.

Eugster, H. P., C. E. Harvie, and J. H. Weare. 1980. Mineral Equilibria in a Six-Component Seawater System, Na-K-Mg-Ca-SO4-Cl-H2O, at 25°C. *Geochimica et Cosmochimica Acta* 44:1335-1347.

Felmy, A. R., and J. H. Weare. 1986. The Prediction of Borate Mineral Equilibria in Natural Waters: Application of Searles Lake, California. *Geochimica et Cosmochimica Acta* 50:2771-2783.

Felmy, A. R., D. Girvin, and E. A. Jenne. 1984. *MINTEQ: A Computer Program for Calculating Aqueous Geochemical Equilibria.* EPA Report 600/3-84-032, U.S. Environmental Protection Agency, Washington, DC.

Fleer, V. N. 1982. *The Dissolution Kinetics of Anorthite (CaAl2Si2O8) and Synthetic Strontium Feldspar (SrAl2Si2O8) in Aqueous Solutions at Temperatures Below 100°C: With Applications to the Geological Disposal of Radioactive Nuclear Wastes.* PhD thesis, Pennsylvania State University, University Park, Pennsylvania.

Freundlich, H. 1926. *Colloid and Capillary Chemistry.* E. P. Dutton and Company, New York, 885 p.

Garrels, R. M., and C. L. Christ. 1965. *Solutions, Minerals and Equilibria.* Harper and Row, New York, 450 pp.

Garrels, R. M., and D. F. Howard. 1957. Reactions of Feldspar and Mica with Water at Low Temperature and Pressure. In *Proceedings of the Sixth National Conference on Clays and Clay Minerals.* Pergamon, New York, pp. 68-88.

Glasstone, S., K. J. Laidler, and H. Eyring. 1941. *The Theory of Rate Processes.* McGraw-Hill, New York, 611 pp.

Glushko, V. P. 1965. *Thermal Constants of Compounds: Handbook in Ten Issues.* All-Union Institute of Scientific and Technical Information, Academy of Sciences of the USSR, Moscow.

Gordon, T. M. 1973. Determination of Internally Consistent Thermodynamic Data from Phase Equilibrium Experiments. *Journal of Geology* 81:199-208.

Grove, D. A., and W. W. Wood. 1979. Prediction and Field Verification of Subsurface-Water Quality Changes During Artificial Recharge, Lubbock, Texas. *Ground Water* 17:250-257.

Guggenheim, E. A. 1935. The Specific Thermodynamic Properties of Aqueous Solutions of Strong Electrolytes. *Philosophical Magazine* 19:588-643.

Guggenheim, E. A., and J. C. Turgeon. 1955. Specific Interactions of Ions. *Transactions of the Faraday Society* 51:747-761.

Gutzow, I., and S. Toschev. 1968. Non-Steady State Nucleation in the Formation of Isotropic and Anisotropic Phases. *Kristall and Technik.* 3:485-497.

Haas, J. L., Jr. 1974. *PHAS20, a Program for Simultaneous Multiple Regression of a Mathematical Model to Thermochemical Data.* U.S. Dept. of Commerce, National Technical Information Service, AD-780 301, 162 pp.

Haas, J. L., Sr. 1985. Thermodynamic Properties of Geologic Materials: Status and Future. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment.* U.S. Nuclear Regulatory Commission Report NUREG/CP-0062, pp. 81-84.

Haas, J. L., Jr., and J. R. Fisher. 1976. Simultaneous Evaluation and Correlation of Thermodynamic Data. *American Journal of Science* 276: 525-545.

Haas, J. L., Jr., G. R. Robinson Jr., and B. S. Hemingway. 1981. Thermodynamic Tabulations for Selected Phases in the System $CaO-AL_2O_3-SiO_2-H_2O$ at 101.325 kPa (1 atm) between 273.15 and 1800 K. *Journal of Physical and Chemical Reference Data* 10:575-669.

Halbach, H., and N. D. Chatterjee. 1982. The Use of Linear Parametric Programming for Determining Internally Consistent Thermodynamic Data for Minerals. In *High-Pressure Researches in Geoscience.* W., Schreyer, ed. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, pp. 475-491.

Halbach, H., and N. D. Chatterjee. 1984. An Internally Consistent Set of Thermodynamic Data for Twenty-One $CaO-Al_2O_3-SiO_2-H_2O$ Phases by Linear Parametric Programming. *Contributions to Mineralogy and Petrology* 88:14-23.

Harvie, C. E. and J. H. Weare. 1980. The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-Cl-SO_4-H_2O System from Zero to High Concentration at 25°C. *Geochimica et Cosmochimica Acta* 44:981-997.

Harvie, C. E., H. P. Eugster, and J. H. Weare. 1982. Mineral Equilibria in the Six-Component Seawater System, Na-K-Mg-Ca-SO_4-Cl-H_2O at 25°C. II, Compositions of the Saturated Solutions. *Geochimica et Cosmochimica Acta* 46:1603-1618.

Harvie, C. E., N. Moller, and J. H. Weare. 1984. The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-H-C1-SO_4-OH-HCO_3-CO_3-CO_2-H_2O System to High Ionic Strengths at 25°C. *Geochimica et Cosmochimica Acta* 48:723-751.

Helgeson, H. C. 1974. Chemical Interaction of Feldspar and Aqueous Solutions. In *The Feldspars.* W. S., MacKenzie, and J. Zussman, eds. Crane, Russak and Co. Inc., New York, pp. 184-217.

Helgeson, H. C., and P. Aargaard. 1985. Activity/Composition Relations Among Silicates and Aqueous Solutions. I: Thermodynamics of Intrasite Mixing and Substitutional Order/Disorder in Minerals. *American Journal of Science* 285:769-844.

Helgeson, H. C., J. M. Delany, H. W. Nesbitt, and D. K. Bird. 1978. Summary and Critique of the Thermodynamic Properties of Rock-Forming Minerals. *American Journal of Science* 278-A:1-229.

Helgeson, H. C., and D. H. Kirkham. 1974a. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. I: Summary of the Thermodynamic/Electrostatic Properties of the Solvent. *American Journal of Science* 274:1089-1198.

Helgeson, H. C., and D. H. Kirkham. 1974b. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. II: Debye-Huckel Parameters for Activity Coefficients and Relative Partial Molal Properties. *American Journal of Science* 274:1199-1261.

Helgeson, H. C., and D. H. Kirkham. 1976. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. III: Equation of State for Aqueous Species at Infinite Dilution. *American Journal of Science* 276:97-240.

Helgeson, H. C., D. H. Kirkham, and G. C. Flowers. 1981. Theoretical Prediction of the Thermodynamic Behavior of Aqueous Electrolytes at High Pressures and Temperatures. IV: Calculation of Activity Coefficients, Osmotic Coefficients, and Apparent Molal and Standard and Relative Partial Molal Properties to 600°C and 5 kb. *American Journal of Science* 281:1249-1516.

Helgeson, H. C., R. M. Garrels, and F. T. MacKenzie. 1969. Evaluation of Irreversible Reactions in Geochemical Processes Involving Minerals and Aqueous Solutions. II: Applications. *Geochimica et Cosmochimica Acta* 33:455-481.

Helgeson, H. C., and W. M. Murphy. 1983. Calculation of Mass Transfer Among Minerals and Aqueous Solutions as a Function of Time and Surface Area in Geochemical Processes. I: Computational Approach. *Mathematical Geology* 15:109-130.

Helgeson, H. C., W. M. Murphy, and P. Aagaard. 1984. Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions. II: Rate Constants, Effective Surface Area, and the Hydrolysis of Feldspar. *Geochimica et Cosmochimica Acta*, 48:2405-2432.

Hemley, J. J., J. W. Montoya, J. W. Marinenko, and R. W. Luce. 1980. Equilibria in the System Al_2O_3-SiO_2-H_2O and Some General Implications for Alteration/Mineralization Processes. *Economic Geology* 75:210-228.

Hildebrand, J. H., J. M. Prausnitz, and R. L. Scott. 1970. *Regular and Related Solutions*. Van Nostrand Reinhold Company, New York, 228 pp.

Holdren, G. R., Jr., and R. A. Berner. 1979. Mechanism of Feldspar Weathering. 1: Experimental Studies. *Geochimica et Cosmochimica Acta* 43:1161-1171.

Honeyman, B. E. 1984. *Cation and Anion Adsorption at the Oxide/Solution Interface in Systems Containing Binary Mixtures of Adsorbents: An Investigation of the Concept of Additivity*. PhD dissertation, Civil Engineering Department, Stanford University, Stanford, California, 383 pp.

Huyakorn, P. S., S. D. Thomas, J. W. Mercer, and H. B. Lester. 1983. *SATURN: A Finite Element Model for Simulating Saturated-Unsaturated Flow and Radioactive Transport*. Prepared by GeoTrans for the Electric Power Research Institute, Palo Alto, California.

Intera Environmental Consultants. 1983. *Geochemical Models Suitable for Performance Assessment of Nuclear Waste Storage: Comparison of PHREEQE and EQ3/EQ6*. Report ONWI-473, prepared for Battelle Memorial Institute, Office of Nuclear Waste Isolation, Columbus, Ohio, 114 pp.

Jackson, K. J. and T. J. Wolery. 1985. Extension of the EQ3/6 Computer Codes to Geochemical Modeling of Brines. *Materials Research Society Symposium Proceedings*. Vol. 44, pp. 507-513.

James, R. O. and G. A. Parks. 1976. *Application of the Computer Program MINEQL to Solution of Problems in Surface Chemistry*. Unpublished addendum to Westall et al. (1976), 35 pp.

James, R. V., and J. Rubin. 1979. Applicability of Local Equilibrium Assumption to Transport Through Soils Affected by Ion Exchange. In *Chemical Modeling in Aqueous Systems*, E. A. Jenne, ed. American Chemical Society, Washington, DC, ACS Symposium Series 93, pp. 225-235.

Javandal, I., C. Doughty, and C.-F. Tsang. 1984. *Groundwater Transport: Handbook of Mathematical Models*. Water Resources Monograph Series 10, American Geophysical Union, Washington, DC, 228 pp.

Jenne, E. A. 1981. *Geochemical Modeling: A Review*. PNL-3574, Battelle Pacific Northwest Laboratory, Richland, Washington.

Jennings, A. A., D. J. Kirkner, and T. L. Theis. 1982. Multicomponent Equilibrium Chemistry in Groundwater Quality Models, *Water Resources Research* 18:1089-1096.

Karickhoff, S. W. 1984. Organic Pollutant Sorption in Aquatic Systems. *Journal of Hydraulic Engineering* 110:707-735.

Keenan, J. H., F. G. Keyes, P. G. Hill and J. G. Moore. 1969. *Steam Tables*. Wiley and Sons, New York, 162 pp.

Kennedy, G. C. 1959. Phase Relations in the System Al_2O_3-H_2O at High Temperatures and Pressures. *American Journal of Science* 257:563-573.

Kent, D. B., V. S. Tripathi, N. B. Ball, J. O. Leckie, and M. D. Siegel. 1988. *Surface-Complexation Modeling of Radionuclide Adsorption in Subsurface Environments*. U.S. Nuclear Regulatory Commission Report NUREG/CR-4807, 113 pp.

Kerrisk, J. 1983. *Reaction-Path Calculations of Ground-Water Chemistry and Mineral Formation of Rainier Mesa, Nevada*. Report LANL-9912-MS, Los Alamos National Laboratory, Los Alamos, New Mexico, 41 pp.

Kincaid, C. T. and R. Morrey. 1984. *Geohydrochemical Models for Solute Migration. Volume 2: Preliminary Evaluation of Selected Computer Codes*. Electric Power Research Institute Report EA-3417.

Kirkham, D. H., J. Walther, J. Delany, and G. Flowers. 1978. *SUPCRT. Unpublished Program Descriptions*. Depart-

ment of Geology and Geophysics, University of California, Berkeley, California, 20 pp.

Kirkner, D. J., A. A. Jenning, and T. L. Theis. 1985. Multi-solute Mass Transport with Chemical Interaction Kinetics. *Journal of Hydrology* 76:107-117.

Kirkner, D. J., T. L. Theis, and A. A. Jenning. 1984. Multi-Component Solute Transport with Sorption and Soluble Complexation. *Advances in Water Resources* 7:120-125.

Knauss, K. G., J. M. Delany, W. J. Beiriger, and D. W. Peifer. 1984. Hydrothermal Interaction of the Topopah Spring Tuff with J-13 Water as a Function of Temperature. In *Scientific Basis for Nuclear Waste Management VIII*, C. M. Jantzen, J. A. Stone, and R. C. Ewing, eds. Boston, Massachusetts, November 26-29. Vol. 44, Materials Research Society Symposia Proceedings, pp. 539-546, 1985 (also Report UCRL-90853, Lawrence Livermore National Laboratory, 1984).

Krupka, K. M. and E. A. Jenne. 1982. *WATEQ3 Geochemical Model: Thermodynamic Data for Several Additional Solids.* Report PNL-4276, Pacific Northwest Laboratory, Richland, Washington, 58 pp.

Krupka, K. M., and J. K. Morrey. 1985. MINTEQ Geochemical Reaction Code: Status and Applications. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste*, G. K. Jacobs and S. K. Whatley, eds. NUREG/CP0062, ORNL/TM-9585, pp. 46-53, U.S. Nuclear Regulatory Commission, Washington, DC.

Lai, S., and J. J. Jurinak. 1972. Cation Adsorption in One-Dimensional Flow Through Soils: A Numerical Solution. *Water Resources Research* 8:99-107.

Langmuir, I. 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *Journal of the American Chemical Society* 40:1361-1403.

Lapidus, L., and N. R. Amundson. 1952. Mathematics of Adsorption in Beds. VI: The Effect of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns. *Journal of Physical Chemistry* 56:984-988.

Lasaga, A. C. 1981a. *Dynamic Treatment of Geological Cycles: Global Kinetics.* pp. 69-110.

Lasaga, A. C. 1981b. Rate Laws of Chemical Reactions. *Reviews of Mineralogy* 8:135-169.

Lasaga, A. C. 1981c. Transition State Theory. *Reviews of Mineralogy* 8:135-169.

Lasaga, A. C. 1984. Chemical Kinetics of Water-Rock Interactions. *Journal of Geophysical Research* 89:4009-4025.

Laszlo, P. 1987. Chemical Reactions of Clays. *Science* 235:1473-1477.

Lewis, G. G., and M. Randall. 1961. *Thermodynamics,* 2nd ed. Revised by K.S. Pitzer and L. Brewer. McGraw-Hill, New York, 723 pp.

Lindberg, R. D., and D. D. Runnells. 1984. Ground Water Redox Reactions: An Analysis of Equilibrium State Applied to Eh Measurements and Geochemical Modeling. *Science* 225:925-927.

Lindstrom, F. T., L. Boersma, and D. Stockard. 1971. A Theory on the Mass Transport of Previously Distributed Chemicals in a Water Saturated Sorbing Porous Medium: Isothermal Cases. *Soil Science* 112:291-300.

Liu, C. W. 1988. *Multiple-Species Chemical Transport Involving Oxidation/Reduction Reactions in Geologic Media.* PhD dissertation, Department of Materials Science and Mineral Engineering, University of California, Berkeley.

Liu, C. W., and T. N. Narasimhan. 1989a. Redox-Driven Multiple Species Reactive Chemical Transport in Groundwater Systems. Part 1: Model Development. *Water Resources Research* 25:869-882.

Liu, C. W., and T. N. Narasimhan. 1989b. Redox-Driven Multiple Species Reactive Chemical Transport in Groundwater Systems. Part 2: Verification and Application. *Water Resources Research* 25:883-910.

Mabey, W., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compounds in Water Under Environmental Conditions. *Journal of Physical and Chemical Reference Data* 7(2):383-415.

MacEwan, D. M. C., and M. J. Wilson. 1984. Interlayer and Intercalation Complexes of Clay Minerals. In *Crystal Structures of Clay Minerals and Their X-Ray Identification*, G.W. Brindley and G. Brown, eds. Mineralogical Society Monograph No. 5 Chapter 3, pp. 197-248.

Maier, C. G., and K. K. Kelley. 1932. An Equation for the Representation of High Temperature Heat Content Data. *Journal of the American Chemical Society* 54:3243-3246.

Mangold, D. C., and C.-F. Tsang. 1987. *Summary of Hydrologic and Hydrochemical Models with Potential Application to Deep Underground Injection Performance.* Lawrence Berkeley Laboratory Report, LBL-23497, 54 pp.

McDuff, R. E., and F. M. M. Morel. 1978. *Description and Use of the Chemical Equilibrium Program REDEQL2.* Technical Report EQ-73-02, Keck Laboratory, California Institute of Technology, Pasadena, California.

Means, J. C., S. G. Wood, J. J. Hassett, and W. L. Banwart. 1982. Sorption of Amino- and Carboxy-Substituted Polynucler Aromatic Hydrocarbons of Sediments and Soils. *Environmental Science and Technology* 16:93-98.

Merina, E., C. Moore, P. Ortoleva, and E. Ripley. 1986. Mineral Zoning in Sediment-Hosted Copper-Iron Sulfide Deposits: A Quantitative Kinetic Approach. Special Publications of the Soceity for Geology Applied to Mineral Deposits. pp. 559-571.

Miller, C. W., and L. V. Benson. 1983. Simulation of Solute Transport in a Chemically Reactive Heterogeneous System: Model Development and Application. *Water Resources Research* 19(2):381-391.

Moore, C. H. 1985. Flow/Reaction Models of Natural Systems. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment.* G. K. Jacobs, and S. K. Whatley, eds. Oak Ridge, Tennessee, October 2-5, 1984, NUREG/CP-0062, ORNL/TM-9585, pp. 93-05, U.S. Nuclear Regulatory Commission, Washington, DC.

Morel, F., and J. J. Morgan. 1972. A Numerical Method for Computing Equilibria in Aqueous Chemical Systems. *Environmental Science and Technology* 6:53-67.

Morrey, J. R. 1981. EQUILIB-*A Computer Program to Predict Complex Aqueous Equilibria Between 0°C and 300°C.* Computers in Chemistry Symposium, National A.C.S. Meeting, Atlanta, Georgia, March 29.

Morrey, J. R., and D. W. Shannon. 1981. *Operator's Manual for EQUILIB-A Computer Code for Predicting Mineral Formation in Geothermal Brines. Vol. 1 and 2.* EPRI Project RP 653-1, Final Report.

Murphy, W. M., and H. C. Helgeson. 1984. Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions. III: Activated Complexes and the pH-Dependence of the Rates of Feldspar, Pyroxene, Wollastonite, and Olivine Hydrolysis. *Geochimica et Cosmochimica Acta* 51:3137-3153.

Murphy, W. M., and H. C. Helgeson. 1987. Thermodynamic and Kinetic Constraints on Reaction Rates Among Minerals and Aqueous Solutions. IV: Retrieval of Rate Constants and Activation Parameters for the Hydrolysis of Pyroxene, Wollastonite, Olivine, Andalusite, and Quartz. *Geochemica et Cosmochimica Acta* 51:3137-3153.

Narasimhan, T. N., A. F. White, and T. Takunaga. 1986. Groundwater Contamination from an Inactive Uranium Mill Tailings Pile. 1, Applications of a Dynamic Mixing Model *Water Resources Research* 22(13):1820-1834.

Naumov, G. B., B. N. Ryzhenko, and I. L. Khodakovsky. 1971. *Handbook of Thermodynamic Data.* Moscow, Atomizdat (translated by G. J. Soleimani, U.S. Geological Survey) National Technical Information Service, U.S. Department of Commerce, Springfield, VA.

Noorishad, J., and C. L. Carnahan. 1985. Development of a Kinetic-Equilibrium Chemical Transport Code. *Transactions of the American Geophysical Union* 66:274.

Noorishad, J., C. L. Carnahan, and L. V. Benson. 1987. *A Report on the Development of the Non-Equilibrium Reactive Chemical Transport Code CHMTRNS.* LBL-22361, Lawrence Berkeley Laboratory, Berkeley, California. 229 pp.

Nordstrom, D. K., L. N. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerar, T. M. Florence, B. Fritz, M. Hoffman, G. R. Holdren, Jr., G. M. Lafon, S. V. Mattigod, R. E. McDuff, F. Morel, M. M. Reddy, G. Sposito, and J. Thrailkill. 1979. A Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems. *Chemical Modeling in Aqueous Systems.* Vol. 110, American Chemical Society Advances in Chemistry Series, pp. 857-892.

Oddson, J. K., J. Letey, and L. V. Weeks. 1970. Predicted Distribution of Organic Chemicals in Solution and Adsorbed as a Function of Position and Time for Various Chemical and Soil Properties. *Soil Science Society of America Proceedings* 34:412-417.

Ortoleva, P. 1985. Modeling Water Rock Interactions. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment,* G. K. Jacobs, and S. K. Whatley, eds. Oak Ridge, Tennessee, October 2-5, 1984, NUREG/CP-0062, ORNL/TM-9585, pp. 87-89, U.S. Nuclear Regulatory Commission, Washington, DC.

Palciauskas, V. V., and P. A. Domenico. 1976. Solution Chemistry, Mass Transfer, and the Approach to Chemical

Equilibrium in Porous Carbonate Rocks and Sediments. *Geological Society of America Bulletin* 87: 207-214.

Parkhurst, D. L., D. C. Thorstensen, and L. N. Plummer. 1980. *PHREEQE—A Computer Program for Geochemical Calculation*. U.S. Geological Survey Water Resources Investigation 89-96.

Perkins, D., E. Essene, Jr., E. F. Westrum, and V. Wall. 1979. New Thermodynamic Data for Diaspore and Their Application to the System Al_2O_3-SiO_2-H_2O. *American Mineralogist* 64:(9-10)1080.

Petrovich, R. 1976. Rate Control in Feldspar Dissolution-II. The Protective Effect of Precipitates. *Geochimica et Cosmochimica Acta* 40:1509-1521.

Petrovich, R. 1981a. Kinetics of Dissolution of Mechanically Comminuted Rock-Forming Oxides and Silicates-I. Deformation and Dissolution of Quartz Under Laboratory Conditions. *Geochimica et Cosmochimica Acta* 45:1665-1674.

Petrovich, R. 1981b. Kinetics of Dissolution of Mechanically Comminuted Rock-Forming Oxides and Silicates-II. Deformation and Dissolution of Oxides and Silicates in the Laboratory and at the Earth's Surface. *Geochimica et Cosmochimica Acta* 45:1675-1686.

Petrovich, R. 1986. Mechanisms and Kinetics of Dissolution and Growth of Silica and Silicates in Aqueous Solutions. *Extended Abstracts.* Fifth International Symposium on Water-Rock Interaction, Reykjavik, Iceland, August 8-17, pp. 428-431.

Petrovich, R., R. A. Berner, and M. B. Goldhaber. 1976. Rate Control in Dissolution of Alkali Feldspar. I: Studies of Residual Feldspar Grains by X-Ray Photoelectron Spectroscopy. *Geochimica et Cosmochimica Acta* 40:537-548.

Phillips, S. L., and L. F. Silvester. 1984. A Database for Nuclear Waste Disposal for Temperatures up to 300°C. *High Temperature High Pressures* 16:81-91.

Pitzer, K. S. 1973. Thermodynamics of Electrolytes. I: Theoretical Basis and General Equations. *Journal of Physical Chemistry* 77:268-277.

Pitzer, K. S. 1977. Electrolyte Theory-Improvements Since Debye and Huckel. *Accounts of Chemical Research* 10:371-377.

Pitzer, K. S., and G. Mayorga. 1973. Thermodynamics of Electrolytes. II: Activity and Osmotic Coefficients for Strong Electrolytes with One or Both Ions Univalent. *Journal of Physical Chemistry* 77:2300-2308.

Pitzer, K. S., and J. J. Kim. 1974. Thermodynamics of Electrolytes. IV: Activity and Osmotic Coefficients for Mixed Electrolytes. *Journal of the American Chemical Society* 96:5701-5707.

Plummer, L. N., and T. M. L. Wigley. 1976. The Dissolution of Calcite in CO_2-Saturated Solutions at 25°C and 1 Atmosphere Total Pressure. *Geochimica et Cosmochimica Acta* 40:191-202.

Plummer, L. N., T. M. L. Wigley, and K. L. Parkhurst. 1978. The Kinetics of Calcite Dissolution of CO_2-Water Systems at 5°C to 60°C and 0.0 to 1.0 Atm CO_2. *American Journal of Science* 278:179-216.

Plummer, L. N., and D. L. Parkhurst. 1985. PHREEQE: Status and Applications. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment*, G. K. Jacobs, and S. K. Whatley, eds. Oak Ridge, Tennessee, October 2-5, 1984, NUREG/CP-0062, ORNL/TM-9585, U.S. Nuclear Regulatory Commission, Washington, DC, pp. 37-45.

Plummer, L. N., D. L. Parkhurst, and D. C. Thorstenson. 1983. Development of Reaction Models for Ground Water Systems. *Geochimica et Cosmochimica Acta* 47:665-686.

Plummer, L.N., B. F. Jones, and A. H. Truesdell. 1976. *WATEQF—A Fortran IV Version of WATEQ, a Computer Program for Calculating Chemical Equilibrium of Natural Waters, User's Guide.* PB-261027, National Technical Information Service, Springfield, Virginia.

Rao, P. S. C., and J. M. Davidson. 1980. Estimation of Pesticide Retention and Transformation Parameters Required in Nonpoint Source Pollution Models. In *Environmental Impact of Nonpoint Source Pollution*, M. R. Overcash, and J. M. Davidson, eds. Ann Arbor Science Publishing, Ann Arbor, Michigan, pp. 23-66.

Prausnitz, J. M. 1969. *Molecular Thermodynamics of Fluid-Phase Equilibria*. Prentice-Hall Inc., Englewood Cliffs, New Jersey, 523 pp.

Reardon, E. J. 1981. K_d's—Can They be Used to Describe Reversible Ion Sorption Reactions in Contaminent Migration? *Ground Water* 19(3):279-286.

Reed, M. H. 1982. Calculation of Multicomponent Chemical Equilibria and Reaction Progresses in Systems Involving Minerals, Gases and an Aqueous Phase. *Geochimica et Cosmochimica Acta* 46:513-528.

Rimstidt, J. D., and H. L. Barnes. 1980. The Kinetics of Silica-Water Reactions. *Geochimica et Cosmochimica Acta* 44:1683-1699.

Roberts, P., M. N. Goltz, and D. M. Mackay. 1986. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer. 3, Retardation Estimates and Mass Balance for Organic Solutes. *Water Resources Research* 22(12):2047-2058.

Robie, R. A., B. S. Hemingway, and J. R. Fisher. 1978. *Thermodynamic Properties of Minerals and Related Substances at 198.15°K and 1 bar (10^6 Pascals) Pressure and at Higher Temperatures.* U.S. Geological Survey Bulletin 1452, 456 pp.

Robinson, G. R. Jr., J. L. Haas Jr., C. M. Shafer and H. T. Haselton Jr. 1982. Thermodynamic and Thermophysical Properties of Mineral Components of Basalts. In *Physical Properties Data for Basalt*, L.H. Gevantman, ed. Chapter I, National Bureau of Standards Report NBSIR 82-2587, 425 pp.

Robinson, R. A., and R. H. Stokes. 1959. *Electrolyte Solutions.* Butterworths, London, 571 pp.

Rubin, J., and R. V. James. 1973. Dispersion-Affected Transport of Reacting Solutes in Saturated Porous Media: Galerkin Method Applied to Equilibrium-Controlled Exchange in Unidirectional Steady Water Flow. *Water Resources Research* 9:1332-1356.

Schellenberg, K., C. Leuenberger, and R. P. Schwarzenbach. 1984. Sorption of Chlorinated Phenols by Natural Sediments and Aquifer Materials. *Environmental Science and Technology* 18:652-657.

Schlitt, W. J., and J. S. Jackson. 1981. In Situ Generation of Acid During Dump Leach Production of Copper. *In Situ* 5:103-131.

Scrivner, N. C., K. E. Bennett, R. A. Pease, A. Kopatsis, S. J. Sanders, D. M. Clark, and M. Rafal. 1986. Chemical Fate of Injected Wastes. *Ground Water Monitoring Review* 6(3):53-58.

Shannon, D. W., J. R. Morrey, and R. P. Smith. 1977. Use of a Chemical Equilibrium Computer Code to Analyze Scale Formation and Corrosion in Geothermal Brines. In *International Symposium on Oil Field and Geochemical Chemistry.*

Society of Petroleum Engineers of ASME, San Diego, California, June 27-29.

Sheindorf, C., M. Rebhun, and M. Sheintuck. 1982. Organic Pollutants Adsorption from Multicomponent Systems Modeled by Freundlich Type Isotherm. *Water Research* 16:357-362.

Shock, E. 1988. Organic and Metastability in Sedimentary Basins. Submitted to the *Journal of Geology* 16:886-890.

Shock, E., and H. C. Helgeson. 1989. Calculation of Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures: Correlation Algorithms for Ionic Species and Equation of State Prediction to 5 kb and 1000°C. *Geochemical et Cosmochemica Acta.*

Shock, E. L., and H. C. Helgeson. 1988b. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperature: Standard Partial Molal Properties of Organic Species. Submitted to *Geochimica et Cosmochimica Acta.*

Sillen, L. G. 1960. Aqueous Hydrolytic species. *Proceedings of the Robert H. Welch Foundation Conferences on Chemical Research* 6:187-234.

Sillen, L. G., and A. E. Martell. 1964. *Stability Constants of Metal-Ion Complexes.* Special Publication No. 17, The Chemical Society, London.

Sjoberg, E. L. 1976. A Fundamental Equation for Calcite Dissolution Kinetics, *Geochimica et Cosmochimica Acta* 40:441-447.

Smith, J. M., and T. J. Raptis. 1986. Supercritical Deep Well Wet Oxidation of Liquid Organic Wastes. In *Proceedings of the International Symposium on Subsurface Injection of Liquid Wastes.* National Water Well Association, March 3-5, 1985, Dublin, Ohio, pp. 715-732.

Sohnel, O. 1982. Electrolyte Crystal Aqueous Solution Interfacial Tensions from Crystallization Data. *Journal of Crystal Growth* 57:101-108.

Solomon, C. 1986. *Reaction Path Modeling of Interaction Between Basalt and Groundwater in the Columbia Plateau, Washington.* Presented at Workshop on Geochemical Modeling, Fallen Leaf Lake, California, September 14-17.

Sposito, G. 1984. *The Surface Chemistry of Soils.* Oxford University Press, New York. 234 pp.

Sposito, G., and S. V. Mattigod. 1980. *GEOCHEM: A Computer Program for the Calculation of Chemical Equilibria in Soil Solutions and Other Natural Water Systems.* Kearny Foundation, University of California, Riverside, California.

Stranski, I. N., and D. Totomanow. 1933. Keimbildungsgeschwindigkeit und Ostwaldsche Stifenregel. *Zeitschrift fur Physikalische Chemie A*163:399-408 pp. 399-408. (Complete citation not available).

Stumm, W., and J. J. Morgan. 1970. *Aquatic Chemistry.* Wiley-Interscience, New York, 583 pp.

Syracuse Research Corporation. 1986. *Using Syracuse Research Corporation's Environmental Fate Data Bases DATALOG-CHEMFATE-BIOLOG.* Syracuse Research Corporation, Syracuse, New York, 31 pp.

Tanger, J. C., and H. C. Helgeson. 1988. Calculation of the Thermodynamic and Transport Properties of Aqueous Species at High Pressures and Temperatures. I: Revised Equation of State for the Standard Partial Molal Properties of Ions and Electrolytes. *American Journal of Science,* 288:19-98.

Theis, T. L., D. J. Kirkner, and A. A. Jennings. 1984. *Multi-Solute Subsurface Transport Modeling for Energy Solid Wastes.* Report DOE/ER-0222, 8 pp.

Truesdell, A. H., and B. F. Jones. 1973. *WATEQ—A Computer Program for Calculating Chemical Equilibrium of Natural Waters.* United States Geological Survey. NTIS PB-220-464, 73 pp.

Truesdell, A. H., and B. F. Jones. 1974. WATEQ—A Computer Program for Calculating Chemical Equilibria of Natural Water. *Journal Research of U.S. Geological Survey* 2:233-248.

U.S. Department of Energy, 1987. Geochemical Retardation Processes. In *Geochemistry, Basalt Waste Isolation Project, Site Characterization Plan.* Section 4.1.3, Chapter 40, pp. 4.1-90 to 4.1-137.

U.S. Environmental Protection Agency. 1985. Report to Congress on Injection of Hazardous Waste. EPA 570/9-85-003. Office of Drinking Water, Washington, DC.

U.S. Enviromental Protection Agency. 1987. Underground Injection Control Program; Hazardous Waste Disposal Injection Restrictions; Amendments to Technical Requirements for Class I Hazardous Waste Injection Wells; and Additional Monitoring Requirements Applicable to All Class I

Wells; Proposed Rule, 40 CFR Parts 124, 144, 146, and 148. *Federal Register,* August 27, pp. 32446-32476.

U.S. Enviromental Protection Agency. 1988. Underground Injection Control Program; Hazardous Waste Disposal Injection Restrictions and Requirements for Class I Wells: Part II Final Rule, 40 CFR Parts 124, 144, 146, and 148. *Federal Register,* July 26, pp. 28118-28157.

Valette-Silver, J. N., J. M. Thompson, and J. W. Ball. 1981. Relationship Between Water Chemistry and Sediment Mineralogy in the Cerro Prieto Geothermal Field: A Preliminary Report. In *Proceedings of Third Symposium on the Cerro Prieto Geothermal Field, Baja California, Mexico.* March 24-26, 1981, San Francisco, California, U.S.A. Lawrence Berkeley Laboratory, LBL-11967, p. 263.

Valocchi, A. J., P. V. Roberts, G. A. Parks, and R. L. Street. 1981. Simulation of the Transport of Ion-Exchanging Solutes Using Laboratory-Determined Chemical Parameter Values. *Ground Water* 19:600-607.

Van Genuchten, M. Th., J. M. Davidson, and P. J. Wierenga. 1974. An Evaluation of Kinetic and Equilibrium Equations for the Prediction of Pesticide Movement Through Porous Media. *Soil Science Society of America Proceedings* 38:29-35.

Van Zeggeren, F., and S. H. Storey. 1970. *The Computation of Chemical Equilibria.* Cambridge University Press, 176 pp.

Walsh, M. P., L. W. Lake, and R. S. Schechter. 1982. A Description of Chemical Precipitation Mechanisms and Their Role in Formation Damage During Simulation by Hydrofluoric Acid. *Journal of Petroleum Technology* 34:2097-2112.

Weare, J. H., J. R. Stephens, and H. P. Eugster. 1976. Diffusion Metasomatism and Mineral Reaction Zones: General Principles and Application to Feldspar Alteration. *American Journl of Science* 276:767-816.

Weres, O., C. H. Jun, and L. Tsao. 1986. New Three-Phase Equilibrium Model (Oil/Gas/Brine) Used To Interpret Production of Liquid Hydrocarbons from a Geopressured Gas Well. In *Proceedings of the 56th California Regional Meeting of the Society of Petroleum Engineers.* Oakland, April 2-4, 1986, Paper SPE 15084, pp. 417-422.

Westall, J. C., J. L. Zachary, and F. M. M. Morel. 1976. *MINEQL—A Computer Program for the Calculation of Chemical Equilibrium Compositions of Aqueous Systems.* MIT Technical Note No. 18, 91 pp.

White, A. F., J. M. Delany, T. N. Narasimhan, and A. Smith. 1984. Groundwater Contamination from an Inactive Uranium Mill Tailings Pile. 1, Application of a Chemical Mixing Model. *Water Resources Research* 20:1743-1752.

Willis, C. and J. Rubin. 1987. Transport of Reacting Solutes Subject to a Moving Dissolution Boundary: Numerical Methods and Solutions. *Water Resources Research* 23:1561-1574.

Wolery, T. J. 1983. *EQ3NR. A Computer Program for Geochemical Aqueous Speciation-Solubility Calculations: User's Guide and Documentation.* UCRL-53414, Lawrence Livermore National Laboratory, 191 pp.

Wolery, T. J. 1986. *Requirements for Development and Use of Scientific and Engineering Software (EQ3/6 Task).* Lawrence Livermore National Laboratory Report (draft).

Wolery, T. J., et al. 1985. EQ3/6: Status and Applications. In *Proceedings of the Conference on the Application of Geochemical Models to High-Level Nuclear Waste Repository Assessment*, G. K. Jacobs, and S. K. Whatley, eds., Oak Ridge, Tennessee, October 2-5, 1984, NUREG/CP-0062, ORNL/TM-9585, pp. 54-65, U.S. Nuclear Regulatory Commission, Washington, DC.

Wollast, R. 1967. Kinetics of the Alteration of K-Feldspar in Buffered Solutions at Low Temperature. *Geochimica et Cosmochimica Acta* 31:635-648.

Wood, B. J., and D. G. Frazer. 1977. *Elementary Thermodynamics for Geologists.* Oxford University Press, 303 pp.

Wood, B. J., and J. R. Holloway. 1984. A Thermodynamic Model for Subsolidus Equilibria in the System $CaO-MgO-Al_2O_3-SiO_2$. *Geochimica et Cosmochimica Acta* 48:159-176.

Wood, B. J., and J. V. Walther. 1983. Rates of Hydrothermal Reactions. *Science* 222:413-415.

Yalkowsky, S. H., S. C. Valvani, W. Y. Kuu, and R.-M. Dannenfelser. 1987. *Arizona Database of Aqueous Solubility: An Extensive Compilation of Aqueous Solubility Data for Organic Compounds.* College of Pharmacy, University of Arizona, Tuscon, Arizona.

Yates, D. A., S. Levine, and T. W. Healy. 1974. Site-Building Model of the Electrical Double Layer at the Oxide/Water Interface. *Journal of the Chemical Society, Farady Transactions* 170:1807-1818.

Zeleznik, F. J., and S. Gordon. 1968. Calculation of Complex Chemical Equilibria. *Industrial and Engineering Chemistry* 60:27-57.

Zemaitis, J. F., Jr., D. M. Clark, M. Rafal, and N. C. Scrivner. 1986. *Handbook of Aqueous Electrolyte Thermodynamics: Theory and Application.* Design Institute for Physical Property Data (DIPPR), American Institute of Chemical Engineers, Inc., New York, New York, 852 pp.
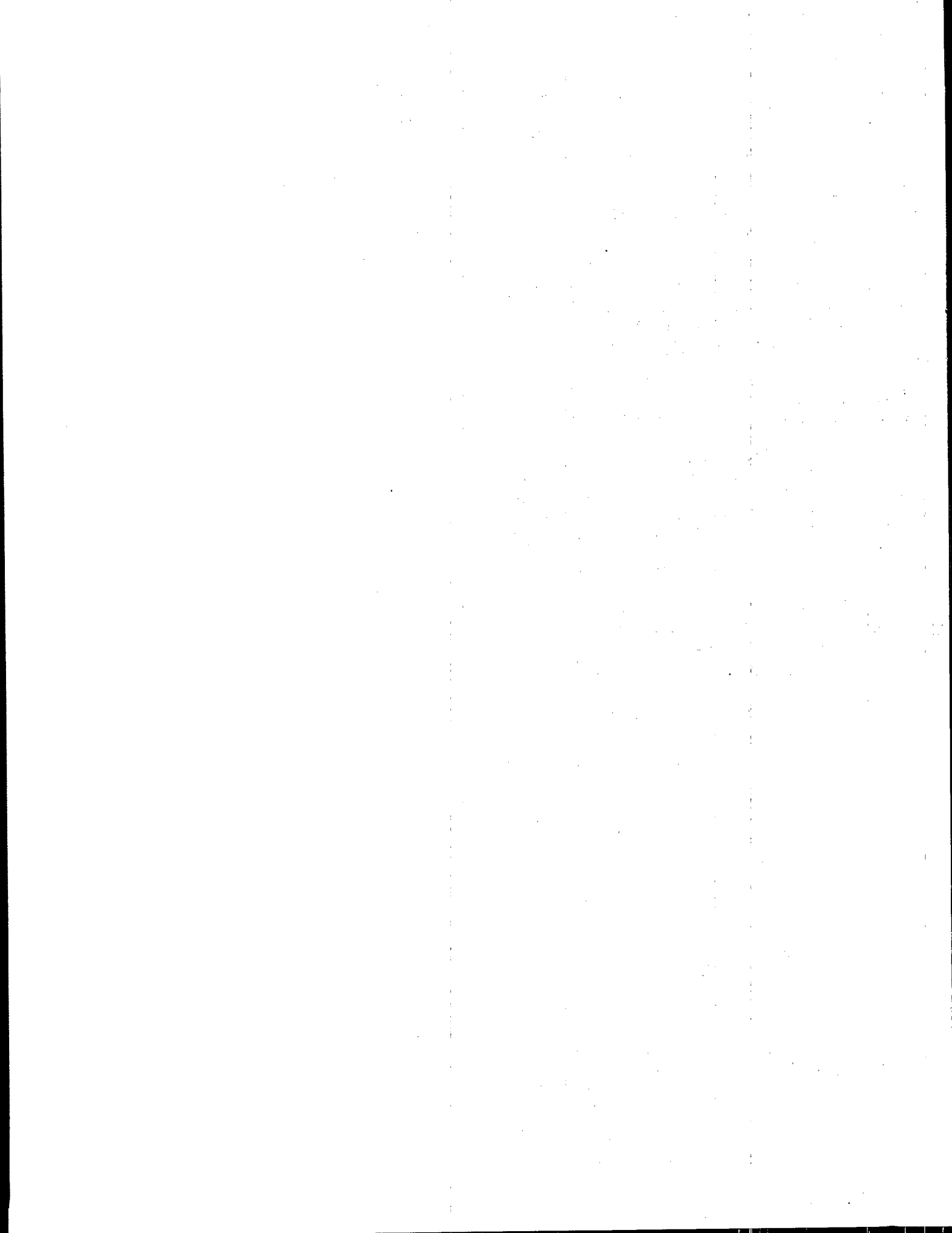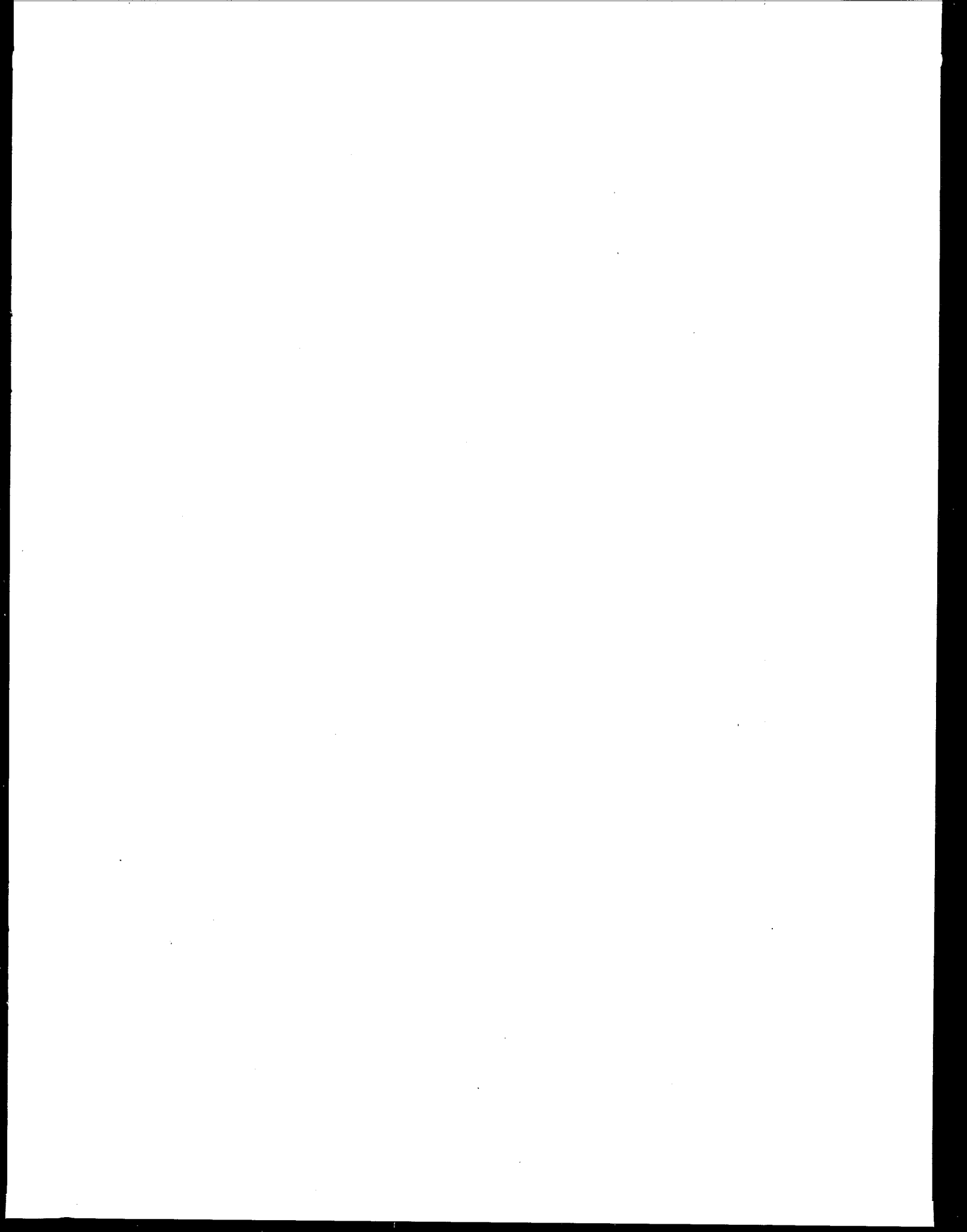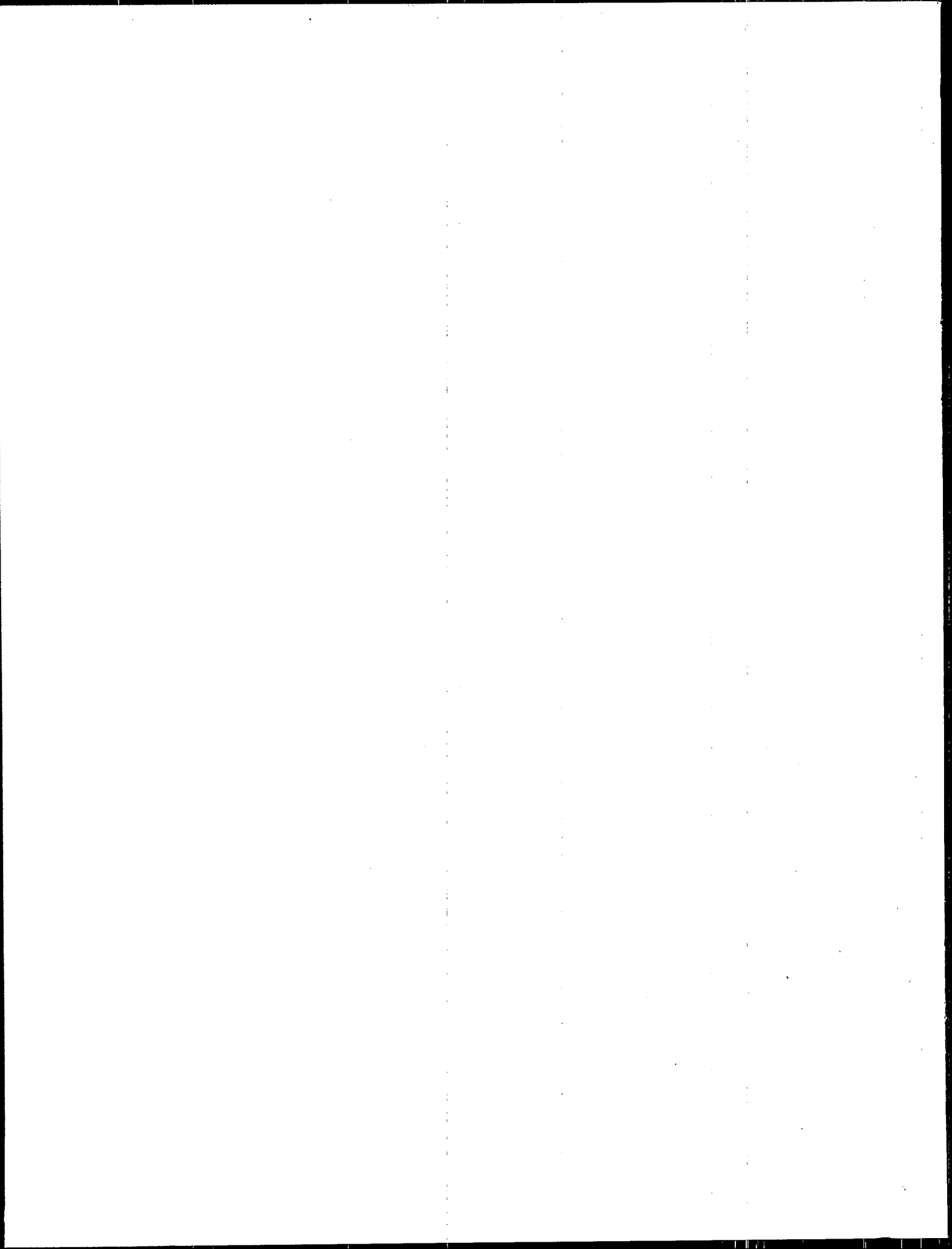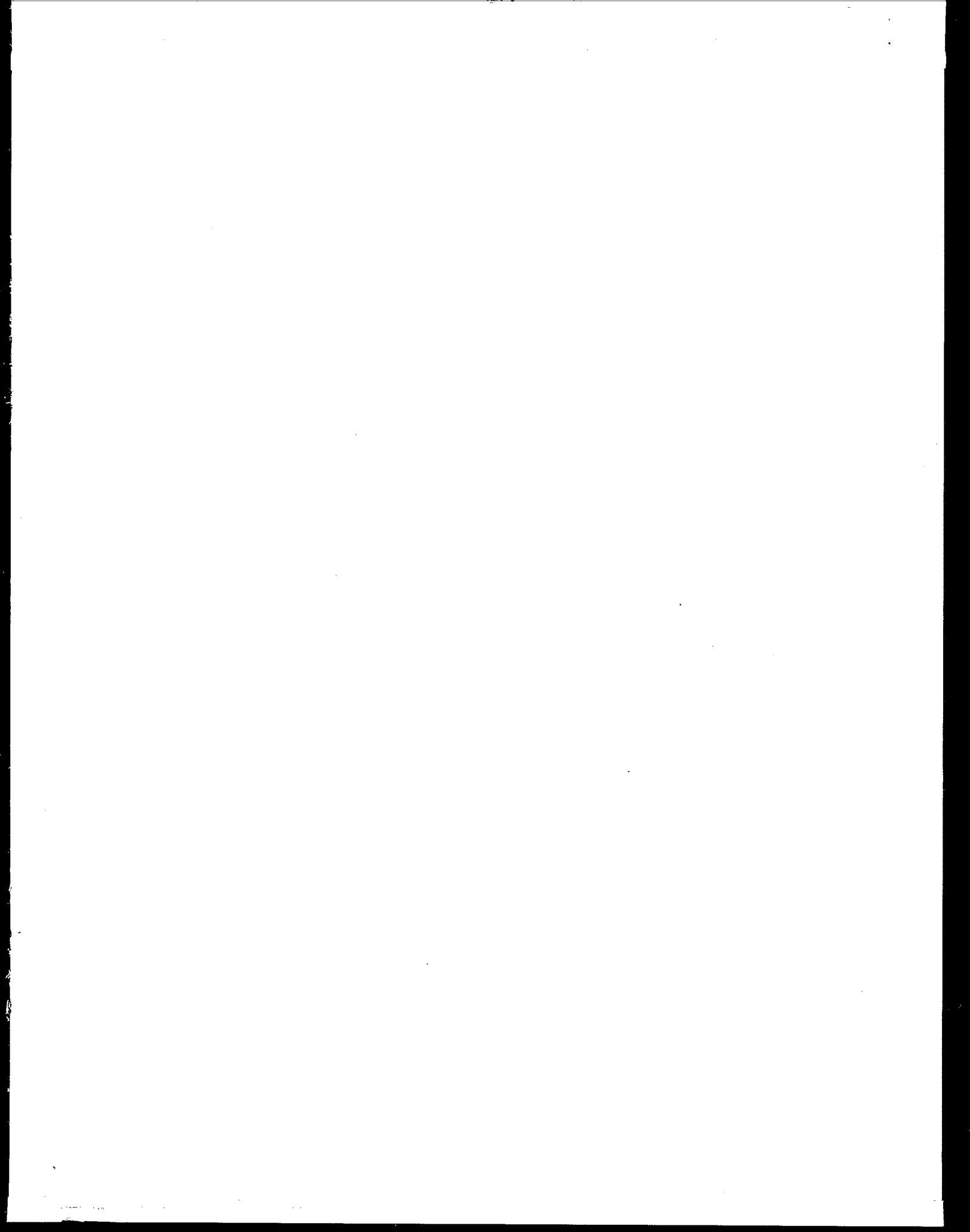
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