LBL-26007
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# Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

## EARTH SCIENCES DIVISION

# Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of Deep Disposal Wells

J.A. Apps

April 1992

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# Current Geochemical Models to Predict the Fate of Hazardous Wastes in the Injection Zones of Deep Disposal Wells

by

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April 20, 1992

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This work was supported by the Underground Injection Control Branch, Office of Drinking Water, U.S. Environmental Protection Agency, through U.S. Department of Energy Contract No. DE-AC03-76SF00098.

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The author welcomes comments, suggestions and recommendations for improving the document in order to make it more useful for interested audiences. He may be reached at 510-486-5193.

## ABSTRACT

On July 26, 1988, the Environmental Protection Agency (EPA) issued amendments to technical requirements for the injection of hazardous wastes in Class C wells. These amendments prohibited the injection of hazardous wastes unless a petitioner could demonstrate that there would be no migration of hazardous constituents from the injection zone of a well for as long as the waste remained hazardous. One means by which this requirement may be met is through the use of geochemical modeling to show that the hazardous waste could be immobilized or converted to innocuous products, or that it could be retarded by adsorption on the rock matrix of the injection zone.

The purpose of the report is to provide a petitioner with background information regarding the current state of the art in chemical theory and modeling capabilities, so that he can use chemical arguments to predict the fate of injected hazardous waste. The report is divided into eight sections: (1) an introduction covering EPA amendments to the technical rules for preparation of a petition and how they relate to geochemical modeling, (2) a discussion regarding what must be modeled in relation to the chemical conditions expected in the injection zone, (3) the thermodynamic models that can be used, (4) the availability of thermodynamic data, (5) modeling of non equilibrium systems, (6) the availability of geochemical modeling computer codes, (7) criteria affecting the satisfactory chemical modeling of waste injection, and (8) conclusions.

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# EXECUTIVE SUMMARY

## Introduction

On July 26, 1988, the Environmental Protection Agency (EPA) issued amendments to the technical requirements for the injection of hazardous waste in Class 1 wells under the Resource Conservation and Recovery Act (40 CFR Parts 124, 1448, 146 and 148). These amendments prohibit the continued disposal of untreated hazardous waste beyond August 5, 1988 in Class 1 wells (and other disposal sites) unless the Administrator determines that prohibition is not required to protect human health and the environment. The prohibition of the injection of hazardous wastes is spelled on in Part 148—Hazardous Waste Injection Restrictions, Subpart B—Prohibitions on Injection.

One way of satisfying this requirement is for an applicant to demonstrate to the Administrator's satisfaction that, to a reasonable degree of certainty, there will be no migration of hazardous constituents from the "injection zone," a legally defined volume of rock surrounding the injection interval in the Class 1 well. The demonstration is submitted as a petition. Regulations governing the form and content of the petition are spelled out in Part 148, Subpart C—Petition Standards and Procedures.

A petitioner can satisfy EPA technical requirements by showing that the hydrogeological and geochemical conditions at the site and the nature of the waste steam are such that it may be reliably predicted that the injected waste will either not migrate out of the injection zone within 10,000 years, or if it does, it will no longer be hazardous. The hazardous constituents can be attenuated through chemical transformation or immobilization. While it is possible to use hydrogeological arguments alone to demonstrate containment of the hazardous waste it is preferable in many cases to provide arguments supporting chemical attenuation or immobilization.

The choice of chemical processes invoked to demonstrate containment depends on the nature of the waste stream, the hazardous constituents, the type and mineralogy of the injection zone rock matrix, and the type of confining beds above the injection zone. Immobilization is achieved through precipitation/coprecipitation, ion exchange or adsorption. Decomposition can occur through neutralization, hydrolysis, oxidation or reduction, the latter two processes sometimes involving bacterial metabolism. Each chemical process requires information, which may or may not be readily available, and therefore it is sometimes necessary to conduct additional laboratory or field studies to acquire the needed information.

## Modeling Requirements

In order to demonstrate containment for periods up to 10,000 years, some form of predictive model is required. When chemical arguments are used, the models must simulate the chemical

thermodynamic or kinetic processes likely to occur in the injection zone while the waste steam is penetrating the rock matrix and mixing with the formation brine. Such modeling presents a serious challenge to the petitioner. Although geochemical modeling has been practiced in various forms for several decades, most has been applied to problems of little immediate relevance to waste injection. Furthermore, the complexity of waste steam chemistry and the demands placed on the petitioner in modeling waste interactions with the formation brine and rock matrix are without precedent. A review of the requirements for geochemical modeling and the availability of suitable geochemical codes is therefore called for.

Class 1 waste wells are most conveniently emplaced in deep sedimentary basins brines containing saline water. Most are located along the Gulf Coast of Texas, Louisiana, Arkansas and Mississippi, and in states overlying the Illinois and Michigan Basins, i.e. Illinois, Indiana, Ohio and Michigan. Two-thirds of the wells are located in Texas and Louisiana, and these receive 90 percent of the injected waste. The injection zones of Class 1 wells are normally arenaceous aquifers confined by argillaceous horizons. A few injection zones are located in limestone. The saline ground waters of injection zones contain between 10,000 and 150,000 $mg.L^{-1}$ of total dissolved solids, the principal solutes being sodium chloride, with smaller concentrations of calcium and magnesium chlorides. The temperatures of the injection zones range from 20–100°C and the pressures range from 50 to 300 bar.

Most deep well injection facilities are operated by the chemical industry of which nearly two thirds of the injected volume originates with the petroleum refining and petrochemical industries, the balance being made up primarily by the metals, minerals and aerospace industries. A survey by Capuano et al. (1989) of Texas waste streams, composing 60 percent ($5.1 \times 10^9$ gallons) of nationwide waste capacity, indicated that between 71 and 87 percent of all hazardous wastes are organic, comprising phenols, organic halogens, nitriles, ketones, aldehydes and carboxylic acids. Substantial amounts of ignitable waste, primarily methyl and butyl alcohol are also injected. Inorganic hazardous waste consists of strong acids, alkalies, cyanide and toxic metal species, particularly nickel.

The most convenient means of demonstrating the fate of the waste in the injection zone is to use a readily available reactive chemical transport simulator, which incorporates all of the needed thermodynamic and kinetic models describing the chemical reactions occurring during advective transport through the subsurface regime. No such dedicated chemical transport simulator is in existence. The petitioner will therefore be obligated to make use of existing computer codes and adapt them to provide partial or complete demonstrations of the fate of various constituents of the waste stream. In this report, the means by which this may be done using currently available software is described. The report is broadly subdivided into sections describing the chemical thermodynamic relations, chemical kinetics, sources of thermodynamic and kinetic data, and the

availability of suitable computer codes. The report concludes with a general section describing various aspects involved in preparing a satisfactory petition in which chemical modeling is used.

**Thermodynamic Models**

All geochemical simulations are concerned with the application of thermodynamic models. Thermodynamic models are systems of equations that relate the thermodynamic properties of phases such as the Gibbs free energy, G, the enthalpy, H, and the entropy, S, to measurable extensive properties such as heat capacity, specific volume and composition, as a function of temperature and pressure. Thermodynamic models may be derived through integration of equations of state, which relate the measurable physical and compositional properties of a phase to intensive parameters such as pressure and temperature.

For convenience, thermodynamic models may be subdivided into four categories,

1. Pure and multicomponent solids
2. Pure and multicomponent fluids
3. Component behavior in liquid aqueous systems
4. Systems modeling interfacial phenomena, e.g., adsorption or bacterial oxidation.

The most commonly used thermodynamic equations in geochemistry are those that permit the calculation of thermodynamic properties of pure solid phases at pressures and temperatures other than the reference conditions of 25°C and 1 bar. The properties usually required are $\Delta H_f^o$ and/or $\Delta G_f^o$ and $S^o$. A number of different forms of relevant thermodynamic equations have been described in the literature, differing primarily in the dependence of the heat capacity, $C_P$, as a function of temperature.

Thermodynamic models for pure solids are reaily available, but those for solid solutions are still evolving. Thermodynamic models for solid solutions have attracted considerable attention in recent years. there are two general approaches to the modeling of the solid solutions. One considers solid solutions to be made up of end member components. The other is the site mixing model, which considers substitutions in a particular site. An alternative to the end member or site mixing approach is the so called polymer model in which a solid solution is considered as being a polymer of its constituent oxides or hydroxides. One such model has been developed by Sposito (1986) to predict the thermochemical properties of clays, and may find application in modeling exchange reactions in clays in the injection zone and confining beds.

The thermodynamic properties of single component fluids and fluid mixtures can be derived from equations of state for single or multicomponent phases respectively. Most such equations of

state are based on models by Redlich and Kwong (1949), Benedict, Webb and Rubin (Benedict et al., 1940) or the corresponding state equations by Lee and Kessler (1975). All use parameters that must be fitted to experimental data, and are usually limited to the maximum P and T ranges of the data. When describing the thermodynamic properties of mixtures, all also require complex mixing rules. Equations of state describing systems containing components, such as $H_2O - CO_2 - CH_4$, are becoming available over the range of concentrations, pressures and temperatures of interest in predictions of deep well injection behaviour. The equation of state for liquid water, which is most commonly used in geochemical modeling, is that developed by Haar et al. (1984). It is also suitable for modeling deep well injection problems.

The development of thermodynamic models to describe the properties of aqueous electrolytes has a long history. These models are of great importance to petitioners, as most relevant chemical reactions take place in aqueous electrolytes such as the waste stream, the formation brine, or mixtures of the two. The difficulty encountered with modeling the properties of components in aqueous electrolytes is the fact that they behave non ideally and require special equation, often with limited ranges of applicability to describe the non ideal behavior. Most model applications in geochemistry use various forms of the Debye-Hückel equation, but are limited in their range of applicability to less than 0.5 $m$. During the last 20 years, equations due to Pitzer, referred to as the Pitzer interaction model, have been finding increasing application, and are particularly useful in modeling strong formation brines of the type encountered in injection zones. The Pitzer interaction model is currently limited, however, by the lack of information on temperature dependent parameters of many electrolytes of interest.

Adsorption is a phenomenon whereby molecular or ionic species attach to the surface of a solid. The process is thermodynamically reversible in principle and therefore the laws of thermodynamics can be applied. Adsorption is one of the principal processes by which many hazardous aqueous species, either organic or inorganic are immobilized, or at least retarded during transport in the injection zone.

The most commonly used parameter to describe adsorption is the linear isotherm, whose slope is defined by the sorption partition coefficient, $K_d$. Such coefficients are particularly applicable to hydrophobic organic components of low solubility, i.e. $\leq 10^{-5} M$ when the concentration is equal to or less than half the saturation concentration. Various means are available for measuring $K_d$, both directly or indirectly. Methods have also been developed for calculating $K_d$ from a theoretical knowledge of the structure of the organic compound.

Other isotherms such as those due to Langmuir and Freundlich have been applied to the aqueous phase adsorption problems. The Langmuir isotherm has very restricted use in systems involving the aqueous phase, but the Freundlich isotherm, although semi-empirical in concept is applicable over a wider range of concentration than the simple linear isotherm.

Adsorption isotherms may be readily incorporated in equations to describe solute transport. Hence, they are preferred over more complex adsorption models, such as those accounting for adsorption on specific sites of mineral surfaces in the presence of the electrical double layer. Otherwise known as surface complexation or site binding models, these models represent the state of the art in describing adsorption thermodynamics. A representative of the class is the triple layer model (TLM), so named for the three surface layers through which the surface electric charge is distributed. For this model, surface sites on a given mineral complex with ions or molecules in solution and their thermodynamic properties are described by equilibrium constants. Although the TLM permits a more accurate representation of competitive adsorption among inorganic sorbents, it is presently of limited practical value to petitioners, as the required thermodynamic data for injection zone conditions in inadequate.

**Thermodynamic Data Bases**

A requirement for any geochemical modeling is carefully compiled internally consistent thermodynamic data. Numerous thermodynamic data bases are available for minerals, organic compounds and aqueous inorganic and organic species. Data is also available on the properties of absorbed species including linear isotherm partition coefficients ($K_d$), octanol-water coefficients, ion exchange constants on clays and surface complexation constants. Care should be exercised in using thermodynamic data compilations to ensure that the data is internally consistent and can be traced to the original source references.

The petitioner may find that insufficient data is available to meet his needs. He will therefore be obligated to cull the literature or conduct experiments to obtain the necessary information. Sometimes it is possible to calculate the thermodynamic properties of phases or aqueous species using various published correlation equations.

**Non Equilibrium Systems**

From the perspective of EPA regulations, chemical reactions involving the waste, ground water and injection zone rock matrix may be divided into three categories: (1) those that occur sufficiently rapidly that the reaction goes to completion and local reversible equilibration in the injection zone may be assumed, (2) that those that require substantially longer than 10,000 years to go to completion and hence it may be assumed that the reaction does not take place in the injection zone, and, (3) those where reaction rates fall between the two extremes and require kinetic information to determine the fate of hazardous constituents in the injection zone. For first order reactions, this translates into a range of specific rate constants falling between $10^{-11}$ and $10^{-6}\ s^{-1}$.

Chemical reactions can be subdivided into heterogeneous and homogeneous reactions. Information in heterogeneous reaction kinetics involving the precipitation or dissolution of rock

forming minerals is relatively sparse, and no methods are currently available to permit their prediction. Interest in mineral reactions is generally limited to neutralization reactions involving acids or alkalies. Under these circumstances, primary interest lies in reactions with carbonates or clays.

A special class of heterogeneous reaction concerns bacterial catalysis. Bacteria that decompose otherwise refractory hazardous constituents, might be usefully employed in the injection zone environment. Although the bacterial destruction of hazardous wastes has not been deliberately used in the injection zones of disposal wells, bacterial decomposition of waste has been observed in the injection zone of at least one disposal well. Because the deep well injection zone environment is usually strongly reducing, very saline, relatively hot and at a pressure many times that of the atmosphere, it would probably be best to use pre-existing bacteria for the purpose intended rather than attempt to adapt foreign strains. A reactive biofilm model, based on a substrate utilization model by Monod (1949), has been developed to describe bacterial consumption of hazardous metabolites and cometabolites. This model, combined with laboratory experimental studies might be used to engineer *in situ* bioreactors surrounding an injection zone.

Many hazardous organic constituents decompose homogeneously through hydrolysis reactions. Compilations of hydrolysis rate constants are available in the literature. According to Mill (1990), rate constants for many hydrolysis reactions can be predicted from structure activity relationships.

**Computer Codes**

The computer code permits the convenient solution of problems using various thermodynamic, kinetic or transport models. For the purpose of modeling the fate of hazardous waste in the subsurface environment, computer codes may be divided into five categories, i.e., those that:

- Reduce and evaluate experimental data in order to obtain thermodynamic or kinetic data.
- Calculate the thermodynamic properties of phases or species at temperatures and pressures other than at standard state conditions, (thermodynamic models).
- Determine the distribution of species at equilibrium, given the principal extensive and intensive parameters in the system, (distribution codes).
- Predict the evolution of a chemical system, either as a function of reaction progress, i.e. the amount of material reacted, or as a function of time, (mass transfer or reaction progress codes). Such codes do not account for the spatial distribution of reactants or products.
- Predict the chemical evolution of a system in which both chemical reactions and transport proceed simultaneously, (reactive chemical transport codes).

Computer codes are available in all five categories, although not all are necessarily suitable for

the preparation of petitions. A variety of distribution of species codes are available for the petitioner, many of which are in the public domain. The petitioner should make his selection of disribution of species code on the basis of its suitability for the problem at hand. Not all of these codes have data bases that are internally consistent, or adequate to model the typical waste stream. Reaction progress codes, while limited in availability may be particularly useful for predicting the long term fate of waste streams. The availability of reactive chemical transport codes, which are suitable for modeling waste transport in the injection zone is limited, and petitioners might be hampered in their ability to conduct comprehensive simulations. The latest versions of many computer codes may be obtained by contacting the authors of the cited references. A few computer codes are proprietary and might require a user fee before they may be used.

**Chemical Modeling**

Several steps are needed to conduct geochemical simulations of the fate of hazardous constituents in the subsurface environment. The first step involves the aquisition of basic information, such as the composition of the waste stream, ground water composition, mineralogy and chemical composition of the rock matrix and hydrologic parameters of the injection zone and confining zones. The second step involves identification of chemical interactions that determine the fate of the hazardous wastes, either by decomposition or immobilization. The third step is to acquire the critical thermodynamic or kinetic information. If not available in the literature, experiments must be designed and carried out to obtain the needed information. The fourth and final step is to conduct simulations of waste transport in the injection zone. Although two- or three-dimensional models may be used, one dimensional models may be all that is required.

In modeling, attention should be placed to various criteria regarding the submission of an acceptable petition. The injection zone environment should be properly characterized and described, and complete chemical analyses of the waste streams should be given together with EPA concentration limits in drinking water, or current analytical detection limits. The mechanisms of decomposition or immobilization of the hazardous waste constituents should be identified and background information given on the information used in subsequent modeling. All modeling should be completely described and the simulations or codes identified and supporting documentation provided to show that the simulations can be varified and validated to the extent possible. The results in relation to EPA technical requirements should be presented in succinct form, and all findings and conclusions summarized. Particular attention should also be paid to quality assurance needs in presenting information.

A very important part of geochemical modeling is ensuring that the computer codes or simulations are properly verified and validated. Numerous problems can arise at all stages of the process from model conception through the final validation phase. Sufficient supporting

information should be provided to permit EPA staff to form an opinion of the quality of the modeling presented. All model predictions should be conservative, and information provided to assure EPA staff that conservative values for all parameters have been used throughout the model exercise. Finally, it is necessary to conduct sensitivity studies of the model through variation of critical parameters, in order to determine how predictions might be affected by parameter uncertainties. Sensitivity studies can be conducted by separately varying critical parameters to establish the impact of parameter changes on model predictions. When a large number of parameters are involved and many costly computer runs might be required, efficient means of input parameter sampling, such as the Latin Hypercube Sampling method may be advisable.

**Conclusions**

Many aspects of geochemical modeling remain at an embryonic state of development regarding predictions of the fate of hazardous constituents in deep underground zones. Although computer codes are available to aid in the modeling process, most are not specifically designed to address the problems posed by deep well disposal, and extra effect will be required by the petitioner, both to adapt codes for his purposes, and to acquire the needed thermodynamic and kinetic data. The development of systematic methods to conduct sensitivity studies is currently under way, but considerable effort may be required to adapt those methods to geochemical problem solving.

Section 1

# INTRODUCTION

## 1.1 Purpose of this Report

As a result of recent EPA amendments to the technical requirements for the injection of hazardous waste in deep injection (Class 1) wells, companies operating such wells are required to petition EPA to show there will be no migration of hazardous waste from the injection zone of the well for as long as the waste remains hazardous. This may be demonstrated in part by predictive models involving chemical waste transformation and/or fluid flow. These models should show, to a reasonable degree of certainty, that the hazardous waste will be destroyed or immobilized in the injection zone. The purpose of this report is to provide a petitioner with background information regarding the current state of the art in chemical theory and modeling capabilities, so that he could use chemical arguments to predict the fate of injected hazardous waste.

The report is divided into eight sections: (1) an introduction covering EPA amendments to the technical rules for preparation of a petition and how they relate to geochemical modeling, (2) a discussion regarding what must be modeled in relation to the chemical conditions expected in the injection zone, (3) the thermodynamic models that must be used, (4) the availability of thermodynamic data, (5) modeling of non equilibrium systems, (6) the availability of geochemical modeling computer codes, (7) criteria affecting the satisfactory chemical modeling of waste injection, and (8) conclusions.

## 1.2 Background

On July 26, 1988, the Environmental Protection Agency (1988) issued amendments to the technical requirements for the injection of hazardous waste in Class 1 wells under the Resource Conservation and Recovery Act (40 CFR Parts 124, 1448, 146 and 148). These amendments prohibit the continued disposal of untreated hazardous wastes beyond August 25, 1988, in Class 1 wells (and other disposal sites) unless the Administrator determines that prohibition is not required to protect human health and the environment.

According to the Environmental Protection Agency (1988)

"Part 148 defines two circumstances under which a waste otherwise prohibited from injection may be injected: (1) when the waste has been treated in accordance with the requirements of Part 268 pursuant to section 3004 (m) of RCRA; or (2) when an applicant has demonstrated to the satisfaction of the Administrator that there will be no migration of hazardous constituents from the injection zone [of a Class 1 well] for as long as the wastes remain hazardous."

A "no migration" petition for injection wells can satisfy the statutory and regulatory requirements in either of two ways.

> "(1) an absence of fluid movement out of the injection zone; or (2) an active process of waste reduction, transformation, or immobilization within the injection zone."

Non hazardous concentrations are determined by EPA to mean those concentrations below the maximum contaminant levels promulgated pursuant to the Safe Drinking Water Act, Carcinogenic Potency Factors, or site specific public health advisories issued by the agency under the auspicies of the Department of Health and Human Services. In the absence of any specific exposure limit, EPA requires that a petitioner show that the concentration of the unspecified constituent be at or below the detection level at the boundary of the injection zone.

EPA understands that it is easier to meet the requirements of the first interpretation than the second, for the requirements of the first are those involving computer simulation of the hydrology, a technique utilized extensively for two decades with proven success, whereas the second requires the prediction of complex chemical processes in sedimentary formations, a skill that is still in its formative stage.

EPA proposes that the petitioner could show under the final rules, that the requirements may be met by demonstrating that the injected hazardous constituents would be transformed to non-hazardous by products or that the concentrations would be reduced by retardation or other physical mechanisms in the injection zone. Furthermore, the EPA proposes that the time period, over which this could occur, can be as long as 10,000 years.

### 1.3 Federal Rules

The rules, which give the petitioner the option of submitting chemical arguments to demonstrate that hazardous constituents would be contained or decomposed in the injection zone, are given in Part 148-Hazardous Waste Injection Restrictions (Environmental Protection Agency, 1988). The following rules are particularly relevant:-

**Part 148-HAZARDOUS WASTE INJECTION RESTRICTIONS**

**Subpart B-Prohibitions on Injection**

**§ 148.10 Waste specific prohibitions - solvent wastes.**

> (a) Effective August 8, 1988, the spent solvent wastes specified in § 261.31 as EPA Hazardous Waste Nos. F001, F002, F003, F004, and F005 are prohibited from underground injection unless the solvent waste is a solvent-water mixture or solvent-containing sludge containing less than 1 percent total F001-F005 solvent constituents listed in Table A of this section.

(b) Effective August 8, 1990, all spent the F001-F005 solvent wastes containing less than 1 percent total F001-F005 solvent constituents listed in Table A of this section are prohibited from injection.

(c) The requirements of paragraphs (a) and (b) of this section do not apply:

* * *

(2) If an exemption from a prohibition has been granted in response to a petition under Subpart C of this Part;

* * *

**Table A**

| | |
|---|---|
| Acetone | Methylene chloride |
| n-Butyl alcohol | Methylene chloride (from the pharmaceutical industry) |
| Carbon disulfide | Methyl ethyl ketone |
| Carbon tetrachloride | Methyl isobutyl ketone |
| Chlorobenzene | Nitrobenzene |
| Cresols and cresylic acid | Pyridine |
| Cyclohexanone | Tetrachloroethylene |
| 1,2-dichlorobenzene | Toluene |
| Ethyl acetate | 1,1,1-Trichloroethane |
| Ethyl benzene | 1,2,2-Trichloro-1,2,2 trifluoroethane |
| Ethyl ether | Trichloroethylene |
| Isobutanol | Trichlorfluoromethane |
| Methanol | Xylene |

**§ 148.11 Waste specific prohibitions - dioxin-containing wastes.**

(a) Effective August 8, 1988, the dioxin-containing wastes specified in § 261.31 as EPA Hazardous Waste Nos. F020, F021, F023, F026, F027, and F028, are prohibited from underground injection.

(b) The requirements of paragraph (a) of this section do not apply:

* * *

(2) If an exemption from a prohibition has been granted in response to a petition under Subpart C of this Part;

* * *

**Subpart C--Petition Standards and Procedures**

**§ 148.20 Petitions to allow injection of a waste prohibited under Subpart B.**

(a) Any person seeking an exemption from a prohibition under Subpart B of this part for the injection of restricted hazardous waste into an injection well or wells shall submit a petition

to the Director demonstrating that, to a reasonable degree of certainty, there will be no migration of hazardous constituents from the injection zone for as long as the waste remains hazardous. This demonstration requires a showing that:

(1) The hydrogeological and geochemical conditions at the sites and the physio-chemical nature of the waste stream(s) are such that reliable predictions can be made that:

(i) Fluid movement conditions are such that the injected fluids will not migrate within 10,000 years:

(A) Vertically upward out of the injection zone; or

(I) Laterally within the injection zone to a point of discharge or interface with an Underground Source of Drinking Water (USDW) as defined in 40 CFR Part 146; or

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

(2) * * *

(IV) * * *

(d) A demonstration may include a showing that:

(1) Treatment methods, the implementation of which shall become a condition of petition approval, will be utilized that reduce the toxicity or mobility of the wastes; or

(2) A monitoring plan, the implementation of which shall become a condition of petition approval, will be utilized to enhance confidence in one or more aspects of the demonstration.

**§ 148.21 Information to be submitted in support of petitions.**

(a) Information submitted in support of § 148.20 must meet the following criteria:

(1) All waste analysis and any new testing performed by the petitioner data shall be accurate and reproducible and performed in accordance with quality assurance standards;

(2) Estimation techniques shall be appropriate, and EPA-certified tests protocols shall be used where available and appropriate;

(3) Predictive models shall have been verified and validated, shall be appropriate for the specific site, waste streams, and injection conditions of the operation, and shall be calibrated for existing sites where sufficient data are available;

(4) An approved quality assurance and quality control plan shall address all aspects of the demonstration;

(5) Reasonably conservative values shall be used whenever values taken from the literature or estimated on the basis of known information are used instead of site-specific measurements; and

(6) An analysis shall be performed to identify and assess aspects of the demonstration that contribute significantly to uncertainty. The petitioner shall conduct a sensitivity analysis to determine the effect that significant uncertainty may contribute to the demonstration. The demonstration shall then be based on conservative assumptions identified in the analysis.

(b) Any petitioner under § 148.20(a)(1)(i) shall provide sufficient site-specific information to support the demonstration, such as;

* * *

(5) Geochemical conditions of the site.

(c) In addition to the information in § 148.21(b), any petitioner under § 148.20(a)(1)(ii) shall provide sufficient waste-specific information to ensure reasonably reliable predictions about the waste transformation. The petitioner shall provide the information necessary to support the demonstration, such as;

(1) Description of the chemical processes or other means that will lead to waste transformation; and

(2) Results of laboratory experiments verifying the waste transformation.

* * *

### 1.4 Relationship of the Rules to Geochemical Modeling

As noted, EPA requires that injected hazardous constituents remain within the injection zone and that none break through to contaminate drinking water (USDW) sources. From the technical viewpoint, this can be achieved if one or more of the following conditions are present.

- The injection zone is isolated from USDW.
- The hazardous constituents are immobilized in the injection zone.
- The hazardous constituents decompose to non hazardous constituents in the injection zone.

Only the last two conditions require an understanding of chemical processes, although both also require specific knowledge of the geohydrologic conditions present in the injection zone, and in paths to USDW or the accessible environment.

From the regulatory point of view, any petition for approval of a Class 1 well must show quite clearly the scientific rationale and degree of confidence in any geochemical arguments used to support the containment capabilities of the proposed disposal method and site. Because of the potential complexity of the legal requirements, and differing ways in which the regulations and technical standards may be interpreted, the author will not dwell on specific criteria by which a submission might be judged, but will instead discuss the tools and techniques that are presently available to prepare a submission that satisfactorily demonstrates containment.

If the petitioner wishes to demonstrate that the hazardous waste will be immobilized in the injection zone, he must consider the following;

1. The mechanism(s) by which the hazardous constituent(s) will be immobilized.
2. The adequacy of existing chemical theory to represent the phenomena in the subsurface environment he wishes to demonstrate.
3. The availability of satisfactory models, which embody the chemical theory.
4. The availability and adequacy of appropriate thermodynamic and kinetic data pertinent to the immobilization process at the temperatures and pressures anticipated in the injection zone.
5. The quality of the experimental data used to generate the pertinent thermodynamic and kinetic data.
6. Whether the subsurface environment has been adequately characterized to permit predictive modeling.
7. The extent to which laboratory or field tests can demonstrate the validity of the model in predicting the immobilization of hazardous constituents in the subsurface environment.
8. The degree of confidence of the predictions, which may be demonstrated through the use of conservative assumptions and sensitivity analyses.

As is well known, the mechanisms leading to "immobilization" in the injection zone, are either precipitation/coprecipitation, ion exchange or adsorption. Complete immobilization is impossible, as all precipitates have a finite solubility and all ion exchange and sorption processes must have finite, though sometimes very small, reversible exchange or sorption coefficients. Metastability and the slow kinetics of heterogeneous processes may further complicate the picture. A satisfactory condition would be one in which a hazardous constituent is so effectively removed from solution that its concentration in solution is decreased to below the health based limit established for that constituent or the current analytical detection limit should there be no specified health based limit. In such a situation, a demonstration that the injection zone has the capacity to precipitate, exchange or sorb that hazardous constituent and that this capacity is accessible to the waste stream, would be necessary. Furthermore, it must be shown that the

hazardous waste will remain immobilized for the next 10,000 years. In reality, many hazardous constituents, particularly water miscible organic species, are not immobilized very effectively. Furthermore, waste streams may contain a multiplicity of hazardous constituents. If satisfactory proof of immobilization of a hazardous constituent cannot be demonstrated, then the petitioner must use other arguments, either to demonstrate isolation of the injection zone, or to demonstrate that the hazardous constituent decomposes.

If the petitioner wishes to demonstrate that the hazardous constituent(s) will decompose to innocuous constituents before the injected waste stream leaves the injection zone, then another set of criteria must be considered.

- The mechanism(s) by which the hazardous constituent is converted to harmless products.
- The rate at which the hazardous constituent decomposes.
- Whether or not catalysts are involved in the process.
- The effect of host rocks, or ground water constituents on the catalytic process.
- The effect of down-hole temperature (and pressure) on the decomposition rate.
- The quality of the kinetic data supporting the predicted decomposition mechanism.
- Whether the subsurface environment has been sufficiently well characterized to permit predictive modeling.
- The extent to which laboratory and field tests can verify the model in predicting destruction of the hazardous constituents in the subsurface environment.
- The degree of confidence of the prediction, which may be demonstrated through the use of conservative assumptions and sensitivity analyses.

Decomposition mechanisms include neutralization, hydrolysis and oxidation or reduction. The latter two may be accelerated through bacterial mediation. Potential problems with a submission where the decomposition of the hazardous constituent is claimed as a criterion for containment include:–

- Side reactions, some of which may not be anticipated, could make predictions of decomposition rates optimistic,
  - — complexing
  - — sorption
  - — poisoning of a catalytic process
  - — formation of unanticipated hazardous by products.
- Misunderstanding or misinterpreting the decomposition mechanism, particularly with respect to reaction product intermediates, which may respond differently in the subsurface

environment when compared with laboratory experiment.

- Confidence in short-term laboratory experiments as a basis for the prediction of long-term decomposition rates.

It is expected that the petitioner would argue for injection zone decomposition, because either the hazardous constituent could not be destroyed economically in a surface installation in a reasonable period of time, or that the presence of other constituents would make deep well disposal a favored disposal option. In the former case, rates may be sufficiently slow that large holding tanks or ponds would be required to allow sufficient time for decomposition. As with the immobilization scenario, residual concentrations of the hazardous constituent at the boundary of the injection zone should be sufficiently low after 10,000 years that it meets the established health based limit, or that its concentration meets the current analytical detection limit when no health based limit has been specified.

The petitioner may wish to consider innovative techniques in which the injection zone can be exploited as a reactor in which added constituents to the waste stream may beneficially react with the hazardous constituents, either immobilizing them or converting them to innocuous products, e.g. through the use of wet combustion, (Smith and Raptis, 1986) or through the addition of a fixation agent such as tetramethyl ammonium ion to a waste stream to modify the injection zone smectite clays and permit enhanced sorption of hazardous organic waste compounds, (Barrer and MacLeod, 1955). Additives might be added, which, when sorbed by a natural substrate, could catalyse the decomposition of waste constituents. If means of accelerating the sorption or decomposition of hazardous constituents are proposed, it should be demonstrated that they are both effective and reliable.

Waste streams may react with the host rock or ground water to produce undesirable side reactions, such as the formation of a separate gas phase or the precipitation of pore clogging solids. Some waste streams may be supersaturated with respect to either benign or hazardous constituents even before injection. Precipitation in the injection zone in the vicinity of the well bore could seriously decrease injection rates unless pumping pressure were to be increased. Higher pumping pressures could exceed EPA mandated limits and could lead to hydrofracturing and bypassing of part of the injection zone by the injected fluid. Therefore, the petitioner should address issues relating to the long term proper functioning of the injection system if failure to do so would compromise the integrity of the injection zone. To ensure hydrogeologic compatibility, the well operator must in any case submit a plan to EPA under Section 146.68 that identifies anticipated reaction products and demonstrates that neither the waste nor the reaction products would adversely affect the injection or confining zone.

The petitioner may wish to operate an injection well to provide a convenient disposal option for a number of plants with differing waste streams. In this situation both the variety and relative quantities of the waste streams, may make it exceedingly difficult to anticipate all possible interaction scenarios. The petitioner may find it difficult to present satisfactory chemical arguments for containment, unless he were to exercise strict control over monitoring the composition and volumes of the waste streams. The petitioner should also be conscious of the need to avoid conflict with Part 148.3 which prohibits "the artifical aggregation of wastes to avoid a land disposal prohibition standard, or mixing of substances that do not either themselves need to be treated or which do not aid in treatment" (Federal register, v. 53, No. 143, p. 28124).

### 1.5 Role of Geochemical Modeling

Geochemical modeling may be used as a predictive tool by which information previously acquired through theory, experiment and testing is utilized to anticipate the geochemical evolution of a system. Because the deep well injection of hazardous waste streams will almost always involve some chemical processes, arguments to support the licensing of a Class 1 well, will often justify the use of geochemical modeling. Geochemical modeling will be only part of any application. Hydrologic modeling, laboratory studies and field tests will also play an essential role in the submission. Geochemical modeling must therefore be coordinated with other components of a submission to be effective.

Predicting the chemical fate of hazardous constituents in the subsurface environment presents a rigorous challenge to the modeler. Although geochemical modeling has been practiced in various forms for several decades, much of it has been applied to problems of little immediate relevance to hazardous waste injection. Hence, there is little precedent for establishing whether such modeling may convincingly demonstrate that a particular injection scenario will perform as planned.

Problems relating to the deep well disposal of hazardous wastes require an understanding of physico chemical phenomena that have been studied as components of many other disciplines,* but scientists are rarely required to integrate the diverse knowledge required to address a technological problem of such complexity. Each sub discipline has its own specialized literature, dispersed through many scientific and technical journals. It is difficult, therefore, to determine whether the state-of-the-art is sufficiently well developed that practical answers might be found for chemical problems relating to hazardous waste disposal.

* The list of disciplines includes soil chemistry, clay chemistry and mineralogy, aqueous geochemistry, boiler water chemistry, hydrometallurgy, the physical chemistry of strong electrolytes, process chemistry and engineering, and hydrometallurgy, physical organic chemistry and environmental chemistry, to name a few.

Finally, it must be emphasized that EPA is not primarily interested in the petitioner providing a quantitative simulation of the fate of injected hazardous waste, but rather a demonstration of effective containment. The use of conservative assumptions in geochemical modeling is encouraged, provided that the assumptions are demonstratable, and that this does not lead to oversimplification and omission of potentially non conservative conditions.

Section 2

# PRELIMINARY CONSIDERATIONS

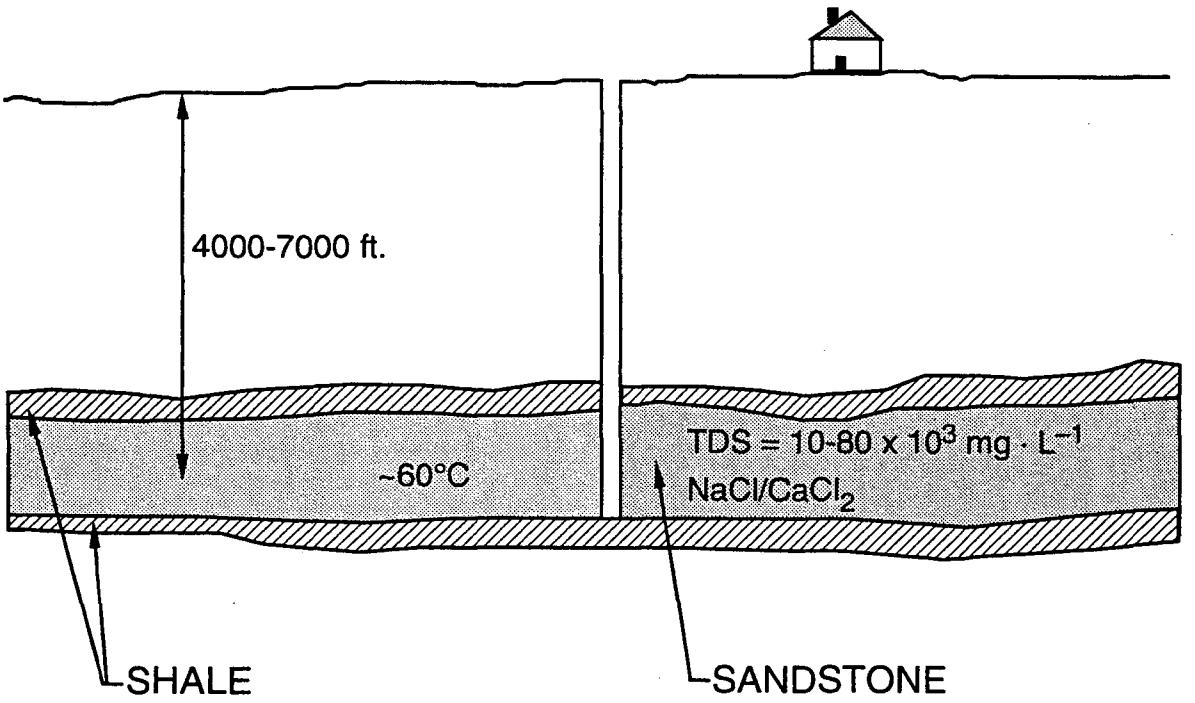
## 2.1 Introduction

Operators pump or allow the waste steam to flow into a deep porous rock formation for a period of years after which they seal the well and the injected waste is allowed to remain in the formation in perpetuity. The injected wastes will be modified, transformed or immobilized by a variety of mechanisms, while simultaneously being subject to migration away from the vicinity of the well. In order to meet EPA technical requirements, the fate of the hazardous waste constituents must be predicted with a reasonable level of confidence to ensure that they do not migrate beyond the injection zone. In order to make such predictions, the processes by which the waste chemical constituents are modified, transformed or immobilized must be known in relation to the environmental conditions of the injection zone. Suitable geochemical models must be used to make the predictions. The choice and level of sophistication of the model, and the amount of information needed to make the necessary calculations depends greatly on the nature and complexity of the waste stream and the processes that might be invoked to demonstrate containment. Before such model choices can be made, the conditions of the injection zone and the range of waste types likely to injected must be identified. The choice of units in geochemical calculations must also be settled. These subjects are discussed further below.

## 2.1 Physical and Chemical Conditions of the Injection Zone

Class 1 hazardous waste wells are most conveniently located in deep sedimentary basins containing saline water. It is not surprising therefore, that such wells are concentrated along the Gulf Coast of Texas, Louisiana, Arkansas and Mississippi and in states overlying the Illinois and Michigan Basins, i.e. Illinois, Indiana, Ohio and Michigan. (Environmental Protection Agency, 1985) Approximately two thirds of the wells are located in Texas and Louisiana, and these receive ninety percent of the injected waste. Injection sites are also concentrated in Texas north of the Oachita uplift and in Oklahoma and Kansas. A relatively small number of wells are located in California and Florida.

The injection zones are normally arenaceous aquifers, confined by argillaceous horizons which may be tens to hundreds of feet thick. Occasionally, the injection zone may be limestone; a beneficial choice for the disposal of acid wastes, provided that the carbon dioxide liberated does not cause operating problems. A typical Class 1 injection zone environment is illustrated in Figure 2.1.




| | wt % |
|---|---|
| Total Clay | 68 |
| Calcite | 9 |
| Quartz | 13 |
| K Feldspar | 3 |
| Plagioclase | 4 |
| Pyrite | 3 |

| | wt % |
|---|---|
| Quartz | 50 |
| Plagioclase | 6 |
| K Feldspar | 6 |
| Calcite | 7 |
| Illite | 5 |
| Kaolinite | 6 |
| Chlorite | 6 |
| Smectite | 10 |
| Mixed layer clays | 4 |

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Figure 2.1. Typical Class 1 Injection Well Environment

The saline ground waters of injection zones, contain at least 10,000 $mg.L^{-1}$ and sometimes over 150,000 $mg.L^{-1}$ of total dissolved solids. The principal constituent of such ground waters is sodium chloride, although significant concentrations of calcium and magnesium chloride may also be present, (Donaldson, 1972; Kreitler and Richter, 1986). Such ground waters are also characteristically associated with oil and gas accumulations. Therefore, the extensive records of oil field brine compositions obtained during petroleum exploitation permit an estimation to be made of their principal chemical constituents and expected concentration ranges. These are summarized in Table 2.1. The injection zone rock matrix usually consists primarily of detrital minerals, i.e. quartz sand, with smaller amounts of plagioclase, potash feldspar and clays. Authigenic minerals, including carbonates and clays may also be present. A representative mineralogical composition of the injection zone is also given in Table 2.1.

### 2.3 The Chemistry of Waste Streams

It is evident, that a necessary requirement for geochemical modeling is that the thermodynamic models used cover the conditions most likely to be encountered during deep well injection.

Most deep well injection facilities are operated by the chemical industry, of which nearly two thirds of the injected volume originates with manufacturers of organic chemicals. Another quarter of the volume originates with petroleum refining and petrochemical industries. The balance is made up by the metals, minerals, and aerospace industries, and commercial facilities receiving waste from many industrial sources. Many large plants have on-site injection wells (Environmental Protection Agency, 1985).

Capuano et al. (1989) have surveyed the composition of waste streams injected into 98 deep disposal wells in Texas between 1985 and 1986. While their survey cannot be considered as representative of the whole country, the quantity of liquid waste injected anually in Texas is substantial ($5.1 \times 10^9$ gallons) and is nearly 60 percent of that injected nationwide. Capuano et al. found that hazardous organic waste comprised 71–87 percent of all hazardous compounds injected in Texas. Of these, non-ignitable hazardous compounds consisted primarily of phenols, organic halogens, nitriles, ketones, aldehydes and carboxylic acids. Substantial quantities of ignitable hazardous waste primarily methyl and butyl alcohol were also injected. The inorganic hazardous waste consisted of strong acids and alkalies, cyanide, and toxic metal species, of which those containing nickel appeared to predominate.

## Table 2.1

## Chemical Parameter Variation in the Injection Zone Environment

| Parameter | Unit | Range | |
|---|---|---|---|
| | | min | max |
| T | °C | 20 | 100 |
| P | bar | 50 | 300 |
| pH | –log *M* | 5.0 | 9.5 |
| Eh | mV | –500. | 0.0 |
| **A. Chemical constituents of the brine[1]** | | | |
| Total dissolved solids | $mg.L^{-1}$ | 10,000. | 250,000. |
| Na | | 1200. | 80,000. |
| K | | 70. | 2,000. |
| Mg | | 1. | 9,500. |
| Ca | | 20. | 36,000. |
| Sr | | 5. | 1,800. |
| Ba | | ? | 100. |
| Mn | | 1. | 6. |
| Fe | | 0.01 | >1,000. |
| Cu | | 0.5 | 3. |
| Zn | | 0.01 | >500. |
| Cd | | 0. | 0.001 |
| Hg | | ? | <0.0001 |
| B | | 4. | 350. |
| Al | | tr. | >100. |
| $HCO_3$(alkalinity) | | 1.0 | 6000. |
| Si | | 2. | 25. |
| Pb | | tr. | >100. |
| $NH_3$(as nitrogen) | | 0. | 450. |
| $PO_4$ | | ? | <1. |
| As | | 0 | 10. |
| $SO_4$ | | 1 | 3000. |
| F | | ? | 5. |
| Cl | | 400. | 150,000. |

[1]Parameter ranges taken primarily from Collins (1975), Kreitler and Richter (1986) and Kreitler et al. (1988).

## Table 2.1 Continued

| Parameter | Unit | Range |
|---|---|---|
| **B. Mineral Assemblage[1]** | | |
| silicates | | |
| quartz | wt% | 30–85 |
| plagioclase | | 3–10 |
| K feldspar | | 3–10 |
| Carbonates | | |
| calcite | | 0–15 |
| dolomite | | 0–15 |
| siderite | | 0–5 |
| Clays | | |
| kaolinite | | |
| smectites | | 0–15 |
| illite | | 0–10 |
| chlorite | | 0–10 |
| mixed layer clays | | 0–10 |
| Accessories | | |
| pyrite | | 0–5 |
| pyrrhotite | | 0–2 |
| heavy minerals | | 0–5 |
| organic matter | | 0–2 |

[1]Parameter ranges taken primarily from Pettijohn (1963, 1965) and Pettijohn et al. (1980).

Table 2.2 summarizes the reported maximum concentrations of both inorganic and organic wastes injected into Texas wells. The inorganic constituents include one third of all elements in the periodic table. The maximum concentrations of some elements are sometimes very high, notably, Na, Fe, Ni, Zn, C (as $CO_3^{--}$) N (as $NO_3^-$ and $NH_3$), P (as $PO_4^{3-}$), S (as $S^{--}$, $SO_3^{--}$ and $SO_4^{--}$) and Cl.

Although the reported maxima are rarely if ever attained in practice, they provide some indication of the requirements for modeling activities.

Over 125 organic compounds are listed in Texas waste streams. Many other compounds not specifically identified are also reported collectively by Capuano et al. (1989) under headings describing their principal functional groups. The summary of organic compound maximum concentrations in Table 2.2, is similarly organized under broad functional grouping as a matter of convenience and to indicate the diversity of compounds injected. It is beyond the scope of this report to list the concentrations of individual organic compounds.

## 2.4 Units of Measurement

The units of measurement used in geochemical modeling have been chosen to facilitate computations. They differ somewhat from those used in chemical process engineering or in hydrogeology, two disciplines that are intimately related to chemical waste disposal by deep well injection. Geochemical modeling is concerned with the thermodynamics and kinetics of chemical processes. For this reason, the basic unit for measuring the amount of a substance is the mole. The mole is defined as the amount of a substance of a system that contains as many elementary entities as there are atoms in 0.012 kg of carbon 12. When the mole is used, therefore, the elementary unit must be specified, whether it be a formular unit for a solid, or ions, complexes or molecules dissolved in a liquid or gaseous phase.

The units of concentration used in geochemical modeling are most commonly the molal concentration, *m*, or the mole fraction, X, for liquids and solids respectively. The molal concentration of a substance is defined as the number of moles of that substance in 1 kg of solvent, usually water. The mole fraction of a substance is the number of moles of that substance divided by the total number of moles of all substances present. The great advantage to using both units of concentration is that they are dimensionless and independent of temperature and pressure.

Thermodynamic temperature is measured in units of Kelvin (K), the secondary standard being degree Celcius (°C), where °C = K–273.15. Although the SI unit for pressure is the Pascal (Pa), most geologists and geochemists still prefer to use the bar (1 bar = $10^5$ Pa) or the atmosphere. With respect to units of energy, the derived SI unit, the Joule (J) is winning increasing acceptance by geologists and geochemists. However, many continue to use the calorie (cal.),

## Table 2.2

## Maximum Concentrations of Chemical Constituents in Waste Streams in Texas[1]

**A. Inorganic Compounds**

| Chemical Constituent | Unit | Maximum Concentrations |
|---|---|---|
| TDS | | >200,000. |
| pH, max | $-\log M$ | 13.8 |
| min | $-\log M$ | 0.03 |
| Na, | $mg.L^{-1}$ | 125,000. |
| K | | 5400. |
| Mg | | 1200. |
| Ca | | 6800. |
| Ba | | 90. |
| $^{226}Ra$ | $pCi.L^{-1}$ | 4000. |
| V | $mg.L^{-1}$ | 25. |
| U | | 120. |
| Cr | | 360. |
| Mo | | 430. |
| Mn | | 340. |
| Fe | | 36,000. |
| Co | | 20. |
| Ni | | 35,000. |
| Cn | | 600. |
| Ag | | 4. |
| Zn | | 10,000. |

[1]Based on a summary of analyses of waste streams injected into Class 1 wells in Texas, as reported by Capuano et al. (1989).

## Table 2.2 Continued

| Chemical Constituent | Unit | Maximum Concentrations |
|---|---|---|
| Cd | $mg.L^{-1}$ | 6. |
| Hg | | 3. |
| B | | 100. |
| Al | | 500. |
| $CO_3$ | | 160,000 |
| Si | | 190. |
| Pb | | 260. |
| $^{210}Pb$ | $pCi.L^{-1}$ | 150. |
| nitrogen (total) | $mg.L^{-1}$ | 16,000. |
| $NO_3$ | | 15,000. |
| $NH_3$ | | 5,000. |
| CN | | 2900. |
| $PO_4$ | | 25,000. |
| As | | 2,500. |
| Sb | | 13. |
| Bi | | 16. |
| sulfide | | 50,000 |
| $SO_3^-$ | | 69,500 |
| $SO_4^-$ | | 81,000. |
| Se | | 65. |
| F | | 10,000. |
| Cl | | 310,000 |
| I | | 10,000. |

Table 2.2 Continued

| B. Organic Compounds | |
|---|---|
| Functional Group | Range of Maximum Concentrations, $mg.L^{-1}$ |
| **Aliphatic Compounds** | |
| alkanes | 200–30,000 |
| halogenated Compounds | 2–400 |
| alcohols | |
| monols | 100–30,000 |
| diols | 130–10,000 |
| triols | 130–50,000 |
| other aliphatic | 4–2113 |
| ethers | 700–1000 |
| aldehydes | 300–5000 |
| ketones | 150–2000 |
| carboxyllic acids | 1500–300,000 |
| dicarboxyllic acid | 2800–40,000 |
| carboxyllic acid dervatives | |
| esters | 100–5000 |
| amides | 650 |
| nitriles | 600–970,000 |
| amines | 100–1400 |
| salts | 600–71,000 |

**Table 2.2 Continued**

| Functional Group | Range of Maximum Concentrations, $mg.L^{-1}$ |
|---|---|
| **Aromatic Compounds** | |
| benzene | 5000 |
| halogenated compounds | 7–95,000 |
| phenols | 3–50,000 |
| acyl benzenes | 620 |
| nitriles | 410–1500 |
| pyridines | 14 |
| borates | 7000 |
| boranes | 400 |
| **Miscellaneous Organic Compounds** | |
| sulfonated compounds | 10,000 |
| chlorinated hydrocarbons (non specific) | 15,000 |
| phosphorous compounds | 100,000 |
| nitrile compounds | 970,000 |
| oil and grease | 1,800 |

where 1 calorie = 4.184 Joule, because data bases built into geothermal codes were compiled in terms of the old units. Units of length are either the meter (m), or multiples thereoff, e.g. μm, cm, km, etc.

Two problems arise in the use of geochemical models. The first is that concentration data needed as input for the geochemical model is often in available only in concentration units that differ from those needed for the model. The most commonly used concentration units are $mg.L^{-1}$, ppm and wt%. Sometimes concentrations are given in terms of molarity ($M$) i.e., moles per liter of solution. These units of measurement may be converted to molalities using the following relations:

$$m = M \frac{\text{weight of solution}}{(\text{weight of solution} - \text{total weight of solutes})} \times \frac{1}{\rho_{soln.}} \tag{2-1}$$

$$= \frac{mg.L^{-1}}{1000.gfw} \times \frac{\text{weigtht of solution}}{(\text{weight of solution} - \text{total weight of solutes})} \times \frac{1}{\rho_{soln.}} \tag{2-2}$$

$$= \frac{\text{ppm} \times 1000 \times \text{weight of solute}}{\text{gfw}\ (10^6 \times \text{weight of solute} - \text{weight of solutes} \times \text{ppm})} \tag{2-3}$$

$$= \frac{\text{wt\%} \times 1000 \times \text{weight of solute}}{\text{gfw}\ (100 \times \text{weight of solute} - \text{wt\%} \times \text{weight of solutes})} \tag{2-4}$$

where gfw is the gram formula weight of the species in solution.

Casual inspection will show, that for very dilute aqueous solutions

$$m \approx M \approx \frac{mg.L^{-1}}{1000 \times \text{gfw}} \approx \frac{\text{ppm}}{1000 \times \text{gfw}} \approx \frac{\text{wt\%} \times 10}{\text{gfw}} \tag{2-5}$$

This equivalence is often applied as a convenient approximation, in geochemical systems involving low total solids content but for concentrated brines and waste streams, such approximations should be used with caution, and avoided whenever possible. As may be noted, molarity and $mg.L^{-1}$ units require density corrections to obtain molality. Such corrections are usually quite small, but become significant if the density exceeds 1.10, or is less than 0.9. All concentration units require a knowledge of the total weight of solutes for their conversion to molality. This may also be approximated through use of total dissolved solids for inorganic systems, but for chemical wastes containing solvents or volatiles, the total weight of solutes may have to be calculated from a complete chemical analysis.

For extremely concentrated solutions, the use of mole fractions rather than molalities is preferred, as the molality of a substance approaches infinity as the concentration of the solute approaches 100 percent. Because most waste streams rarely contain such high concentrations of solutes that water becomes a minor component, the use of mole fractions for aqueous systems in

geochemical modeling is not a significant issue. Mole fractions are conveniently used, however, in describing solid solutions and adsorption phenomena.

Section 3

# THERMODYNAMIC MODELS

## 3.1 Introduction

All geochemical simulations are concerned with the application of thermodynamic models. Thermodynamic models are systems of equations that relate the thermodynamic properties of phases such as the Gibbs free energy, G, the enthalpy, H, and the entropy, S, to measurable extensive properties such as heat capacity, specific volume and composition, and measurable intensive variables such as pressure and temperature. They can be derived by the integration of equations of state (EoS) often making necessary approximations or simplifications to permit the use of tractable equations. Thermodynamic models are incorporated in more complex algorithms, i.e., geochemical models, to calculate other thermodynamic properties of a phase or phases, given known input constraints such as pressure, temperature or bulk composition.

An EoS relates the measurable physical, such as specific volume, and compositional properties of a phase as a function of intensive parameters such as pressure and temperature. One purpose of an EoS is to correlate the measured physical properties over regions where no experimental measurements have been made. An EoS is valid, however, only over a specified range of temperatures, pressures or compositions. Outside that range, it could prove to be seriously defective. The better EoSs permit reasonable extrapolations beyond regions of measurement. EoSs also permit the derivation of continuous thermodynamic properties, such as the Gibbs free energy, through integration. They are therefore particularly important in describing the properties of fluids and gases, where variations in the physical and thermodynamic properties over the range of measurements can be quite substantial.

Thermodynamic models, required to predict the fate of waste streams in the injection zones of deep wells, range from extremely simple to very complex. For convenience, they can be subdivided into four categories.

(1) Pure and multicomponent solids

(2) Pure and multicomponent fluids

(3) Component behavior in liquid aqueous systems

(4) Systems involving interfacial phenomena, e.g. adsorption or bacterial oxidation.

Those relevant to each category and appropriate to injection problems are discussed in the following sections.

### 3.2 Pure and Multicomponent Solids

The injection zone rocks constitute a multicomponent heterogeneous assemblage. The distribution of phases (minerals) in this system at thermodynamic equilibrium can be predicted using the specific volume, $V^o$, the heat capacity, $C_P^o$, as a function of temperature, and the enthalpy of formation, $\Delta H^o_{f,T_r,P_r}$, where $T_r$ and $P_r$ is the reference temperature and pressure respectively in the thermodynamic system. The derivative functions, such as the compressibility, $\beta$, and the thermal expansivity, $\alpha$, are of minor importance to solid phase equilibria under deep well injection conditions. From low temperature heat capacity measurements, the entropy, $S_{T_r,P_r}$, of a phase may be computed. Then $\Delta G^o_{f,T_r,P_r}$ may be calculated from the relation;

$$\Delta G^o_{f,T_r,P_r} = \Delta H^o_{f,T_r,P_r} - T_r \Delta S^o_{f,T_r,P_r} \tag{3-1}$$

provided that the entropies of the participating elements are known.

Calculating the thermodynamic properties of phases at conditions other than at, $T_r$, and $P_r$, requires equations embodying certain model assumptions. Typical of such equations are those used, by Helgeson and his coworkers, e.g., Delany and Helgeson (1978) and Helgeson et al. (1978), and by Berman et al. (1985) and Berman (1988), by Robinson et al. (1982), and by Powell and Holland (1985), Holland and Powell (1985), Powell and Holland (1988) and Holland and Powell (1990). The equations derived and used by Delany and Helgeson (1978), for example, are:

$$S^o_{P,T,i} - S^o_{P_r,T_r,i} = a_i l\,n(T/T_r) + b_i(T-T_r) - \frac{c_i}{2}\left[\frac{1}{T^2} - \frac{1}{T_r^2}\right]. \tag{3-2}$$

$$H^o_{P,T,i} - H^o_{P_r,T_r,i} = a_i(T - T_r) + \frac{b_i}{2}(T^2 - T_r^2) - c_i\left[\frac{1}{T} - \frac{1}{T_r}\right] + V^o_{P_r,T_r,i}(P - P_r), \tag{3-3}$$

$$G^o_{P,T,i} - G^o_{P_r,T_r,i} = - S_{P_r,T_r,i}(T - T_r), + a_i(T - T_r - T l\,n(T/T_r)) - \frac{(b_i T T_r^2 + c_i)(T - T_r)^2}{2T_r^2 T} + V^o_{P_r,T_r,i}(P - P_r), \tag{3-4}$$

Equations (2) through (4) incorporate two assumptions, that the heat capacity of a mineral can be represented by the Maier-Kelley equation (Maier and Kelley, 1932) describing the heat capacity on a function of temperature:-

$$C_{P_r,T,i} = a_i + b_i T + c_i T^{-2} \tag{3-5}$$

where a, b and c are empirical coefficients, and that the molal volume of a mineral is independent of pressure and temperature, i.e.

$$V^{o}_{P,T,i} = V_{P_r,T_r,i} \cdot \tag{3-6}$$

These two assumptions permit the prediction of the $\Delta S^{o}_{p,T,i}$, $\Delta H^{o}_{p,T,i}$ and $\Delta G^{o}_{P,T,i}$ to within an acceptable degree of accuracy at pressures $\leq$ 50 kbar and 1000°C, ranges that go far beyond those necessary for deep well injection calculations. The equations are embodied in the computer codes, SUPCRT, (Kirkham et al., 1978), and SUPCRT92 (Johnson et al., 1992), which permit the calculation of the above thermodynamic parameters for reactions among solid phases and water expected in a deep injection well environment.

Differences between thermodynamic equations used by different groups of investigators depend primarily on variations in the form of the heat capacity equation, and whether or not mineral expansivity or compressibility is taken into account. For example, Berman (1988) employs a heat capacity equation of the form

$$C_{P_r,T,i} = a_i + b_i T^{-0.5} + C_i T^{-2} + d_i T^{-3} \tag{3-7}$$

which ensures that the heat capacity approaches the high temperature limit predicted by lattice vibrational theory ($Cp = 3R + \alpha^2 VT/\beta$) (Berman and Brown, 1985). Berman (1988) has also employed a parametric equation to correct mineral volumes for pressure and temperature. Such refinements, while they have no significant impact in predicting injection zone conditions from standard state conditions, i.e. $P_r$ = 1 bar and $T_r$ = 25°C, these refinements may be important then using experimental data at elevated temperatures and pressures to calculate the properties of minerals at standard state conditions, as discussed further in Section 4.2.

Although the thermodynamic properties of many pure stoichiometric minerals have been determined, natural systems are comprised primarily of minerals that are multicomponent solid solutions. The impact of mineral solid solutions on the migration of hazardous wastes very variable, and in many cases is of little importance to the petitioner, e.g. the substitution of alkalies earth metal ions in feldspars or carbonates.

In contrast, solid solutions of the exchange sites of clays, and perhaps zeolites and manganese oxides, may be of considerable importance to the petitioner, depending on the nature of the waste injected. Many cations can be readily exchanged on natural clays and zeolites, thereby making these minerals very effective scavengers for 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.

A solid solution may be described in terms of variations of the thermodynamic properties i.e. $C_P$, S, $\Delta H_f$ as a function of its composition, or in terms of the exchange reaction between two

or more participating species in a coexisting aqueous phase. The former approach possesses the advantage that both variations of the mineral composition, and its stability in relation to other minerals may be modeled, whereas in the latter case, the thermodynamic properties of the exchange reaction are treated independently of the thermodynamic properties of the mineral in which the exchange reaction takes place. Which approach should be used depends on the nature of the waste stream. If the waste stream contains aggressive reagents, such as strong acids and heavy metals, for example, then an equation of state describing the properties of the mineral in terms of its composition must be used, because both the mineral stability and its exchange properties must be modeled. In contrast, equations simply describing multicomponent ion exchange may be all that are necessary to describe the retardation of heavy metals in a waste stream that does not cause the exchanger to decompose.

Predicting the behavior of mineral solid solutions is a subject that has attracted considerable attention in recent years. An excellent review is given by Wood and Frazer (1977). A more recent derivation of intrasite mixing in silicate minerals has been prepared by Helgeson and Aargaard (1985). Currently, there are two general approaches to the modeling of solid solutions. One considers the solid solution to be made up of components representing the end members, (Bourcier, 1985). Thus for olivine, a binary system $(Mg_{1-x},Fe_x)_2SiO_4$ the end members are $Mg_2SiO_4$ and $Fe_2SiO_4$. Therefore the solid solution can be considered a mixture of

$$1-x(Mg_2SiO_4) + x(Fe_2SiO_4)$$

The other is the ''site mixing model'' approach. In this approach, individual structural sites in the crystal lattice of a solid solution are considered to be positions where ionic substitution or ordering can occur. Thus the solid solution is formally represented as $(Mg_{1-x}Fe_x)_2^{I}SiO_2$ where $Fe^{++}$ substitutes for $Mg^{++}$ on the (I) site. Helgeson and Aargaard (1985) derived the general thermodynamic relations for site mixing and compared their derivations with earlier literature on the subject. In a companion paper Aargaard and Helgeson (1983) utilized the theory to investigate the assumed ideal mixing of atoms on sites in montmorillanites, illites, and mixed layer clays.

Scrivner et al. (1986) successfully applied regular solution theory described by Garrels and Christ (1965) with a mixing rule by Hildebrand et al. (1970) to analyse 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 in the prediction of hazardous waste uptake on clays, (and zeolites, if they are present).

An alternative to the end member and site mixing models is the so called polymer model, which was pioneered by Nriagu (1975) and subsequently refined by Mattigod and Sposito (1978) and Sposito (1986) to predict the thermochemical properties of 2:1 layer type phyllosilicates.

The latest embodiment of the model (Sposito, 1986) is based on the assumption that the Gibbs free energy $\Delta G_r^o$, for the formation reaction of the clay from its constituent hydroxide components, thus:

$$nC + n5Mg(OH)_2(s)(OH)_z(s) + n1Si(OH)_4(s) + n2Al(OH)_3(s) + n3Fe(OH)_3(s)$$
$$+ n_4Fe(OH)_2(s) = C_r[Mg_{n5}Fe(II)_{n4}Fe(III)_{n3}Al_{n2}Si_{n1}O_{10}(OH)_2(s)$$
$$+ (X + \sum_{i=1}^{5} niZ_i - 12)H_2O(l) \tag{3-8}$$

where

$$\Delta G_r^o = \Delta G_f^o\ [\text{clay mineral}] + (x + \sum_{i=1}^{5} niZ_i - 12)\Delta G_f^o[H_2O(l)]$$
$$- n\Delta G_f^o[C(OH)_z(s)] - \sum_{i=1}^{5} ni\Delta G_f^o[\text{hydroxides}] \tag{3-9}$$

is linearly related to the product of the charge of the half-cell layer and the crystallographic ionic radius of the interlayer exchangeable cation, $C^{z+}$, divided by the charge, z.

$$|\Delta G_r^o| = A + B\left[\frac{xR}{z}\right] \tag{3-10}$$

where A and B are empirically determined parameters, respectively 41.34 and 921.66, when $|\Delta G_r^o|$ is in $kJ.mol^{-1}$, and R is in nanometers.

Krupka et al. (1988) adapted the clay polymer model to model cation exchange reactions

$$A^{m+}(aq) + mX^-(s) = AX_m(s) \tag{3-11}$$

where $A^{m+}$ is an exchangeable cation, $AX_m(s)$ is the clay loaded with the exchangeable cation $A^{m+}$, and $mX^-(s)$ is the negatively charged clay minus the exchangeable cation. Through application of Eqns. (3-9) and (3-10) to calculate $\Delta G_f^o$ of the clay, together with calibrations with laboratory and field cation exchange experiments, application of the Vanselow convention (Vanselow, 1932) to model activity coefficients of species on the exchange sites, and specification of the standard state of the exchanger, they were able to generate a series of cation exchange constants that could be used to model the distribution of cations on the clay exchange site as a function of aqueous solution composition. Although certain features of this exchange model require further improvement, its representation as "half cell" exchange reactions, i.e. Eqn. (3-11) facilitates their incorporation in equilibrium constant type models (see Section 6.3). The exchange model has been incorporated in the ECHEM computer code and the FASTCHEM simulator whose development was sponsored by the Electric Power Research Institute (Morrey, 1988).

### 3.3 Pure and Multicomponent Fluids

In the event that a $CO_2$ rich or organic phase partitions in the subsurface environment, it will be necessary to calculate its stability in relation 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. Rather complex equations of state are sometimes required to describe the PVT properties, of multicomponent fluids, particularly in the region around the critical phase. The problem becomes even more acute if water, a polar fluid, is one of the participating components.

The ideal gas law is

$$PV = nRT \tag{3-12}$$

where P, V, R and T are the pressure, molar volume, gas constant and absolute temperature, respectively, and n is a constant depending on the units chosen. This law works well only for gases at pressures significantly below, and temperatures significantly above, those of the critical points of the gases under consideration. Deviations from ideality have been accomodated by various modifications to the ideal gas law, ranging from the relatively simple, such as the Van der Waal's EoS, to those that are extremely complex. The development of such EoS has been reviewed by Prausnitz (1969), and Walas (1985). Among those that have found widespread applications are the Redlich Kwong EoS (Redlich and Kwong, 1949), the hard sphere modified Redlich-Kwong (HSMRK) EoS, e.g. Holloway (1977), Kerrick and Jacobs (1981) and Bowers and Helgeson (1983), the Benedict-Webb-Rubin EoS (Benedict et al., 1940) and corresponding state equations such as that by Lee and Kesler (1975). All of these EoSs utilize parameters that have been fitted to experimental data, and are usually limited to the ranges of P and T of the experimental data.

The most probable occasion when the petitioner would find a need for such equations of state is when a $CO_2$ rich fluid phase forms as a result of strong acid neutralization by carbonates in the injection zone. It is remotely possible that the decomposition of organic compounds might also lead to the formation of a methane rich fluid. Under some waste stream conditions a thermodynamic model, which is capable of relating the fluid phase composition to that of a coexisting brine, may be required. The fluid phase would consist primarly of $CO_2$–$CH_4$ with minor concentrations of water vapor under injection zone P-T conditions. Recently, Duan et al. (1992a) Duan et al. (1992b) have developed very precise equations of state for $CH_4$, $CO_2$ and $H_2O$ between 0 and 1000°C and 0 and 8000 bar using a modified Lee-Kesler EoS. Subsequently, they extended the EOS for the pure end members to the binary and ternary system using selected mixing rules. Model predictions appear to be within experimental accuracy over the range from

50–1000°C and 0–1000 bar. The fluid phase EoS for methane has also been used to predict methane solubility in saline brines by Duan et al. (1992c). This last study covers the range from 0–250°C, 1–1600 bar and NaCl concentrations to $\approx 6\ m$. The development of a thermodynamic model relating the solubility of $CO_2$ fluid in saline brines would be welcomed by some petitioners.

Liquid water, possessing a variable heat capacity, thermal expansivity and compressibility, even over the range of temperatures and pressures expected in an injection well, must also be accommodated with a carefully calibrated EoS. That frequently used in past geochemical evaluations is by Keenan et al. (1969). This EoS is highly suitable for modeling the properties of pure water under injection well conditions, and was adapted by Helgeson and Kirkham (1974a) for use in the SUPCRT code. More recently, the EoS developed by Haar et al. (1980, 1984) has found increasing acceptance and is used in the SUPCRT92 code (Johnson et al. 1992).

### 3.4 Chemical Components in Liquid Aqueous Systems

Ground waters and aqueous waste streams are electrolyte solutions composed of the solvent (water), and the solute. The solute consists of an electrically neutral collection of charged (i.e. positive and negative) ions and complexes, and neutral molecules representing the dissolved chemical components. The ground water in the injection zone contains many chemical components, most of which are also found in the coexisting mineral assemblage. If the ground water and all coexisting minerals are in thermodynamic equilibrium, the chemical potential of each component is the same in all phases. In order to be able to determine the composition of a ground water in equilibrium with the coexisting minerals, a thermodynamic model is required in which the potentials of the chemical components can be related to their concentrations in solution.

The concentrations of chemical components in an aqueous electrolyte cannot be related simply to the chemical potentials of components in coexisting minerals or precipitates because the solution behaves "non ideally," the consequence of charged and neutral species interacting with the solvent and the formation of complexes. Thermodynamic equations are therefore required that adequately model the non ideal behavior. This may be acccomplished through the use of an electrolyte model describing the thermodynamic properties of the aqueous electrolyte. The choice of model and its level of sophistication depend on the nature of the problem to be addressed.

Electrolyte models are also required when it is desired to predict interactions of the waste stream with the displaced ground water or minerals composing the rock of the injection zone or arresting layers. This is an important consideration in the deep underground disposal of hazardous wastes, because a successful model, would in principle, permit an accurate estimate to be

made of the equilibrium concentration of a hazardous constituent in the injection zone, which could be compared with EPA Water Quality Standards to determine whether it meets EPA's criterion for being non hazardous.

The development electrolytes models as a function of temperature, pressure and composition has been slow. Satisfactory methods for dealing with dilute solutions with an aggregate solute molality of less than 0.1 *m* have been available for over 50 years, but accurate equations describing the behavior of strong mixed electrolytes typical of saline ground waters in an injection zone, or waste streams containing heavy salt loads, are still under development. Systems of strong mixed electrolytes with several components, however, can now be modeled at 25°C.

The formalism adopted for electrolyte models is to define the standard state partial molal properties of a chemical component, whether a salt that dissociates into ions upon dissolution, or an ionic species or molecule, as that of a hypothetical one-molal solution of the component as it would behave at infinite dilution.* To predict the ground water or waste stream behavior in the injection zone, two steps are required (1) calculation of the standard state partial molal properties, i.e. $\Delta\overline{H}_f^o$, $\Delta\overline{G}_f^o$, $\overline{S}^o$, $\overline{C}_P^o$, of the participating species under injection zone conditions, (2) modeling the interactions of those species in the ground water or waste stream under conditions that deviate from standard state conditions. While it would be desirable, from the user's viewpoint, to have an equation integrating both functions, it has not generally been achieved in practice. In the following sections, some currently available thermodynamic equations of potential use to the petitioner are discussed, including useful features and limitations.

### 3.4.1 Standard State Partial Molal Properties of Dissolved Species

Given the availability of standard state partial molal properties of a dissolved species at 25°C and 1 bar, the petitioner will want to know what those same properties are in the injection zone at 60°C and 150 bar, for example. Because of the relatively small temperature difference, and the compensating effects of temperature and pressure, a rough approximation that 25°C, 1 bar properties are similar to those in the injection zone is adequate for order of magnitude estimates, i.e. the error introduced in predicting the equilibrium concentrations of a component in solution is unlikely to exceed a factor of 10, and in most cases would be considerably less.

A more precise method of estimation is to assume that the change in heat capacity of a component is constant over the range of pressure and temperatures under consideration. Then

$$\Delta\overline{H}_{r,T}^o = \Delta\overline{H}_{r,T_r}^o + \Delta\overline{C}_{P,f,T_r}^o (T-T_r) \qquad (3\text{-}13)$$

*For an extended discussion of the definition of the standard state of aqueous species, see Garrels and Christ (1965) p. 52–54.

$$\Delta\bar{S}^{o}_{f,T} = \Delta\bar{S}^{o}_{f,T_r} + \Delta\bar{C}^{o}_{P,f,T_r} \ln\frac{T}{T_r} \tag{3-14}$$

Since $\Delta\bar{G}^{o}_{f,T} = \Delta\bar{H}^{o}_{f,T_r} - T\Delta S^{o}_{f,T}$

$$\Delta\bar{G}^{o}_{f,T} = \Delta\bar{G}^{o}_{f,T_r} + \Delta\bar{C}^{o}_{P,f,T_r}(T-T_r) - \Delta C^{o}_{P,f,T_r} T \ln\frac{T}{T_r} \tag{3-15}$$

This approach was popularized by Criss and Cobble (1964), for the calculation of equilibrium constants at elevated temperatures and has been used extensively in many applications. In general, the assumption of constant heat capacity of reaction, $\Delta C^{o}_{P_r,T_r}$, 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). For the calculation of standard state properties under conditions in the injection zone, the method is generally sufficient for petition preparation, as the errors introduced in predicting the concentration of a component in solution are within the level of uncertainty of $\Delta\bar{G}^{o}_{f}$ of that component at 25°C and 1 bar.

Helgeson and his co-workers have formulated an EoS to predict the standard state partial molal thermodynamic properties of ionic and molecular species in aqueous solution over a range of temperatures between 0 and 600°C and pressures between 1 and 5000 bars. Referred to as the HKF EoS, after its principal authors; Helgeson, Kirkham and Flowers, it has been under development for fifteen years. Progress can be followed in a series of papers by Helgeson and his co-workers (Helgeson and Kirkham, 1974 a,b, 1976; Helgeson et al., 1981). A major improvement in the model by Tanger and Helgeson (1988) has eliminated some deficiences in earlier versions.

The basic premise of the model is that the partial molal properties of ions and molecular species can be evaluated in terms of non electrostatic and solvation contributions. The non electrostatic contribution can be further subdivided into intrinsic and solvent collapse properties. Provided that the partial molal volume, $\bar{V}^{o}$, the partial molal heat capacity, $\bar{C}^{o}_{P}$, and the partial molal heat of formation of an ionic species, $\Delta\bar{H}^{o}_{f}$ are known at the reference temperature and pressure respectively, in this case at 298.15 K and 1 bar pressure, it is possible to estimate $\bar{S}^{o}_{298}$, and $\Delta\bar{G}^{o}_{298}$ as well as the standard state properties at any other pressure and temperature within the pressure-temperature region of applicability, when a series of model parameters are evaluated for that particular species. Shock and Helgeson (1988a) provide guidelines for calculating the model parameters as well as giving a summary of the respective 298 K, 1 bar pressure values and the model parameters for a large number of common inorganic ionic species. Data for many water miscible low carbon number organic species and inorganic neutral species have been similarly compiled by Shock and Helgeson (1989) and Shock et al. (1989).

The modified HKF equation of state is also incorporated in a revised version of the SUPCRT code, SUPCRT 92 (Johnson et al., 1992). Documentation for an earlier version is given by Kirkham et al. (1978).

The HKF equation of state has the advantage over the constant heat capacity approach in that the effect of pressure is also taken into account, and will therefore yield more accurate estimates of relevant partial molal properties under injection zone conditions. However, the corrections from 25°C, 1 bar conditions will be small, and like the constant heat capacity approach, may not result in an overall improvement of any predictive geochemical models in which these corrections are incorporated.

The principal advantage in using the HKF EoS for dissolved aqueous species is predicting their partial molal properties at temperatures above 200°C and at pressures over 50 bars. Although its application introduces a level of refinement that would not normally be required in the preparation of petitions, the SUPCRT codes in which the HKF EoS is incorporated, are convenient to use and provide a framework for systematically developing an internally consistent data base for the modeling of geochemical problems in which an aqueous phase participates.

### 3.4.2 Aqueous Electrolyte Models

It is beyond the scope of this report to discuss the development of aqueous electrolyte models. Many excellent textbooks, e.g. Lewis and Randall (1961), Robinson and Stokes (1959) and papers by Pitzer (1977, 1991) provide reviews of the subject. Certain aspects, however, bear directly on attempts to simulate the thermodynamic and kinetic behavior of waste streams in saline aquifers, and these are discussed further in the following paragraphs.

To relate the concentration, $m_i$, of substance, i, to its thermodynamic properties the term activity, $a_i$, species of i, is introduced. Species i may refer to a charged species or to a dissolved salt. $a_i$ is related to the concentration of i in solution by:

$$a_i = m_i \gamma_i \tag{3-16}$$

where $\gamma_i$ is as the activity coefficient, $\gamma_i$ can vary substantially in value, depending on whether the species is charged or neutral, on the nature and total concentration of dissolved constituents and on temperature, but it always approaches unity at infinite dilution.

If the species, i, is a dissolved salt which dissociates into $\nu_+$ positive and $\nu_-$ negative ions, the mean ionic activity, $a_\pm$, is defined as:

$$a_\pm = (a_+^{\nu+} . a_-^{\nu-})^{\frac{1}{\nu}} \tag{3-17}$$

The mean ionic molality, $m_{\pm}$ is defined as

$$m_{\pm} = m_i(\nu_+^{\nu+} + \nu_-^{\nu-})^{\frac{1}{\nu}} \tag{3-18}$$

and the mean ionic activity coefficient is defined as:

$$\gamma_{\pm} = (\gamma_+^{\nu+} . \gamma_-^{\nu-})^{\frac{1}{\nu}} \tag{3-19}$$

where $\nu = \nu_+ + \nu_-$

The derivation of these relationships is given by Garrels and Christ (1965).

For charged aqueous species, Debye and Hückel (1923) and Debye (1923, 1924) successfully developed the necessary theory to relate activity to concentration, known familiarly as the Debye-Hückel equation:

$$-\log \gamma_i = \frac{A \mid z_i^2 \mid \sqrt{I}}{1 + B\mathring{a}_i\sqrt{I}} \tag{3-20}$$

where

A and B = two temperature dependent "Debye-Hückel" parameters

$\mid z_i \mid$ = absolute value of charge

$\mathring{a}$ = parameter which defines the electrostatic radius of the ion.

I = ionic strength, where $I = \frac{1}{2}\sum_i c_i z_i^2$.

The Debye-Hückel expression is successful in predicting the activity coefficient of a species in dilute solutions less than 0.1 molal, but, as will be shown below, is insufficiently precise to be of practical value in solutions whose concentrations of dissolved constituents are in the molal range. Because many waste streams and all saline ground waters in injection zones contain concentrations of dissolved constituents far greater than the range of applicability of the Debye-Hückel equation, some means is needed to extend its range of validity. Several attempts have been made over the years to achieve this objective. Two empirical forms, which have been particularly popular in geochemical modeling, are the "$B^{\bullet}$ extension" of the Debye-Hückel expression and the Davies equation.

The $B^{\bullet}$ extension:

$$-\log \gamma_i = \frac{A \mid z_i^2 \mid \sqrt{I}}{1 + B\mathring{a}_i\sqrt{I}} - B^{\bullet}I \tag{3-21}$$

is similar in form to that originally proposed by Guggenheim (1935) and Guggenheim and Turgeon (1955) and its value was demonstrated by Pitzer and Brewer in Lewis and Randall (1961). It has been utilized in several distribution of species codes, PATH (Helgeson et al., 1969), FAST-PATH (Schlitt and Jackson, 1981) and PHREEQE (Parkhurst et al., 1980) and EQ3/6, (Wolery, 1983). The $B^{\bullet}$ parameter is adjustable and is 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. However, in practice, every mixed electrolyte would require a specific setting of $B^{\bullet}$, which would have to be determined empirically. For hazardous waste streams with significant concentrations of dissolved salts other than NaCl, the need to adjust $B^{\bullet}$ for each composition is an inconvenience. Furthermore, this empirical extension of the Debye-Hückel equation becomes unreliable at ionic strengths greater than about 0.5 molal, which is considerably lower than that of many deep saline ground waters and waste streams.

The other empirical extension of the Debye-Hückel equation is due to Davies (1962). For single ions, this is:

$$-\log \gamma_i = Az_i^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.2I\right]. \tag{3-22}$$

The equation is based on the reasonable concordance of a number of 1-1 (e.g. NaCl) and 1-2 (e.g. $CaCl_2$) electrolytes, and also gives fairly good estimates out to about 0.5 molal, e.g. see Butler (1964). However, it suffers from the same disadvantages as the $B^o$ parameter extension of the Debye-Hückel equation. 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 codes, and is an option for the latest version of EQ3/6. A convenience of the Davies equation is that a determination of å is not required, which, for many species, is not known. The Davies equation is often preferred, therefore, even at concentrations where the more rigorous Debye-Hückel expression, Eqn. (3-20) would yield more precise results.

Several other extensions of the Debye-Hückel equation have been formulated to deal with the computation of activity coefficients in high ionic strength mixed electrolytes. The problem of finding a satisfactory method has been the focus of considerable attention both in academia and in industry. (Zemaitis et al., 1986) gave an extensive review and comparison of various equations for computing either individual ion activity coefficients or mean activity coefficients of salts in single and multicomponent strong electrolytes.

One model, which is gaining increasing acceptance in the field of geochemistry is that due to Pitzer and his co-workers, e.g. see Weare (1987). Pitzer (1973) reviewed the original molecular model upon which the Debye-Hückel equation was based and calculations of the radial distribution function for this model. He found that the Debye-Hückel equation could be extended in a

relatively simple manner to yield equations that approximate rigorous theory very well (Pitzer, 1977). The equation for the mean activity coefficient of a symmetrical electrolyte is, according to Pitzer (loc. cit).

$$\ln \gamma_{\pm} = -z^2 A_{\phi}\left[I^{1/2}/\left(1 + bI^{1/2}\right) + (2/b)\ln\left(1 + bI^{1/2}\right)\right] +$$
$$m\left\{2\beta^{(0)}_{MX} + (2\beta^{(1)}_{MX}/\alpha^2 I)\left[1 - \left(1 + \alpha I^{1/2} - \alpha^2 I/2\right)\exp(-\alpha I^{1/2})\right]\right\} +$$
$$m^2(3C^{\phi}_{MX}/2) \qquad (3\text{-}23)$$

where b, x, $\beta^{(0)}_{MX}$, $\beta^{(1)}_{MX}$ and $C^{\phi}_{MX}$ are adjustable parameters obtained by fitting osmotic coefficients for some 200 electrolytes (Pitzer and Mayorga, 1973), and $A_{\phi}$ is the temperature dependent Debye-Hückel parameter. According to Pitzer (loc. cit), the parameter, b, is the same for all solutes and is optimized at 1.2; $\alpha$ is 2.0 for all 1-1 and many other electrolytes. The remaining coefficients, the so-called interaction parameters, because they reflect electrostatic interactions between ions of like and opposing charges are specific for each ionic interaction, but do not change regardless of the bulk composition of the electrolyte. The determination of interaction parameters involving three or more unlike ions requires the fitting of osmotic coefficient data of mixed electrolytes with the binary interaction parameters fixed. Somewhat more complicated expressions for activity coefficients are required, (Pitzer and Kim, 1974). Pitzer has recently summarized the current state of knowledge regarding the interaction model in a recent publication (Pitzer, 1991).

The great advantage of Pitzer's method, is that it can model multicomponent electrolytes to very high ionic strengths with remarkable accuracy, often to the limits of saturation of such salts as sodium chloride. The ability of the Pitzer interaction model to model strong mixed electrolytes is illustrated in Figure 3.1, where it is compared with two other models. Several studies, e.g. Eugster et al. (1980), Harvie and Weare (1980), Harvie et al. (1982, 1984) Felmy and Weare (1986) have used the Pitzer interaction model in simulating brine-salt equilibria in natural evaporite systems. These studies convincingly demonstrate the potential of the model to simulate the properties of saline brines with similar compositions in deep injection zones.

The disadvantages of the Pitzer model stem primarily from the lack of sufficient data on the interaction parameters and their temperature dependence for many important electrolytes and minor components. Furthermore, the basic premise of the model is that it accounts for electrostatic interactions between ionic species, thereby eliminating the need to account explicitly for ion pair formation, but it cannot account for strong covalently bonded complexation, e.g. chloride complexes of lead and mercury. Thus, systems, in which covalent bonding of aqueous complexes

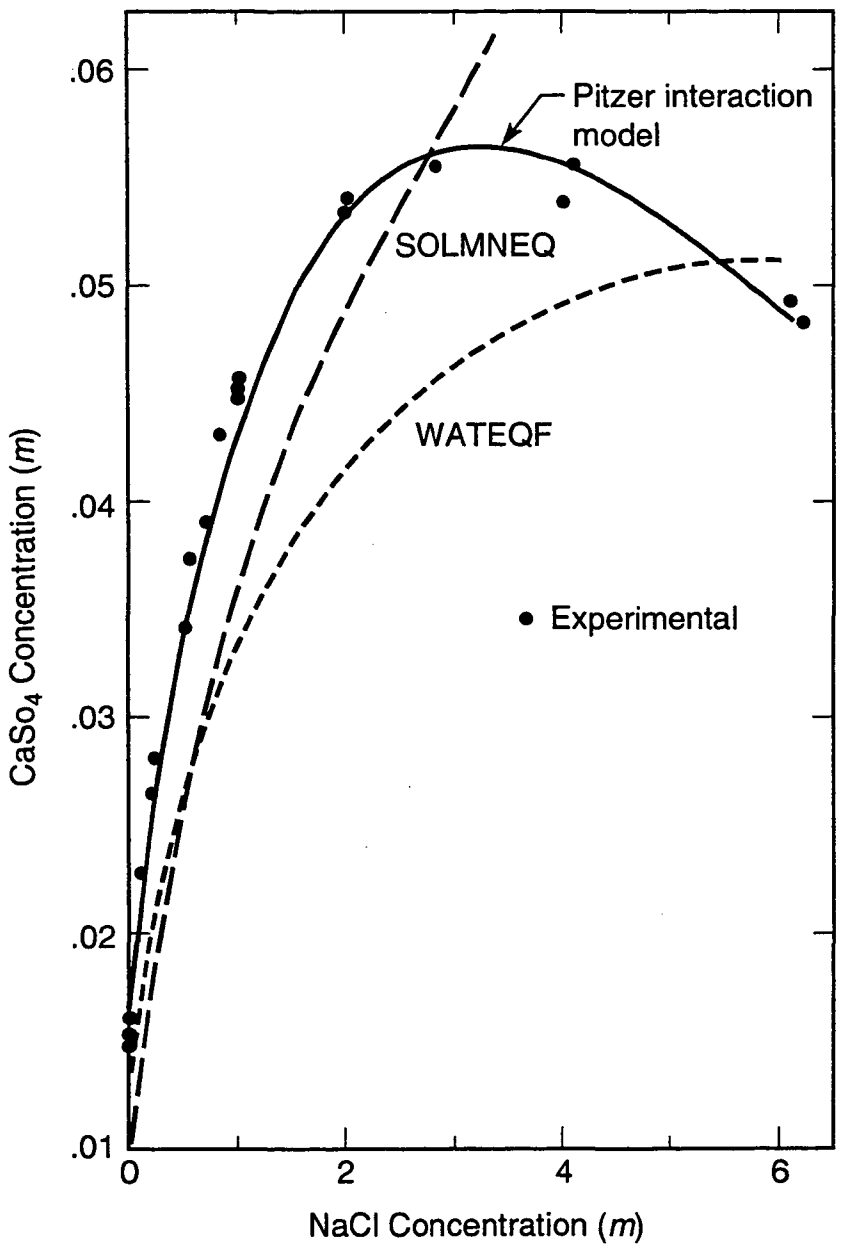


Figure 3.1. Comparison of Predicted Solubilities of Gypsum as a Function of NaCl Concentration Using SOLMINEQ, WATEQ, and the Pitzer Interaction Model with Experimentally Determined Solubilities (after Harvie and Weare, 1980)

occur, must involve the formulation of hybrid models. This is no easy undertaking, particularly with complex systems such as may be encountered during hazardous waste injection. Another minor problem is that applications of the model involve the use of mean activity coefficients for dissolved salt components rather than individual ion activity coefficients. The reason for this choice is that single ion activity coefficients are not normally measurable by thermodynamic methods, and transformation of the interaction equations to account for single ions results in additional terms that are also not presently measurable. Therefore, some effort is required to reconcile published standard state partial molal properties of charged species with equivalent neutral salts. In spite of these serious practical disadvantages, the Pitzer interaction model may find immediate application in modeling the neutralization of strong acids in injection zones.

## 3.5 Adsorption

### 3.5.1 Introduction

Adsorption is a phenomenon whereby molecular or ionic species attach to the surface of a solid. The process is thermodynamically reversible in principle, and therefore the laws of thermodynamics may be applied to describe the distribution of species between the surface adsorbent and the surrounding fluid phase.

Adsorptive phenomena are of major importance in retarding the transport of many potentially hazardous inorganic and organic compounds in soils, stream and river sediments, alluvia, and in the subsurface environment. If the waste stream chemical composition does not significantly affect the stability of the solid phases in the injection zone and contains hazardous constituents that adsorb on the mineral surfaces, then it may only be necessary to model the adsorption behavior of those species during waste transport to demonstrate containment in the injection zone.

Adsorption behavior under subaqueous conditions can be very complex, particularly at high sorbate concentrations, and where numerous different species, both inorganic and inorganic compete for adsorption sites. At low concentrations i.e. $<<10^{-3}$ *m*, however, quite simple relationships may be used to predict hazardous species transport. These are discussed further in the following paragraphs.

With some water miscible organic species, the amount adsorbed by a soil or sediment at a given aqueous concentration is directly proportional to the quantity of contained organic matter, e.g. see Westall (1987). It has also been found in soils and shallow sediments that mineral surfaces respond as adsorbents in quite different ways depending on the quantity of organic material present e.g. see Hassett et al. (1980) (cited in Karickhoff (1984)), regarding the sorption of biquinoline and pyrene. Soil scientists believe that the organic content of soils and sediments is present as a coating on mineral grains forming the matrix of the soil or sediment. The organic

layer inhibits , or at least retards adsorption of constituents dissolved in the aqueous phase on the mineral surfaces. Occasionally, however, the organic content is sufficiently low, that the mineral surfaces are exposed to the adsorbate. The organic coating responds quite differently to adsorption than does the uncoated mineral surface, which may have undergone alteration and weathering. Hence a bimodal sorptive behavior is sometimes observed. It has become common practice among soil scientists, therefore, to consider sorption by soils and sediments to be a function of both the organic coating and the mineral surface. This practice is probably applicable also to the rock matrix of deep well injection zones, as there is strong evidence for an organic coating on sand grains in oilfield reservoir rocks (Hyne, 1986). In the following sections adsorption on matrix surfaces is considered.

### 3.5.2 The Sorption Partition Coefficient, $K_d$

The sorption partition coefficient, otherwise known on the $K_d$ value is used by soil scientists to describe adsorption of inorganic or organic compounds on soils. $K_d$ is defined as the distribution of a given species between the solid and the solution, expressed a ratio of concentration, S, of sorbent adsorbed per unit mass of solid, to the concentration per unit volume of solution, C, expressed as $\frac{[M]\ [L]^3}{[M]\ [M]}$ ($ml.g^{-1}$ in c.g.s. units or $m^3.kg^{-1}$ in SI units.)

A common experimental procedure for determining the $K_d$ of a particular substance involves agitation of a suspension of a known particulate mass of soil or other solid in a solution of defined volume, and known concentration of sorbent. After allowing a specified time to elapse, the concentration of the sorbent in solution is measured, and the amount sorbed is calculated by comparing the initial and final concentrations in solution. The experiment can be repeated at different concentrations and a series of data points obtained. A graph of sorbed concentration versus aqueous concentration should yield a straight line passing through the origin with a slope of $K_d$. Hence

$$S = K_d C \tag{3-24}$$

$K_d$ measurements must be carefully conducted to ensure that sorption alone causes depletion of the sorbent in the solution. Precipitation may occur, which could lead to a calculated $K_d$ value with little meaning if the presence of precipitates were not recognized.

A second approach is to set up a column of soil or sediment and arrange for a steady state saturated flow of solvent (i.e. water) through the column. At a specified time, a pulse of adsorbing solute is introduced in the influent. The effluent is then monitored for the breakthrough and time dependent distribution of adsorbing solute in the effluent. The shape of the resulting elution curve is a measure of many potential variables, including non linearity of the isotherm, mass

transfer and sorption kinetics, dispersion and convection within the column.

A column packed with adsorbing materials may be considered as representing a stack of batch reactors in series. For very simple cases, where diffusion, dispersion, convection, isotherm non linearity and reaction kinetics play an insignificant role, a column elution study may be used to obtain a $K_d$ value of a sorbing species. For further details, the reader is referred to Schweich and Sardin (1981), who have reviewed the theory relating to sorption processes in batch reactors and columns.

The theoretical basis for the relationship between adsorbed and solute concentrations following a linear sorption isotherm with a constant $K_d$ may be derived as follows (Karickhoff, 1984). At equilibrium, the fugacity, fi, of a given chemical component is the same at the surface, (S) and in the aqueous phase, (aq). Therefore

$$f_i(\mathrm{S}) = f_i(\mathrm{aq}) \tag{3-25}$$

also

$$f_i(\mathrm{aq}) = \phi_i(\mathrm{aq})C_i \tag{3-26}$$

and

$$f_i(\mathrm{S}) = \phi_i(\mathrm{S})X_i \tag{3-27}$$

where $\phi_i(\mathrm{aq})$ and $\phi_i(\mathrm{S})$, are the respective fugacity coefficients in the aqueous and surface phases respectively, and $C_i$ and $X_i$ are the concentrations in the respective phases. Since

$$\frac{f_i(\mathrm{aq})}{f_i^{\circ}(\mathrm{aq})} = \gamma_i C_i \text{ and } \frac{f_i(\mathrm{S})}{f_i^{\circ}(\mathrm{S})} = \lambda_i X_i \tag{3-28}$$

$$\phi_i(\mathrm{aq}) = f_i^{\circ}(\mathrm{aq})\gamma_i \quad \text{and} \quad \phi_i(\mathrm{S}) = f_i^{\circ}(\mathrm{S})\lambda_i \tag{3-29}$$

where $f_i^{\circ}(\mathrm{aq})$ and $f_i^{\circ}(\mathrm{S})$ are the fugacities of the sorbing substance in its standard states. Equating fugacities and rearranging

$$X_i = K_d C_i \tag{3-30}$$

where

$$K_d = \frac{\phi_i(\mathrm{aq})}{\phi_i(\mathrm{S})} = \frac{f_i^{\circ}(\mathrm{aq})\gamma_i}{f_i^{\circ}(\mathrm{S})\lambda_i} = \beta\,\frac{\gamma_i}{\lambda_i} \tag{3-31}$$

It is clear from the devivation that $K_d$ incorporates the activity coefficients of species, i, in both aqueous and surface phases. So long as the relationship $\frac{\gamma_i}{\lambda_i}$ remains constant, or varies only

slightly, an approximately linear relationship will be observed, as would be expected at very low concentrations. Karickhoff et al. (1979) estimates an upper limit of $10^{-5}$ *M* for hydrophobic solutes or half their solubility in water. In aqueous systems $\gamma_i$ for a slightly soluble hydrophobic neutral organic compound, i, is expected to vary only slightly with increasing concentration of i, and would become invariant upon saturation of i. However, $\lambda_i$ may be expected to vary substantially, depending on the extent to which adsorption sites become saturated with i. Under these circumstances, the sorption isotherm may then become non linear. It has been found that the sorption isotherm may then be approximated by

$$X_i = K_F C_i^{\frac{1}{n}} \tag{3-32}$$

where $K_F$ is the Freundlich sorption constant, and n is the Freundlich parameter. This modification of the linear isotherm is discussed in a subsequent section. The relationship $\frac{\gamma_i}{\lambda_i}$ may also be extremely sensitive to environmental changes. Therefore large differences may be expected if the conditions under which a $K_d$ value is determined differ from those in the injection zone, e.g. see Reardon (1981). Table 3.1 adapted from an earlier publication (Apps et al., 1977) lists some of the variables and the impact they could have on $K_d$ if not controlled to replicate injection zone conditions.

The second problem with the application of measured $K_d$ value is the referencing of an adsorption process to the mass of the sediment rather than to its surface area. If the sediment retains a similar reactive surface area in its disaggregated form as *in situ*, as would be expected of unconsolidated sediments and soils, the measurement of $K_d$ on disaggregated material would introduce inconsequential errors. However, the disaggregation of a coherent rock by crushing and grinding will lead to a much larger specific surface area than is present in the injection zone. Furthermore, the newly exposed surfaces will not be representative, and may sorb differently than those normally in contact with the ground water. $K_d$ values acceptable for incorporation in geochemical models should therefore be made under physical conditions similar to those found in the subsurface environment unless a correlation can be established between the conventional method of measurement and *in situ* conditions.

A $K_d$ experiment is usually completed within a few days, whereas the hazardous waste steam may be in contact with the host rock for ten thousand years. The extent of sorption attained in a simple short-term $K_d$ determination may reflect metastable equilibrium or incomplete attainment of equilibrium. Over longer periods of time, surface structural changes, redox reactions, pore diffusion, interlayer diffusion in clays or body diffusion in solids may lead to significant changes to the initially determined value as the system trends towards equilibrium.

## Table 3.1

## Factors influencing $K_d$ for an adsorbent, based on conditions expected in a subsurface injection zone.

| Parameters | Principal effect | Injection zone conditions | Potential variation in $K_d$ |
|---|---|---|---|
| 1. Solution chemistry | | | |
| a. Major components | Ionic strength, complexing. | Determined by host rock chemistry and by other factors including the leaching chemistry of the waste product. | Difficult to predict probably $10^{-3}$ to $10^{+3}$ |
| b. Minor components | Complexing | Same as above. | Same as above. |
| c. pH | Complexing, hydrolysis. | 5.0 - 8.5 Buffering by heterogeneous and homogeneous reactions keep the pH range within narrow limits. | $10^{-5}$ to $10^{+5}$ |
| d. Eh | Change in redox state. | Variable, over a narrow range, usually reducing. | Up to $10^{10}$ or even more |
| 2. Hazardous constituent concentration | Supersaturation Polymerization, colloid formation. Metastable equilibrium. | Very variable concentration. Could range from 0 to 10,000 $mg.L^{-1}$. | Difficult to estimate, but could be very large for inorganic amphoteric species near the isoelectric point (~ $10^6$). |
| 3. Flow rate | Metastable equilibrium, colloid transport. 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 lead to different thermodynamic controls (0 to $10^6$) |

## Table 3.2 Continued.

| Parameters | Principal effect | Injection zone conditions | Potential effect on $K_d$ |
|---|---|---|---|
| 4. Permeability | Flow rate (see above). | 1 to $10^{-5}$ md. | Same as above. |
| 5. Surface area | Adsorption. | ~ $10^2$ $cm^2/g$ Fractures, microfractures, intergranular pores. | ~ $10^3$ |
| 6. Temperature | Complexing, solubility, adsorption. | 10 to 150°C | Up to $10^3$ |

Attempts to desorb a pollutant leads to observations of a similar phenomenon, in that the sorbent is slow to enter the aqueous solution and reestablishment of a new equilibrium state is slow. This hysteresis effect has lead some investigators to treat sorption as essentially an irreversible phenomenon, e.g. see Karickhoff (1980), Van Genuchten et al., (1974), and Di Toro and Horzempa (1982). In as much as the initial $K_d$ value is usually lower than those measured after longer times, the approach is conservative in that the initial $K_d$ of a hazardous constituent, will, when employed in a transport equation, over-predict the migration rate. For this reason, and because of their apparent simplicity, $K_d$ values have frequently been incorporated in models of hydrologic systems to simulate chemical transport, assuming that the conditions postulated in the model are identical to those in which the experiment to measure $K_d$ was conducted, and that the $K_d$ measurement reflects reversible equilibrium, which is rarely the case.

A potential disadvantage to the approximation that a short-term $K_d$ measurement reflects reversible equilibrium is that its use in transport models results in optimistic predictions of the recovery of pollutants from aquifers requiring decontamination. Although this problem is not germane to questions regarding confinement of hazardous waste in the injection zone, it does highlight one of the limitations in assuming reversibility when measurements have not demonstrated this to be the case.

As noted above, the exposed mineral surfaces in soils and shallow aquifers are prone to become coated with a layer of organic matter, especially matter containing carboxyllic groups, which attaches to silicate surfaces by ligand exchange. Bacterial cultures also grow on mineral surfaces and accumulate waste products of metabolism. The surfaces therefore become hydrophobic and preferentially adsorb hydrophobic compounds. Extensive evidence, (cited in Karickhoff, 1984) and by Chiou et al. (1983) supports the contention that the adsorption capacity is quantitatively related to the concentration of organic matter in sediments and soils. Therefore, the $K_d$ of uncharged hydrophobic organic compounds on a given soil may be predicted, where

$$K_d = \frac{\phi_i(aq)}{\phi_i(S_{oc})} \cdot f_{oc} \tag{3-33}$$

where $\phi_i(S_{oc})$ the fugacity coefficient of substrate, i, on the organic carbon substrate, and $f_{oc}$ is the fraction of organic matter present, or

$$K_{oc} = \frac{\phi_i(aq)}{\phi_i(S_{oc})} \tag{3-34}$$

Karickhoff (1984) cites several studies demonstrating the close correlation between the "carbon referenced sorption" and many soils with different organic carbon contents. The implication is that for a given uncharged hydrophobic compound, the behavior of the organic substrate is very

similar from one soil to the next. It has been further demonstrated that $K_{oc}$ for a given compound can be predicted from its solubility in water and its melting point, e.g. Karickhoff (1981) obtained

$$K_{oc} = -0.83 \log X_s - 0.01(mp-25) - 0.93 \tag{3-35}$$

where r = 0.93, for 47 organic compounds from five chemical families. Here $X_s$ is the mole fraction solubility and mp is the melting point in °C for a given compound.

A logical application of this concept is to take advantage of a pure organic compound that mimics, or at least possesses similar chemical properties to the naturally occurring organic coating. Laboratory measurement of the partition coefficient of a sorbing compound between the aqueous phase and the selected pure organic phase can then be used as a proxy for the organic coating. The pure organic compound selected for this purpose is octanol ($CH_3(CH_2)_6CH-OH$). The measured octanol/water partition coefficient, $K_{ow}$, can be expressed thermodynamically in terms similar to that of $K_d$ and $K_{oc}$, thus:

$$K_{ow} = \frac{C(oct)}{C(aq)} = \frac{\phi_i(aq)}{\phi_i(oct)} = \beta \frac{\gamma_i(aq)}{\gamma_i(oct)} \tag{3-36}$$

Because the solubility of octanol in water is low, $\phi_i(aq)$ remains nearly constant and equivalent to that of Eqn. (3-34). Hence, by combining Eqn (3-34) with Eqn. (3-36), a relationship between $K_{oc}$ and $K_{ow}$ is obtained:

$$K_{oc} = \frac{\phi_i(oct)}{\phi_i(S_{oc})} . K_{ow}$$

The regression of experimental data has established empirical correlations between $K_d$, $K_{oc}$ and $K_{ow}$ (Karickhoff 1984; Westall, 1987) that permit the calculation of $K_d$ from $K_{ow}$ and the organic content of a sediment or soil. $K_{ow}$ values for organic compounds may be obtained from reference manuals describing the properties of pollutants (Environmental Protection Agency, 1983), or they may be calculated (Karickhoff, 1984; Sims et al., 1988).

The preceding discussion is strictly applicable only to hydrophobic neutral organic compounds. Extension of the principles to hydrophobic ionizable and ionic organic compounds is somewhat more complex, but the same approach as that applied to hydrophobic neutral organic compounds can be applied in some instances. In situations where organic species are ionized, where inorganic species are potential sorbates, or where the organic content of the soil or sediment is low, sorption may take place on both hydrophobic and non hydrophobic surfaces, necessitating the use of a mixed model. In this case, $K_d$ becomes a function of both types of surface and the $K_d$ for a given species is dependent on contributions from both. Sediments, soils, and rocks are, however, composed of a number of minerals, each possessing differing non

hydrophobic surface characteristics. The sorption isotherm for such an assemblage may be quite complex and not amenable to approximation by a single $K_d$ value. Sometimes adsorption on one surface predominates and the isotherm remains linear or can be approximated by a Freundlich isotherm, but in general, more complex representations of adsorption behavior are required.

The direct measurement of sorption of a hazardous constituent during flow through a core from the injection zone under simulated down-hole conditions could allow an immediate estimate to be made of the sorption capacity and potential retardation in the injection zone. The results would probably be conservative, because the test would be of relatively short duration, and longer term processes involving diffusion into micropores or solid state ion exchange would not be observed. The injected formation would be relatively permeable and contain only minor concentrations of such sorbents as smectites, which would be more likely to be found in adjacent confining zones. The appropriate design of such an experiment would permit calculation of a $K_d$ for incorporation in a transport model.

### 3.5.3 Langmuir and Freundlich Isotherms

Because of the maximum aqueous concentration limitations imposed by the linear isotherm, various other isotherms have been explored in the hope that the distribution coefficient for a given adsorbate might be predicted at higher aqueous concentrations. Two well known forms of the sorption isotherm are due respectively to Langmuir and to Freundlich.

The basis for measurement of the Langmuir adsorption isotherm is that the surface of the adsorbing substrate, S, is covered by a monolayer of solvent, $Y_1$ and solute molecules, $Y_2$, in competition with each other. This formulation was originally applied to gas adsorption on a metal surface by Langmuir (1918). The reaction can be written thus,

$$Y_2(aq) + SY_1 = SY_2 + Y_1(aq) \tag{3-38}$$

for which the equilibrium constant, is

$$K = \frac{X_{SY_2} \cdot \lambda_{SY_2} \cdot C_{Y_1} \gamma_{Y_1}}{C_{Y_2} \cdot \gamma_{Y_2} \cdot X_{SY_1} \cdot \lambda_{SY_1}} \tag{3-39}$$

where $X_{SY_1} + X_{SY_2} = 1$, where $C_{Y_1}$ and $C_{Y_2}$ are aqueous concentrations, and where $\lambda$ and $\gamma$ are the respective activity coefficients of the sorbed and aqueous species.

Let $x_{SY_2} = X_{SY_2} \cdot x$, where x is the total number of moles of adsorption sites per gram and $x_{SY_2}$ is the number of moles of sorption sites occupied by the adsorbing solute per gram.

If $\frac{\lambda_{SY_2}}{\lambda_{SY_1}} \approx 1$, and for very dilute solutions, if $\gamma_{Y_2} \approx 1$, and letting $b = K/C_{Y_1} \cdot \gamma_{Y_1}$, we get

after rearranging,

$$\frac{C_{Y_2}}{x_{SY_2}} = \frac{1}{x.b} + \frac{C_{Y_2}}{x} \tag{3-40}$$

This expression, analogous to the gas adsorption equation due to Langmuir (1918), is known as the Langmuir adsorption equation. Note that a plot of concentration ratio, $\frac{C_{Y_2}}{x_{SY_2}}$ versus $C_{Y_2}$ should give a straight line with an intercept of $\frac{1}{x.b}$ and slope of $\frac{1}{x}$. Kincaid and Morrey (1984) have shown that the Langmuir adsorption equation is valid only at an extremely low concentration of the adsorbing solute and at fixed pH.

A fundamental assumption implicit in the derivation of the Langmuir adsorption equation, is that the surface activity coefficients of the adsorbing species are unity, i.e. adsorption behavior is ideal. Experience has shown that b varies with $\theta$, the fraction of surface occupied, suggesting that this assumption is not valid. Adamson (1982) points out that if the variation in b and $\theta$ is attributed entirely to a variation in the heat of adsorption then it is possible to derive an adsorption isotherm, where

$$\frac{x_{SY_2}}{x} = \theta = aC_{Y_2}^{1/n} \tag{3-41}$$

and where a is a constant and 1/n, the intensity of adsorption is such that n is greater than unity. This form is named after Freundlich (1926), who first made extensive use of it in many applications. The Freundich isotherm is usually rearranged and the observed adsorbence is plotted logarithmically, thus

$$\log x_{SY_2} = \log K_F + N\log C_{Y_2} \tag{3-42}$$

log $K_F$, the intercept, is the Freundlich sorption constant and N is the slope, which usually has value less than unity. A representation of a typical Freundlich isotherm is illustrated in Figure 3.2. Because N contains embedded in it a number of parameters that cannot easily be derived independently, the Freundlich isotherm equation remains an empirical formulation, albeit with some theoretical basis. Each Freundlich isotherm must be measured where all parameters other than sorbent concentration, e.g. pH, Eh, temperature and solution composition are kept 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 it has been used successfully in measuring the adsorption of a variety of metal ions on clays as part of the Civilian Radioactive Waste Management Project of the Department of Energy (1987), and in the sorption of organic species on clays and soils (Means et al., 1982; Sheindorf et al. 1982).

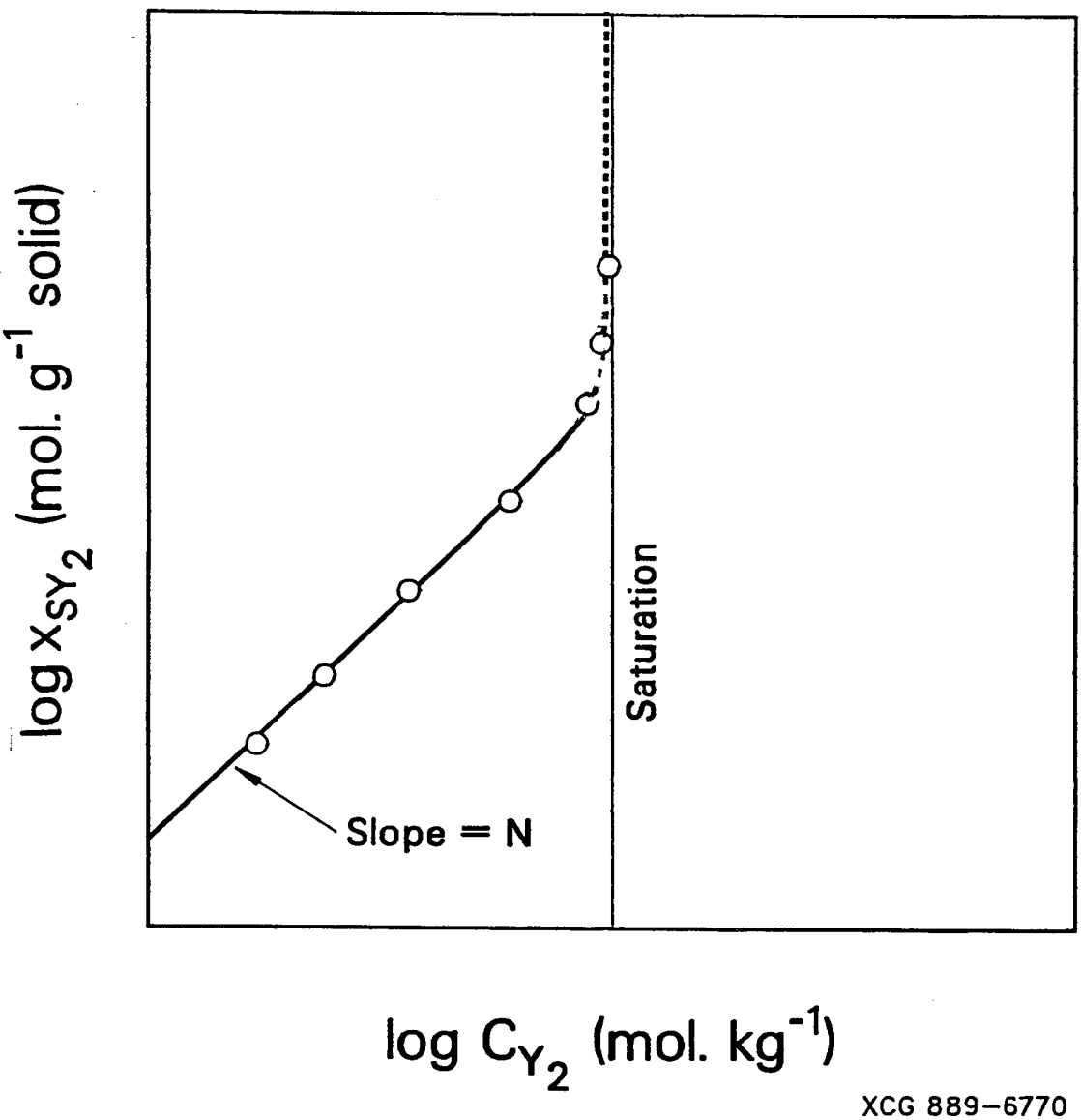


Figure 3.2. Representation of a Freundich Isotherm

### 3.5.4 Incorporation of Sorption Isotherms in Transport Equations

An attractive feature of sorption isotherms in that they may be very conveniently incorporated into transport equations. They have therefore frequently been used in hydrologic models to predict the transport of organic contaminents or radionuclides in the subsurface environment, e.g. the one dimensional differential equation used to describe solute transport, (after Javandal et al., 1984), is normally written as;

$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_j}\right] - \frac{\partial}{\partial x_j}(Cv_i) - \frac{C'W^*}{\phi} + \sum_{k=1}^{N} R_k = \frac{\partial C}{\partial t} \tag{3-43}$$

where

$$v_i = \frac{-K_{ij}}{\phi}\frac{\partial h}{\partial x_j} \tag{3-44}$$

and

| | |
|---|---|
| $C$ | solute concentration |
| $v_i$ | seepage or average pore water velocity in the direction $x_i$ |
| $D_{ij}$ | dispersion coefficient tensor |
| $C'$ | solute concentration in the source or sink fluid |
| $W^*$ | volume flow rate per unit volume of the source or sink |
| $\phi$ | effective porosity |
| $h$ | hydraulic head |
| $K_{ij}$ | hydraulic conductivity tensor |
| $R_k$ | rate of solute production in reaction *k* of *N* different reactions |
| $x_i$ | Cartesian coordinate. |

Recalling that

$$S = K_d C \tag{3-24}$$

and

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t} \tag{3-45}$$

The rate of solute production is

$$\sum_{k=1}^{N} R_k = -\frac{\rho_s}{\phi}\frac{\partial S}{\partial t} \tag{3-46}$$

Hence, by substituting Eq. (3-45) into Eq. (3-46) which is then substituted into Eqn. (3-43), the following equation is obtained:

$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_i}\right] - \frac{\partial}{\partial x_i}(Cv_i) - \frac{C'W^*}{\phi} = R\frac{\partial C}{\partial t} \tag{3-47}$$

where

$$R = \left[1 + \frac{\rho_s K_d}{\phi}\right] \tag{3-48}$$

and where R is known as the retardation factor. It is assumed that the sorption reaction is locally reversible. Thus it is possible in principle to estimate the degree of retardation expected for a given sorbent.

Substitution of the Freundlich isotherm in a differential equation to describe solute transport, follows that for the distribution coefficient, $K_d$, thus

$$\frac{\partial S}{\partial t} = KNC^{N-1}\frac{\partial C}{\partial t} \tag{3-49}$$

and

$$\frac{\partial}{\partial x_i}\left[D_{ij}\frac{\partial C}{\partial x_j}\right] - \frac{\partial}{\partial x_i}(Cv_i) - \frac{C'W^*}{\phi n} = \left[\frac{\rho_s}{\phi}KNC^{N-1} + 1\right]\frac{\partial C}{\partial t} \tag{3-30}$$

When desorption experiments indicate that the Freundlich adsorption process is not reversible, separate expressions for sorption and desorption are sometimes incorporated in transport equations, e.g. see Van Genuchten et al. (1974). Clearly, if the adsorption process does not show reversibility, then the implicit assumption that the Freundlich isotherm is an approximation of a thermodynamic process, as indicated in equation (3-41) and (3-42), is incorrect and the Freundlich isotherm has no theoretical basis. It would be preferable instead to use kinetic rate equations to describe the sorption process, e.g. Lapidus and Amundson (1952), Lindstrom et al. (1971) or Oddson et al. 1970, as cited in Van Genuchten et al. (1974).

### 3.5.5 Surface Complexation Models

Although linear sorption isotherms may find broad application in the modeling of the transport of hydrophobic organic compounds at very low concentration, and other isotherms may be used to extend the applicable hydrophobic organic concentration range, or to model the transport of ionic organic or inorganic species, their use in predicting the transport of hazardous species in

the injection zone may be limited by other factors.

In situations where the injected waste stream reacts with the injection zone host rock or ground water, and substantial changes in pH, Eh, ionic strength or ionic concentrations are expected, where competition exists among dissolved species for adsorption sites, or where hydrophobic surfaces are minimally present, more complex models are required. Unfortunately, increasingly complex models require the precise measurement of more parameters and a more rigorous definition of the conditions to be modeled.

In order to appreciate the successful modeling of adsorption processes over a wide range of solute concentrations in the aqueous phase, a brief description is given of the phenomena observed at the mineral-aqueous phase interface and how they have been formulated.

Mineral surfaces are invariably electrically charged, the charge arising from unsatisfied valences caused by the discontinuity in a crystal structure, or from polarization of molecules or atoms at the interface. Minerals in sediments and soils are usually negatively charged. The charge, which is intrinsic to the mineral, is referred to as a permanent structural charge. In the aqueous phase, this charge is partially satisfied with a tightly coordinated layer of so called potential determining ions, which bind to the exposed functional groups of the mineral. The surface charge resulting from this coordinated layer of ions may be either negative or positive. To preserve electrical neutrality a diffuse layer of counter-ions must accumulate in the aqueous phase adjacent to the surface. The resulting interfacial structure containing the surface layer with its attendant tightly coordinated ions and the diffuse layer of counter-ions is referred to as the electrical double layer.

The distribution of ionic species in the coordinated and diffuse layers are some function of the surface properties of the mineral and the activities of competing solutes in the aqueous phase. To predict quantitatively the adsorption of given solute, an electrostatic model is required that reproduces the behavior of the electrical double layer in relation to the solute species. The history of the development of such models and their current implementation spans a period of more than eighty years. Historical reviews are given by Bolt (1982), Bolt and Van Riemsdijk (1982), Sposito (1984), Westall (1987) and Davis and Kent (1990). At the heart of most models are variations of the Gouy-Chapman-Stern (GCS) model, based on the work of Gouy (1910), Chapman (1913), Stern (1924) and Grahame (1947). In the GCS model, the electrical double layer is described in terms of the charge per unit area of surface, $\sigma$, where

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \tag{3-51}$$

the subscripts o, $\beta$ and d referring to the permanent structural charge, the coordinated surface charge and the diffuse layer respectively; and where $\sigma_d$ can be calculated from the Gouy-Chapman equation for symmetrical electrolytes:

$$\sigma_d = -0.1174\ \sqrt{I}\ \sinh\frac{ze\psi_o}{2kT} \tag{3-52}$$

where

e = fundamental charge

k = Boltzmann constant

T = absolute temperature.

$\psi_o$ = electric potential at the surface.

I = ionic strength.

The other component of such models is the assumption that the mineral surface consists of one or more sites upon which species bind or complex, for which a modified form of the law of mass action applies. Determination of the binding constants for all participating species in a potential waste stream for each site on each mineral under the range of environmental conditions expected in the injection zone is one of the major hurdles confronting users of the more complex electrostatic models.

An example of one such model is a triple layer model (TLM), which has been refined, developed and tested over a number of years by faculty and research staff at Stanford University, e.g. Davis and Leckie (1978, 1980) and Kent et al. (1988). This model describes the surface of a mineral in terms of a site binding model, developed by Yates et al. (1974), and is combined with a surface-binding model by Davis et al. (1978).

This TLM can best be described by reference to Figure 3.3, adapted from Kent et al. (1988), with respect to a single oxide surface, such as silica ($SiO_2$) or corundum ($Al_2O_3$). The aqueous interface is subdivided into three layers, o (= surface) $\beta$, and d (= diffuse) layers. Each layer has an associated electrical potential, $\psi_i$, charge density, $\sigma_i^o$, capacitance, $C_i^o$, and dielectric constant $\varepsilon_i$. The interlayer spacings, $\beta$, $\gamma$ and d are as designated on the figure. It is further assumed that protons bind at the o plane, whereas electrolyte ions bind at the $\beta$ plane.

The surface, S, is assumed to be coated with hydroxyl groups, and that each surface site is represented by SOH. 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), thus:

$$SOH + H_s^+ = SOH_2^+\ ;\ \beta^+ = \frac{\left\{SOH_2^+\right\}}{\left\{SOH\right\} a_{H^+} \exp\left[\frac{-e\psi_o}{kT}\right]} \tag{3-53}$$

$$SOH = SO^- + H_s^+ \;;\; \beta^- = \frac{\left\{SO^-\right\} a_{H^+} \exp\left[\frac{-e\psi_o}{kT}\right]}{\left\{SOH\right\}} \tag{3-54}$$

$$SOH + X_s^- + H_s^+ = SOH_2^+ X^- \;;\; \beta^{an} = \frac{\left\{SOH_2X^-\right\}}{\left\{SOH\right\} a_{H^+} a_{x^-} \exp\left[\frac{-e\psi_\beta - e\psi_o}{kT}\right]} \tag{3-55}$$

$$SOH + M_s^+ = SO^-M^+ + H_s^+ \;;\; \beta^{cat} = \frac{\left\{SO^-M^+\right\} a_{H^+} \exp\left[\frac{e\psi_\beta - e\psi_o}{kT}\right]}{\left\{SOH\right\} a_{M^+}} \tag{3-56}$$

where:

$H_s^+, M^+s, X_s^-$ = ions in the bulk electrolyte near the surface.

$\beta^+, \beta^-, \beta^{an}, \beta^{cat}$ = intrinsic equilibrium constants.

The experimental terms relate the concentrations of the ions at their respective surface planes to those in the bulk solution. It is also assumed that the triple layer is electronically neutral, according to Eqn (3-51), i.e.

$$\sigma_o + \sigma_B + \sigma_d = 0$$

$\sigma_o$ and $\sigma_\beta$ can be related to the concentration of the sorbed ionic species by a factor F/S where F is the Faraday constant, and S is the surface to volume ratio. $\sigma_d$, the diffuse layer charge can be calculated from the Gouy-Chapman equation, Eqn. (3-52).

Many investigations have been conducted on a variety of oxide substrates and their adsorption behavior has been successfully modeled over a range of environmental conditions. Unfortunately, simple oxide surfaces are not the only surfaces a waste stream will encounter in an injection zone. Indeed, the adsorption capacity due to simple oxides may represent only a small fraction of the total adsorption capacity of the injection zone rock matrix.

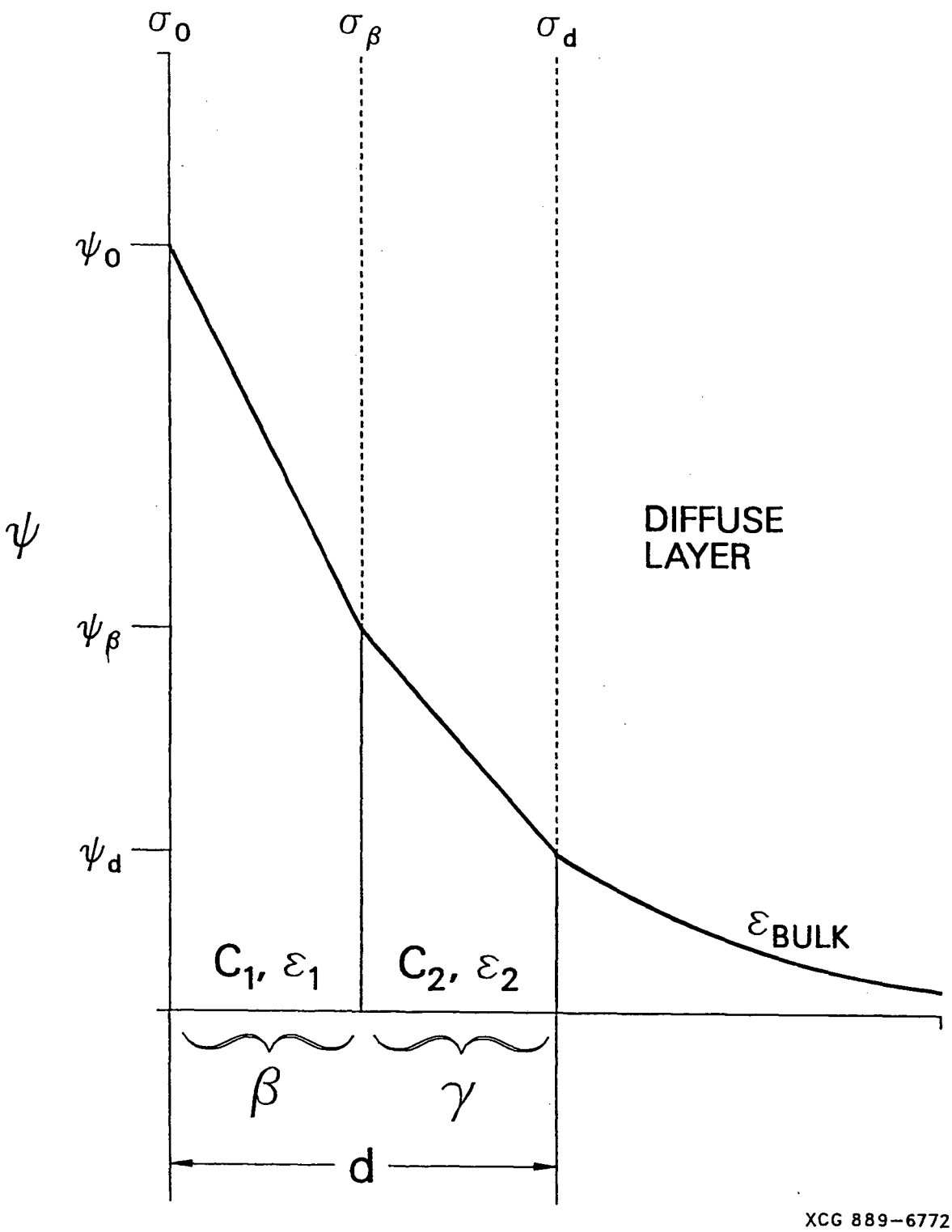


Figure 3.3. Representation of the Triple Layer Model for Adsorption (after Kent et al. 1988)

Kent et al. (1988) have classified minerals into four categories:

1. Simple oxides
2. Multiple surface-site minerals
3. Fixed charge minerals
4. Salt type minerals

The simple oxides represent the most tractable and easiest surfaces to model with the TLM. Somewhat more complicated are the "multiple site" minerals, such as silicates, aluminosilicates and complex oxides. Among these are the feldspars, which commonly occur as detrital or secondary minerals in deep aquifers. These minerals differ from oxides in that they possess more than one chemically distinct surface site. For example, potash feldspar, $KAlSi_3O_8$ would expose both SiOH and AlOH surface groups. However, Kent et al. (1988) note that data sets adequate to characterize the sorption properties of aluminosilicates do not exist. Thus the petitioners would be required to develop not only the necessary data but test a two or more site TLM, a formidable task if not affiliated with a university department specializing in such work.

Simple oxides and multiple surface site minerals have 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. In contrast, fixed charge minerals are represented as having a permanent negative charge due to the presence of substitutions in the lattice that are compensated by electrostatically bound exchangeable cations. Among these belong the clays, the zeolites and manganese oxides.

The ubiquitous presence of clays, their large surface area and cation exchange capacity make them extremely important as adsorbents, and they are expected to dominate the total adsorption capacity of the injection zone. Zeolites and manganese oxides are normally of lesser importance, as deep sedimentary aquifers, unless contaminated by ashfalls, are unlikely to contain zeolites, except laumontite, whereas manganese oxides are present only in minor amounts, or have been replaced by manganese containing carbonates. Both mineral groups, however, may be artificially created in an injection zone, through interaction of an alkaline waste stream with the preexisting clays and other matrix minerals.

To characterize the surface chemical properties of fixed charge minerals, requires measurement of both ion exchange and adsorption reactions. Although significant achievements have been made in the area, a database does not exist that would permit the prediction of clay mineral adsorption over a wide range of clay compositions and environmental conditions. Thus, the petitioner would again be at a serious disadvantage

in using the TLM unless he were to conduct extensive rigorous fundamental studies in support of his application. Similar problems apply to zeolites and manganese oxides, with the added complication that the latter group are also sensitive to the oxidation state of the system.

The fourth category are salt type minerals such as calcite ($CaCO_3$) and gypsum ($CaSO_4 \cdot 2H_2O$). In these minerals, the structure is an array of ionicly bonded anions and cations. The salt surface is likewise a grid like array of negatively and positively charged sites corresponding to a section through the ionic lattice of the solid. Kent et al. (1988) pointed out that the surface charge and potential is controlled by the relative abundance of the constituent ions in the associated solution, and only indirectly on the pH of the solution.

Adsorption on salts has not been investigated with any thoroughness, and potential adsorption mechanisms are speculative. For example, Kent et al. (1988) cite such reactions as

$$-Ca^+ + A_s^- = -Ca^+A^- \tag{3-57}$$

for anionic ($A_s^-$) adsorption or for cationic ($M_2^{2+)}$ or anionic ($A_s^{2-)}$ exchange, respectively, i.e.

$$-Ca^+ + M_2^{2+} = -M^+ + Ca_s^{2+} \tag{3-58}$$

$$-CO_3^- + A_s^{2-} = -A^- + CO_3^{2-} \tag{3-59}$$

Carbonates are frequently an important constituent of saline aquifer host rocks. Therefore, the mechanisms cited above would be of importance in the removal of heavy metals, for example. A careful study to evaluate the effect of surface ion exchange would be a necessary characterization step.

Finally, the behavior of organic matter with respect to molecular and ionic inorganic species should be considered. Kerogen is often an important constituent of shales. Kerogen may 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, may be reactive adsorbents. The specific surface area of organic detritus could be quite large and make a significant contribution to the total adsorption capacity of the sedimentary rock comprising the injection zone. (Sposito, 1984; Karickhoff, 1984). Associated surface complexation reactions similar to those given in Eqns. (3-52) to (3-55) might also be developed to describe surface adsorption reactions on organic material.

Regardless of the type of mineral substrate to be investigated for its adsorptive properties, careful characterization of the material being studied is a necessary pre-requisite for the TLM. The specific surface area must be measured, usually by the BET method, as well as the surface site density, and whether or not the sites are of more than one type. As with simpler adsorption experiments, it is essential that the exposed surfaces be representative of the undisturbed material, and not be comminuted or disaggregated.

Formulation of the TLM assumes experimental characterization of the adsorbent properties as a suspension or slurry in the aqueous phase. However, with changing suspension concentrations, particles come into contact with each other and, modify the apparent surface properties of the adsorbent. Still greater effects have been observed in the properties of two different adsorbents when mixed. It would have been advantageous if the sorption properties of an aggregate of different adsorbents were additive, obeying the so called the Linear Adsorbtivity Model (LAM). However, experimental studies reported by Honeyman (1984), and unpublished studies conducted by Dr. R. Myer, ORNL (personal communication) reveal that major non linear effects on adsorption are sometimes observed with mixtures. The LAM may therefore be an exception rather than the rule.

Even if the surface area and the density of a material can be properly characterized, a complete analysis of its adsorption characteristics would require a lengthy series of painstaking experiments in which the adsorption capacity is examined over a wide range of pH, ionic strength and coexisting solution compositions, including variation in the total concentration of adsorbate(s). Only then would it be possible to compute the appropriate binding constants for the material being investigated. Such an analysis will of necessity require a corresponding electrolyte model which accurately replicates the thermodynamic properties of the solute species. Conventional models in which a single parameter extension of the Debye-Hückel equation for individual ion activity coefficients is used, as in the MINEQL code (Westall et al., 1976) are limited to an ionic strength of 0.1 for accurate modeling, or 0.5 for less precise interpretations. As noted earlier, 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)

The incorporation of any site complexation model in transport equations is a challenging proposition, especially if the resulting model is to have widespread application. One successful implementation has been made by Krupka et al. (1988) in which a substantial simplification of a surface complexation model was developed to calculate the adsorption behavior of aqueous constituents on hydrated ferric oxide (HFO-). This so

called specific ion adsorption model was designed for incorporation in FASTCHEM™, a proprietary code developed under Electric Power Research Institute sponsorship, to predict the subsurface transport of leachates from utility fly ash impoundments (Hostetler et al., 1989). In shallow soils and sediments, reactive amorphous or microcrystalline precipitates of ferric iron often form from supersaturated solution on the surfaces of mineral grains. An empirical measure of the amount of such reactive material may be obtained from the amount of ferric iron readily dissolved by a hydroxylamine hydrochloride solution.

The model is essentially a single site model in which the negatively charged sorbent, HFO-, may complex with one or two protons to form HFO-$H^o$ and HFO–$H_2^+$, thus:

$$HFO- + H^+ = HFO-H^o \quad , \tag{3-60}$$

and

$$HFO- + 2H^+ = HFO-H_2^+ \quad . \tag{3-61}$$

The respective surface acidity constants were adjusted to fit experimental data with an additional constraint on the second constant that the point of zero charge (pzc) occurred at pH = 8.11. With the exception of $H^+$ for which two site complexation reactions were permitted, all other species were permitted only one reaction. Electrostatic terms were also ignored. Thus, the only parameters requiring adjustment were the constants for site binding reactions of various aqueous species with the HFO- site as a function of total mass balance and species concentration in the aqueous phase. Examples of such reactions include

$$HFO- + SO_4^{--} + 2H^+ = HFO-H_2SO_4^- \tag{3-62}$$

$$HFO- + CrO_4^{--} + 2H^+ = HFO-H_2CrO_4^- \tag{3-63}$$

$$HFO- + Cd^{++} = HFO-Cd^+ \tag{3-64}$$

The complexation constants were adjusted so that the differences between model predictions and experimental data for the single species were minimized. The experimental data reported in the literature, were obtained at low adsorbate concentrations, low surface adsorbate densities and low ionic strengths, and restricted to 25°C. Because the model does not incorporate electrostatic terms, it is insensitive to ionic strength, and is therefore inconsistent with experimental data at higher ionic strengths (Krupka et al., 1988).

The development of the hydrated ferric oxide specific-ion adsorption model for FASTCHEM™ is a useful development, which goes beyond the limitations of simple

isotherms by accounting for competitive site occupancies of ionic species as a function of pH, and illustrates the potential of site complexation models. Its limitations, restriction to a hydrated ferric oxide adsorbent, lack of ionic strength dependence, single site occupancy, and model dependent site binding constants limit its flexibility and applicability, especially with respect to typical highly saline injection zone conditions found in Class 1 wells.

### 3.5.6 Applicability of Adsorption Models to Injection Zone

Adsorption undoubtedly plays an important role in retarding hazardous wastes and confining them to the injection zone. The choice of adsorption model by the petitioner is constrained by its applicability to the waste stream composition and the chemistry of the injection zone rock matrix and ground water. Available information is drawn primarily from extensive research that has addressed issues pertinent to environmental conditions in soils and shallow sediments rather than deep injection zones. With respect to the adsorption of hydrophobic non-polar organic compounds with limited aqueous solubility, much of the literature presumes the presence of organic coatings and residues on the principal adsorbents. The presence of similar organic material in the injection zone would be expected, especially in aquifers containing oil field brines. However the nature of such material and its sorbing characteristics requires clarification. If the only constraint on the waste stream were the presence of hazardous non-polar organic compounds at low concentrations, i.e. $<10^{-5}$ $m$, then the judicious use of relevant $K_d$ values in reactive transport models may be sufficient for predictive purposes.

For polar organic and ionic organic, or inorganic hazardous wastes in low to moderate concentrations, i.e. $<10^{-3}$ $m$, Freundlich isotherms obtained under site specific conditions may suffice. For waste streams containing high concentrations of hazardous constituents that compete for site occupancies, or modify or destroy the adsorbent, however, substantially more complex models would be required for accurate simulations of waste transport in the injection zone. The TLM would, if sufficiently well developed, fulfil the the need for competitive adsorption, especially of inorganic hazardous constituents.

Site complexation models, such as the TLM, for all their sophistication, are presently of limited value. This is because:

(a) Site binding constants have been determined only for a limited range of simple oxides with only one type of surface site.

(b) The petitioner would be required to conduct extensive fundamental studies of common clays and other minerals found in a typical injection zone matrix. There is considerable uncertainty that he would be successful.

(c) No satisfactory model has been developed that would permit predictions of adsorption properties of mixtures of sorbents based on the properties of individual sorbents.

(d) No satisfactory means of measuring and interpreting the sorptive properties of intact host rock in relation to site complexation models has been developed.

(e) Present site complexation models are restricted in their application to coexisting electrolytes with ionic strengths much less than unity.

For those situations where these limitations are not fatal, the petitioner can take advantage of the TLM using the MINEQL code which embodies the model, (Westall et al., 1976), or the MINTEQ code which combines MINEQL with WATEQ (Felmy et al. 1984; Krupka and Morrey, 1985).

Section 4

# THERMODYNAMIC DATA BASES

## 4.1 Introduction

It is frequently necessary to reduce experimental data from the literature or elsewhere in order to derive needed thermodynamic data to solve geochemical problems. Usually, it is preferable first to derive reference state properties of a phase i.e. $\Delta H^o_{f,Tr,Pr}$, $\Delta G^o_{f,Tr,Pr}$, $S^o_{Tr,Pr}$, and $C^o_{Pr,Tr}$, and $V^o$, or the corresponding partial molal properties for an aqueous species at the reference 25°C and one bar or one atmosphere pressure, and then use thermodynamic equations to predict the properties at the conditions required for the simulation. The temperature difference between the normally accepted reference state and the injection zone is usually only 5 to 50°C, whereas the pressure difference is between 50 and 300 bars. Such differences lead to small but sometimes significant changes in the thermodynamic properties of participating species. The magnitudes of such changes should be estimated when it is suspected that failure to account for them would increase the uncertainty of model predictions. As noted in Section 3, corrections for pressure and temperature should also be made when interpreting laboratory experimental measurements or field measurements if the precision of the measurements justifies such a course of action.

Thermodynamic data can be retrieved through a variety of techniques. The most precise usually involve direct calorimetric methods of measuring 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. From these measurements, the respective values of $S^o_{f,P_r,T_r}$ and $\Delta H^o_{f,P_r,T_r}$ may be derived as well as their functional dependence on P, and T.

Numerous other methods are available for computing the thermodynamic properties of a phase or species by less direct methods, e.g. from phase equilibria, solubility (miscibility) electrochemical or spectrometric data or even, in the case of geochemical reactions, phase relations and groundwater compositions observed in the field. A discussion of the techniques used is given in Robinson et al. (1982). Often, the thermodynamic characterization of a phase or species is made using a combination of techniques, some of which may be redundant. Reconciling the results from differing sources of information, and reaching a consensus as to what is the "best value" for a particular thermodynamic parameter, is an art practiced by specialists at various institutions and universities around the world. However, the petitioner may discover that "best values" may not

be available for the minerals or species with which he must contend. Therefore, he may be forced to conduct his own critical evaluations.

Because of the importance of the thermodynamic properties of chemical substances to industry and the sciences, many compilations have been published over the years. Two of the largest are the JANAF (Joint Army, Navy and Air Force) Tables (Chase et al. 1979), and a Russian counterpart, the "Thermal Constants of Compounds" (Glushko, 1965). Both publications include a large range of inorganic solids, liquids, gases and aqueous species. Compilations restricted to geochemical interests include that by Robie et al. (1979) and a Russian counterpart, Naumov et al. (1971). All of these compilations reference original source material, and the data published have received careful scrutiny. However, the petitioner will find that the information presented therein may have to be reconciled with more recent material, or may require an independent reevaluation in response to his specialized needs. In particular, it should be noted that recent studies in the field of geochemistry have focussed on statistical e.g. Holland and Powell (1990) or linear programming methods, e.g. Berman (1988) to ensure internal consistency of thermodynamic data sets.

In the following sections, the availability, reliability and suitability of reference state thermodynamic data is discussed in relation to geochemical modeling needs for the petitioner.

### 4.2 Minerals

In recent years, internally consistent thermodynamic data of mineral phases have been compiled and evaluated, using information derived from both 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) and Holland and Powell (1985, 1990). These compilations serve to highlight inconsistencies between independent sets of experimental data, and to influence the direction of further research towards resolving them. Estimation of the thermodynamic properties of minerals normally requires the application of "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. Specific techniques for refining the data and reconciling inconsistencies vary with investigator. The traditional method, used by Helgeson et al. (1978) is to compare various data sets and make judgemental decisions as to which set(s) are more likely to be correct or of better quality.

Statistical techniques are then used to refine the data and obtain "best values" of the thermodynamic parameters, usually starting with a reference standard such as corundum or quartz, and progressing sequentially from well established mineral thermodynamic properties to those that are less well characterized. This method is conceptually satisfying in that it permits the investigator to start from a secure base, and concentrate on the evaluation of specific subsets of experimental data. However, it possesses a disadvantage in that errors can be propagated rather than distributed.

More recent efforts are being made to eliminate, or at least mitigate inconsistencies in earlier compilations. New techniques are being employed in which internally consistent functions are used to analyse related thermodynamic parameters, and large numbers of data sets are analyzed simultaneously in order to find those that are consistent. The first method involves 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 first described by Haas and Fisher (1976) and was used by them in several compilations, e.g. Haas et al. (1981) and Robinson et al. (1982). It has also been applied by Holland and Powell (1985, 1990).

The second technique, suggested by Gordon (1973) and utilized by Halbach and Chatterjee (1982, 1984), Chatterjee (1984), Berman et al. (1985) and Berman (1988) is to employ linear programming methods, whereby all data sets are again compared simultaneously. Haas (1985) lists the relative advantages of the two methods. Regardless of the approach used, the most important requirement is that the investigator assume a very critical attitude towards the data, and that he ensure that the maximum number of independent checks are available to verify the selected thermodynamic parameters. It is often better to test separate combinations of data sets, where one or more inconsistencies are detected, so that reasons for the inconsistencies might be clarified.

The data sets employed in computing the thermodynamic properties of minerals include the usual calorimetric, phase equilibrium, and solubility data. Most of the data currently available for minerals falls into the first two categories. With the exception of quartz, and readily soluble salts such as the carbonates and sulfates, few solubilities on rock forming minerals have been made. This constitutes a serious deficiency in present mineral thermodynamic databases, as they are often used extensively in the prediction of mineral solubilities in groundwater systems. In other words, the databases have not been adequately "verified" through independent tests.

Direct comparison between different thermodynamic compilations e.g. between Helgeson et al. (1978) and Berman et al. (1985) often show major inconsistencies in the

properties of a number of minerals. This arises from interpreting the same data in different ways, or in using different techniques to estimate thermodynamic parameters for minerals where no experimental data are available. The consequences of such differences on model predictions can be small if the data from one compilation alone is used, because the data are internally consistent and errors introduced in the thermodynamic properties of one species are often inadvertently offset by compensating errors in other species to ensure consistency with experimental observations. However, large and unpredictable errors in model prediction can result from the indiscriminate selection of thermodynamic properties from different databases, or from a selected database when the thermodynamic properties, derived from high temperature phase equilibrium or calorimetric data, are used to predict mineral solubilities under injection zone conditions.

Another source of error is the inadequate characterization of the mineral(s) under consideration. This most often arises in the interpretation of laboratory phase equilibrium studies where equilibration times were relatively short, or the temperature was relatively low. In such situations, fine crystallite size, site disorder, metastable polymorphs, or unknown contaminants can drastically affect the perceived equilibrium state. The original investigator was often unaware of the complications and therefore failed to take note of, or characterize his reaction products with the rigor required. In other situations, the experimental set-up itself apparently resulted in wholly erroneous results, such as the phase equilibria data obtained by a uniaxial press when a vapor phase participated in the reaction, (see Delany and Helgeson 1978, regarding the work of Kennedy (1959).

In spite of the difficulties inherent in the computation of mineral thermodynamic data, much progress has been made in recent years. The database selected by the petitioner should be screened for inconsistencies, and he should ensure that it is internally consistent. This last consideration is often overlooked by *ab initio* users of computer codes and, as noted above, can be a major source of error. In mineral thermodynamic databases, all minerals should be referenced to the oxides, metals or other primary reference standards. Unfortunately, thermodynamic databases used in many geochemical computer codes are often compiled from a variety of independent sources without the referencing required.

Although internally consistent thermodynamic data bases for minerals have become more comprehensive in recent years, thermodynamic data for many mineral phases of relevance to host rock - groundwater interactions are either poorly determined or totally lacking. This applies particularly to the clays. Clays are for the most part solid solutions, and satisfactory models to describe the thermodynamics of solid solutions are only

in the formative stages (see Section 3.2). Clays are finely crystalline. Therefore, a significant contribution to their thermodynamic stability is the surface free energy (Stumm and Morgan, 1970), a factor that is usually omitted in the thermodynamic modeling of rock-water interactions.

Many other detrital minerals and alteration products are solid solutions, e.g. feldspars, pyroxenes, amphiboles, zeolites, carbonates and sulfates. Not only have generally accepted solid solution models not been formulated for use in reactive transport modeling studies, but even the thermodynamic properties of some of the end members remain in doubt, e.g. anorthite (Chatterjee et al., 1984; Berman, 1988).

Finally, it should be recognized that waste streams may contain substantial concentrations of electrolytes, such as mineral acids. The petitioner might find it necessary to conduct his own literature search and generate his own thermodynamic data for unusual phases that might precipitate during reaction of these waste stream components with the injection zone rock matrix. (see Section 6.2).

### 4.3 Organic Compounds

When waste streams contain organic compounds, they are for the most part dissolved in the aqueous phase. Occasionally, immiscible organic compounds may be pumped underground, either entrained in the aqueous phase as globules or micelles, or as an organic liquid. As may be noted from Section 2, the range of organic compounds requiring consideration is substantial. Many have not been characterized in terms of $\Delta G_f^o$, $\Delta H_f^o$, $S^o$ and $V^o$, although such information alone is of value only if it is to be used to predict the relative stabilities of different organic compounds as a function of temperature and pressure.

Most organic compounds in injected waste streams are unstable in the subsurface environment and will ultimately decompose. Kinetic data concerning their decomposition is therefore often of greater interest than their thermodynamic properties. For those organic compounds that are water miscible, and whose decomposition rates are very slow or are poorly known, sorption mechanisms to demonstrate containment might be required. Their sorptive properties can be characterized using either a measured or predicted linear isotherm constant, $K_d$. Because $K_d$ can be related empirically to $K_{oc}$, the sorption constant for organic carbon in soils, and $K_{ow}$, the octanol-water partition coefficient, and to the solubility of the organic compound in water (see Karickhoff, 1984), information that contributes to the determination of any of these parameters is of interest to the petitioner.

Thermodynamic compilations for $C_1$ and $C_2$ compounds may be found in Wagman et al. (1982). Data for these and more complex organic compounds may also be found in Cox and Pilcher (1970), Domalski (1972), Stein and Barton (1981), and Domalski et al. (1984).

If the thermodynamic properties of an organic compound are not available, it is possible to estimate the properties by considering the organic compound to be a collection of constituent fragments, each fragment contributing to the thermodynamic property. Various methods using this approach have been formulated, e.g. see Janz (1958) and Shaub (1982a, b), the precision achievable varying with the complexity of the organic compound and the sophistication of the model. For most compounds, an order of magnitude estimate of $\Delta G_f^o$ at the 25°C may be adequate to predict the sorption properties for petitions, e.g. see Leo et al. (1971) and Leo (1975).

Data on water solubilities and octanol-water partition coefficients have been compiled by Banerjee et al. (1980), Pearlman et al. (1984) and the Environmental Protection Agency (1983). A very large compilation of organic compound solubilities has also been made by Yalkowsky et al. (1987). Physical property data are also available in computer compilations prepared by the Syracuse Research Corporation (1986). Solubilities of gases in water have been compiled by Wilhelm et al. (1977). Water solubilities of polynuclear aromatic and heteroatomatic compounds have been measured by Sarna et al. (1984). Equivalent octanol-water coefficients of indolizine and 2-phenylindolines have also been determined by Lins et al. (1982) using high pressure liquid chromatography.

For those compounds for which solubilities are unknown, methods are available, as for thermodynamic properties, for their calculation. Nirmalakhandan and Speece (1989) compared three different methods for computing the solubilities of organic compounds, and concluded that the "Connectivity-Polarizability" approach was able to predict log S (*M*) with an absolute average error of 0.22, an accuracy that should certainty be adequate for most petitions. Methods to calculate the $K_{ow}$ and $K_d$ values, either directly or through solubility measurements are summarized by Karickhoff (1984). Sims et al. (1988) also describe and tabulate calculated $K_d$ values for 56 EPA listed hazardous chemicals.

It should be remembered that calculated $K_d$ values are valid only to a maximum concentration equal to about half the saturation concentration of the organic compound. Furthermore, where complex mixtures of organic compounds are present, competition for adsorption sites may result in effective $K_d$ values that differ from those calculated under conditions, where no competition is assumed. Experimental verification of the calculated

$K_d$, using realistic mixtures would be preferable, if there is reason to doubt the calculated values.

## 4.4 Aqueous Species

### 4.4.1 Inorganic Species

In common with other thermodynamic data bases, the standard state properties for aqueous species, i.e. $\Delta\overline{H}_f^o$, $\Delta\overline{G}_f^o$, $\Delta\overline{S}^o$, $\Delta\overline{C}_p^o$, consist either of uncritical compilations from various literature sources, or those where the data have been "critically reviewed," and the "best values" selected. Critical review entails going back to the original sources, and sometimes reevaluating the raw data, identifying potential sources of error and reconciling discrepancies. Incomplete or questionable data may be augmented, rejected or accepted through the use of correspondence plots, e.g. 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 may be reconciled using techniques, such as those adopted by Cobble et al. (1982) Phillips and Silvester (1984) or through the use of more elaborate models such as the HKF EoS (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 notable titration techniques developed by Sillen and his coworkers (Sillen, 1962). The petitioner should be fully aware of the techniques, assumptions and models used in the critical review. Critically reviewed data should be available in the standard state, i.e. that of a hypothetical one molal solution with unit activity (e.g. see Garrels and Christ, 1965) and not in an uncorrected form at the ionic strength of a supporting electrolyte such as a non complexing perchlorate. The petitioner should preserve a healthy skepticism when confronted with claims for the existence of a poorly substantiated complexes, whose only justification is that its existence permitted the investigator to obtain a better fit to his data.

Uncritical compilations are often very comprehensive e.g. Sillen and Martell (1964), and are a wealth of information. They serve both to assess the level of knowledge regarding a particular complex, and the level of agreement between different investigators. They are important sources of information upon which a critical review might be based. Other compilations of potential interest to the petitioner are those by Martell and Smith (1974) and by Perrin (1979,1982).

### 4.4.2 Organic Species

Thermodynamic properties of organic molecules in the aqueous phase will be of particular interest to may petitioners. To calculate such properties, usually requires some knowledge of reactions involving hydration of the species, thus

$$Y_o(g,l,s) = Y_o(aq) \tag{4-1}$$

where the subscript, o, refers to any organic species. $\Delta G_r^o$ of such a reaction can be computed from solubility studies, which, combined with the $\Delta G_f^o$ of the pure substance in its gaseous, liquid or solid state, will yield $\Delta \overline{G}_f^o$ of the molecular species in solution. Temperature dependent aqueous solubilities permit determination of $\Delta \overline{H}_f^o$ and $\Delta \overline{S}^o$ for the hydrated species. Compilation of the thermodynamic properties of hydration for many organic species have been made, e.g. Cabani et al. (1981), Abraham (1982, 1984). Shock and Helgeson (1988a) have recently compiled listing of thermodynamic properties of aqueous organic species, for use with the HKF EoS. Comprehensive compilations of thermodynamic properties, and dissociation constants of aqueous organic species may also be found in Sillen and Martel (1964), Christensen et al. (1967), Perrin (1972), Martell and Smith (1974) and Perrin (1979). As with corresponding compilations for inorganic liquids, discretion should be used in their application. It is at all times advisable to check the original sources, and to conduct a literature search for more recent data, before using the information in geochemical models.

### 4.5 Adsorbed Species

The thermodynamic properties of adsorbed species are limited primarily to reference temperature and pressure values, (25°C and 1 atm pressure). Compilations based on the TLM model have been summarized (Kent et al., 1988), but as noted in Section 3.5.4, most such data pertains only to oxide substrates. Properties are usually given as dissociation constants. Recently, Dzombak and Morel (1990) have advanced the concept of tabulating model independent surface complexation constants of sorbed species, and have compiled such constants for species binding on hydrous ferric oxide.

Organic and organometallic species adsorb on clays through a variety of mechanisms, (e.g. see MacEwan and Wilson, 1984 and Laszlo, 1987). A vast body of literature describing sorption on clays and organophilic substrates exists in an uncompiled form. Many studies have been conducted on specially cleaned and characterized clays whose sorption properties might bear little relation to those found *in situ*, except where no organic matter is present. Information is available in the form of various sorption isotherms, exchange constants, e.g. Bruggenvert and Kamphorst (1982) or $K_d$ values, e.g. see

Schellenberg et al. (1984) and Karickhoff (1984) for references. There is a pressing need for a survey of such information and the development of standard procedures for presenting adsorption data in a model independent form.

### 4.6 Miscellaneous

The preceding three sections are devoted to well defined phase and species whose thermodynamic properties can, in principle, be precisely determined. During deep well injection, other substances can form or are already present, whose thermodynamic properties are not so easily characterized. These include such diverse phases as kerogen, colloids, micelles, organic liquids, amorphous gels, and adhering surface material and organic slimes of ill defined composition or structure. Such substances may play a dominant role in mobilizing or immobilizing hazardous waste constituents. Geochemical models generally do not account for such materials. If organic liquids are expected to separate from the aqueous phase, then a model designed to determine the partitioning of organic compounds between aqueous, oil and gas phases for a specified bulk composition, temperature and pressure, which was developed by (Weres et al., 1986), and embodied in the computer code RELAX, could be of interest to petitioners.

Colloids may affect the distribution of hazardous species in the injection zone. A review of colloid transport processes is given by McCarthy and Zachara (1989). Because of their mass, colloids diffuse through the aqueous phase at rates that are orders of magnitude less than molecular or ionic species. They are therefore likely to be transported and disperse hydrodynamically in the same manner as the waste stream solvent, but are unlikely to diffuse into the pores of the rock matrix to any extent. Colloids are also prone to adsorption and to gravitational settling. Consequently, they may not be a significant factor in the migration of hazardous constituents, after hazardous waste injection has terminated (Apps et al., 1982, p. 70–80).

Section 5

# NON-EQUILIBRIUM SYSTEMS

## 5.1 Introduction

Many reactions in an injection zone proceed sufficiently rapidly that local reversible equilibrium may be assumed with reasonable confidence. Among these are most homogeneous reactions in the aqueous phase, (with the exception of some oxidation-reduction reactions) and surface sorption or ion exchange reactions. At the other end of the spectrum are some reactions where rates are so slow that equilibrium is not attained, even after 10,000 years. In this case, hydrologic arguments alone would have to be used to demonstrate containment. Several categories of chemical reactions proceed sufficiently slowly that local equilibrium cannot be assumed, yet substantial progress towards equilibrium is achieved within the 10,000 year time frame. For predictive modeling purposes, we need to know the range of magnitudes of those rate constants, $k_i$ ($s^{-1}$), of chemical reactions that fall between the two extremes must be quantified.

The attenuation of a species in solution to nonhazardous levels, whether through sorption, precipitation or decomposition, is dependent, not only on the rate constant, but also on the initial concentrations of it and other participating species, as well as the substrate area and reaction site density when a heterogeneous reaction is involved. The reaction rate order for decomposition of a hazardous constituent will vary, depending on the mechanisms involved. Many decomposition reactions are, however, first order with respect to the concentration, which greatly simplifies the reaction scheme. If the reaction is first order, then

$$\frac{dC_i}{dt} = -k_i C_i \tag{5-1}$$

where $k_i$ is the first order rate constant. By rearranging, integrating and normalizing the concentration to the initial concentration at t = 0, the following expression is obtained;

$$t_{C_t} = \frac{\ln C_{i,t}}{k_i} \tag{5-2}$$

$$\text{or } \log k_i = \log (\ln C_{i,t}) - \log t_{C_t} \tag{5-3}$$

Figure 5.1 shows a graph where log $k_i$ ($s^{-1}$) is plotted against log t (yrs) for various attenuations in concentration, from $10^{-1}$ to $10^{-10}$ times. For a range of attenuation factors between $10^{-1}$ and $10^{-10}$ of the initial concentration, and for reaction half lives greater than one year, it is evident that rate constants greater than $10^{-6}.s^{-1}$ are of little concern because the hazardous constituent will be immobilized or destroyed in the vicinity of the injection well.* At the other extreme, if the rate constant is less than $10^{-11}s^{-1}$, then the attenuation will not be significant in 10,000 years. For irreversible first order reactions to be of interest to the petitioner therefore, the rate constant would generally fall between $10^{-11}$ and $10^{-6}$ $s^{-1}$.

Of reactions that may necessitate a kinetic treatment, the following is a short list.

1. Heterogeneous precipitation of secondary minerals or solid phases from solution.
2. Oxidation/reduction reactions in the aqueous phase.
3. Hydrolysis, decarboxylation, dechlorination etc. of organic compounds.
4. Bacterial destruction of nitrogen compounds, hydrocarbons and halogenated hydrocarbons.

## 5.2 Heterogeneous Reactions

During the late fifties with increasing concern over pollution due to acid mine drainage, geochemists began to focus their attention on slow surface controlled dissolution reactions involving the oxidation of sulfides in abandoned coal and nonferrous metals mines, and in waste and spoils heaps from such mining operations. Simultaneously, the first tentative studies were made concerning the disolution kinetics of silicates (e.g. Garrels and Howard, 1957). Conceptually allied with geochemical and environmental studies, but developing independently were investigations covering the hydrometallurgical treatment of ores to recover metals. This research concentrated on many issues that are identical to those of present concern (Burkin, 1966, 1983). The introduction of new techniques for characterizing and observing surfaces, such as ESCA, SIMS and SEM provided an added incentive to correctly interpret the dissolution or precipitation mechanisms involved.

*If the constituent forms a pore blocking precipitate, it will of course be of concern to the well operator.

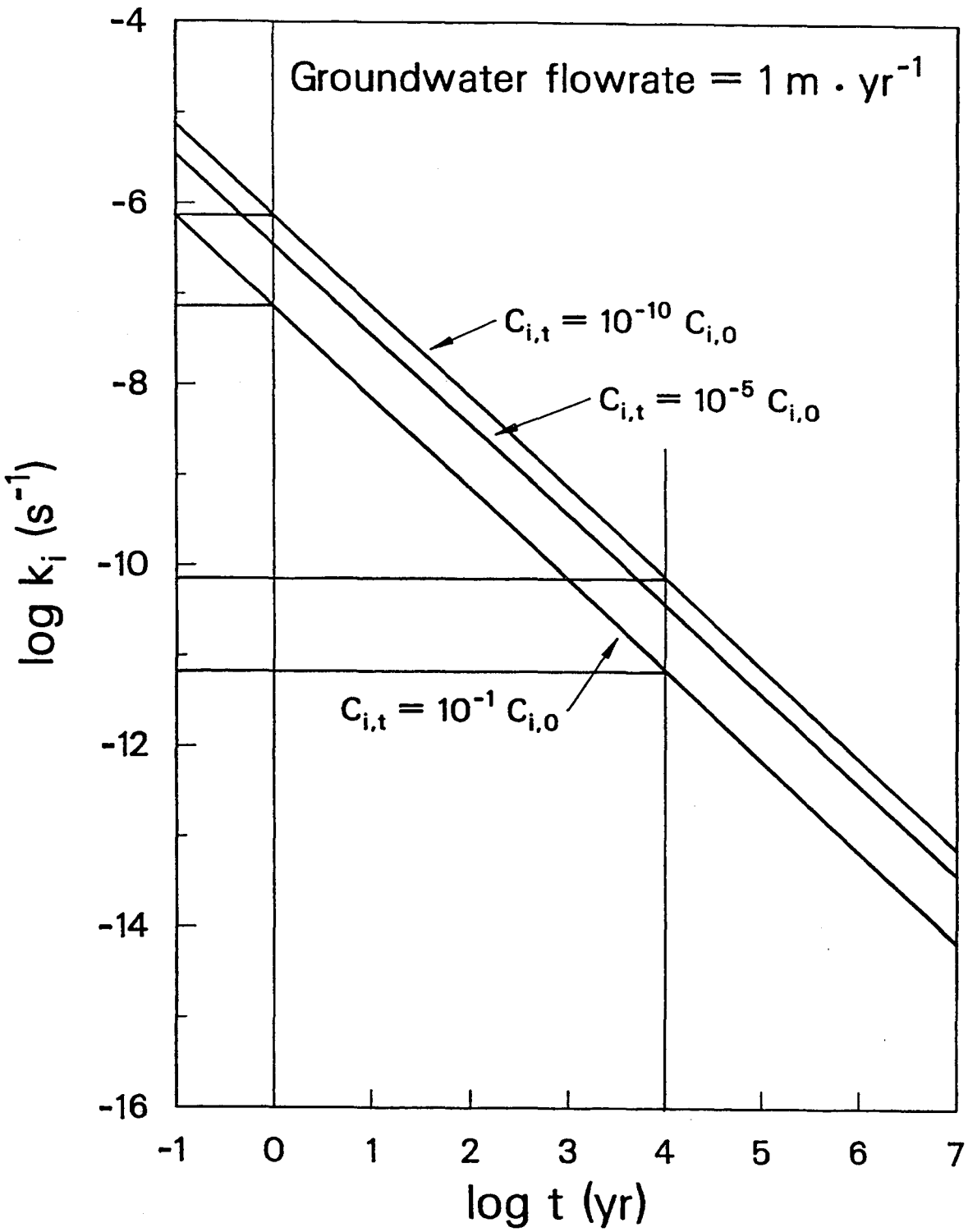


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Figure 5.1. Plot of the First Order Rate Constant Versus Time for Given Attenuation Ratios

With the exception of carbonate dissolution and clay decomposition by strong acids, most heterogeneous reactions involving the dissolution or precipitation of solid phases, particularly aluminosilicates, occur slowly at injection zone temperatures, in relation to the 10,000 year containment period after injection. The amount of information presently available regarding the kinetics of precipitation or dissolution of relevant phases is sparse, despite of the considerable interest shown by the geochemistry community in recent years. Geochemical research has tended to address certain specific issues such as feldspar weathering (Wollast 1967; Helgeson, 1974; Weare, et al., 1976; Petrovic, 1976; Petrovic 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, 1986) or carbonates e.g. Nancollas and Reddy (1971), Sjoberg (1976), Plummer and Wigley (1976) and Plummer et al., (1978), and sulfates such as gypsum and anhydrite (Lebedev and Lekhov, 1990). Dissolution or precipitation studies on other minerals are uncommon, (Lasaga, 1981b, 1984).

Only during the last decade, have attempts been made to develop a comprehensive theoretical understanding of the kinetics of mineral dissolution and precipitation in multicomponent heterogeneous systems, e.g. 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 utilized as a basis for interpreting heterogeneous reactions. The general theory regarding dissolution kinetics by Aargaard and Helgeson (1982) is quite complicated, yet it does little to elucidate or quantify actual mechanisms of dissolution or precipitation, which must be determined by experiment. Unfortunately, the interpretation of experiments can be further complicated by incongruent dissolution or precipitation and secondary nucleation effects as well as mechanisms in which $H^+$, $OH^-$ or other dissolved species may catalyse the reaction.

When a solution is grossly undersaturated or supersaturated with respect to a given mineral, dissolution or precipitation rates are a function of the surface area of the mineral (or more accurately the growth or dissolution sites on the surface, e.g. see White and Peterson (1990) and the rate is zero order, or independent of the concentrations of reactants in solution. Wood and Walther (1983), in evaluating dissolution rates of a number of rock forming aluminosilicates, quartz and corundum, found that reaction rates were consistent with the equation.

$$\log k \approx 2{,}900/T - 6.85 \qquad (5\text{-}4)$$

where all data were normalized to the number of gram atoms of oxygen per square centimeter of mineral surface. This unifying concept regarding dissolution or precipitation rates far from equilibrium is attractive. Unfortunately, more recent studies, e.g. Murphy and Helgeson (1987, 1989), raise serious questions as to the validity of this simple model. Furthermore, in situations where extreme supersaturation occurs, precipitation of the thermodynamically most stable phase does not normally occur. In fact, the nucleating and precipitating phase is a complex function of the degree of supersaturation, the surface tension of the precipitating phase (Söhnel, 1982) and the growth mechanism (Stranski and Totomanow, 1933; Gutzow and Toschev, 1968; Dibble and Tiller, 1981).

As equilibrium is approached, back reactions, which are dependent on the activities of the species in solution, begin to assert a retarding effect on the reaction rate. The participating species and the associated rate laws cannot be readily identified except through experiment. Petrovich (1986) has surveyed the literature and attempted to develop a generalized scheme to explain the kinetics of aluminosilicate precipitation and dissolution.

Although the dissolution and precipitation kinetics of rock forming minerals is of considerable interest to geochemists studying fundamental processes of rock-water interactions, the subject is of concern to petitioners only when major perturbations in the host rock mineralogy would result from interactions with the waste steam. This situation is most likely to occur when waste steams containing high concentrations of inorganic acids or alkalies are introduced in the injection zone, and where, in the case of acid waste streams, the matrix carbonate is insufficient to neutralize the acid. In the absence of carbonates, acidic waste streams will attack clays such as illites and smectites, converting them into kaolinite or amorphous silica. In contrast, alkaline wastes will attack clays and convert them into zeolites. In both cases, the ion exchange capacity of the rock matrix can be altered substantially. Therefore, if the waste stream were to contain other hazardous constituents requiring attenuation through adsorption, the kinetics of clay decomposition or zeolite formation and the stability limits of these mineral groups should be understood. Information on the kinetics of smectite dissolution may be found in Čičel and Novák (1976) and Novák and Čičel (1978), who also cite earlier studies on the subject.

Other heterogeneous reactions, in which aqueous species are adsorbed on the surfaces or coatings on the minerals are generally quite rapid in relation to the time frame of interest to the petitioner or EPA. Karickhoff (1984), in discussing adsorption kinetics in soils, notes that the process appears in some cases to proceed indefinately. Attempts at desorbing organic compounds from soils are similarly hindered kinetically, sometimes taking over 30 days to achieve greater than 90 percent recovery. Modeling of sorption

kinetics has been only partially successful, according to Karickhoff (*loc cit*), and in any case, is unlikely to be of concern to predictions of hazardous waste transport over periods exceeding a few years.

### 5.3. Reactions in which Bacteria Participate

A growing literature attests to the important role of bacteria in decomposing many hazardous organic contaminants in soils, (Abriola, 1987). Hence the concept of using the injection zone as a bioreactor, in which hazardous organic compounds are destroyed, has considerable appeal, particularly for those compounds that are not readily decomposed through abiotic processes. Inadvertent bacterial decomposition of waste products in formations surrounding injection wells has already been observed, e.g. see Goolsby (1972), Kaufman et al. (1973), Leenheer et al. (1976), Pascale and Martin (1978) and Ehrlich et al. (1979). Deliberately engineering the injection zone and waste stream to take advantage of bacterial decomposition as a means of destroying hazardous wastes does not appear to have been practiced, although bacterial remediation of a polluted aquifer has been successfully accomplished (Nagel et al., 1982). Major issues that must be addressed include the availability of bacteria that can be adapted to function effectively, if not flourish, under the temperatures and pressures of the injection zone, the availability of substrates to permit bacterial sustenance, whether the hazardous waste constituents are primary or secondary substrates and whether bacterial growth might compromise the permeability of the injection zone.

The existence of bacteria in deep subsurface reducing environments has been debated for over fourty years. Soviet literature summarized in Kuznetsov et al. (1963) interpreted many field and laboratory observations as strong evidence for the existence of *in situ* bacteria in deep geologic formations. Western studies have until recently been inconclusive, but there is now a growing climate of opinion that bacteria can exist and may actually flourish under such conditions. If this is indeed the case, they might be profitably adapted to catalyze the destruction of hazardous organic wastes.

Bacteria require energy to function, and most do so by catalyzing chemical reactions that are otherwise kinetically hindered. All reactions that supply the needed energy involve coupled oxidation and reduction. The so called aerobic bacteria utilize dissolved oxygen as the electron acceptor in the oxidation of reduced organic compounds to less reduced compounds or carbon dioxide. Anaerobic bacteria take advantage of other electron acceptors, such as $SO_4^{--}$, $NO_3^-$, $N_2$ or $CO_2$ to oxidize organic compounds, hydrogen, $Fe^{++}$ or $H^+$ in the absence of oxygen, the oxidants being reduced to $H_2S$ or $HS^-$, nitrogen or ammonia as the case may be. The oxidation products of anerobic bacteria may

include methane or $Fe^{+++}$, the latter being removed from solution as a ferric salt or hydrated ferric oxide.

Ehrlich (1972), in reviewing the role of biota in underground waste injection, noted that subsurface environments used for deep well injections are quite strongly reducing with a near neutral pH. Under such conditions, only anaerobic bacteria can live, as no oxygen is present. The subsurface environment could be modified by adding oxygen or other oxidents to the waste stream to provide a favorable environment for aerobic bacteria. The amount of oxygen required for the destruction of organic compounds in the waste streams could, however, be such that the solubility of oxygen in the aqueous phase would be exceeded. Recourse would therefore have to be made to using other more soluble oxidants that could be too toxic to bacteria or too expensive when compared with other waste disposal methods.

As a practical matter, it appears that the most convenient approach would be to permit bacterial adaptation to the waste stream with minimal adjustment to its composition, other than providing adequate substrates to sustain bacterial growth, and the necessary reagents to oxidize all of the hazardous waste. In so doing, it may also be unavoidably necessary to oxidize other waste compounds in the waste, even though they are not considered hazardous by EPA. This situation may actually be advantageous, because, as Bouwer and McCarty (1984) point out, if a hazardous compound is a primary substrate, bacteria cannot decrease the concentration of that substrate below a residual concentration necessary to substain a bacterial colony, that residual concentration, possibly being above permitted levels. If, however, the hazardous constituent is not the primary substrate, then its concentration may be decreased to concentrations deemed non-hazardous, while the primary non hazardous substrate is sustaining the bacteria.

Although the ground water in the injection zone may on occasion be substantially in equilibrium with respect to both heterogeneous and homogeneous redox equilibria, the waste stream, by its very nature, will not be in redox equilibrium, otherwise bacteria could not exploit any energy differences for sustenance. Therefore, a redox state for the waste stream cannot be specified. It is also probable that the waste stream contains dissolved oxygen, which must be consumed before anaerobic bacteria can utilize other oxidants as a source of energy, Figure 5.1. After Bouwer and McCarty (1984), illustrates progressively more reducing conditions as oxidants in the waste stream are consumed sequentially. In an injection zone it is presumed that a series of annular reaction zones would be established around the injection well during injection, each reaction zone representing the region in which a given oxidant acts as the primary energy source.

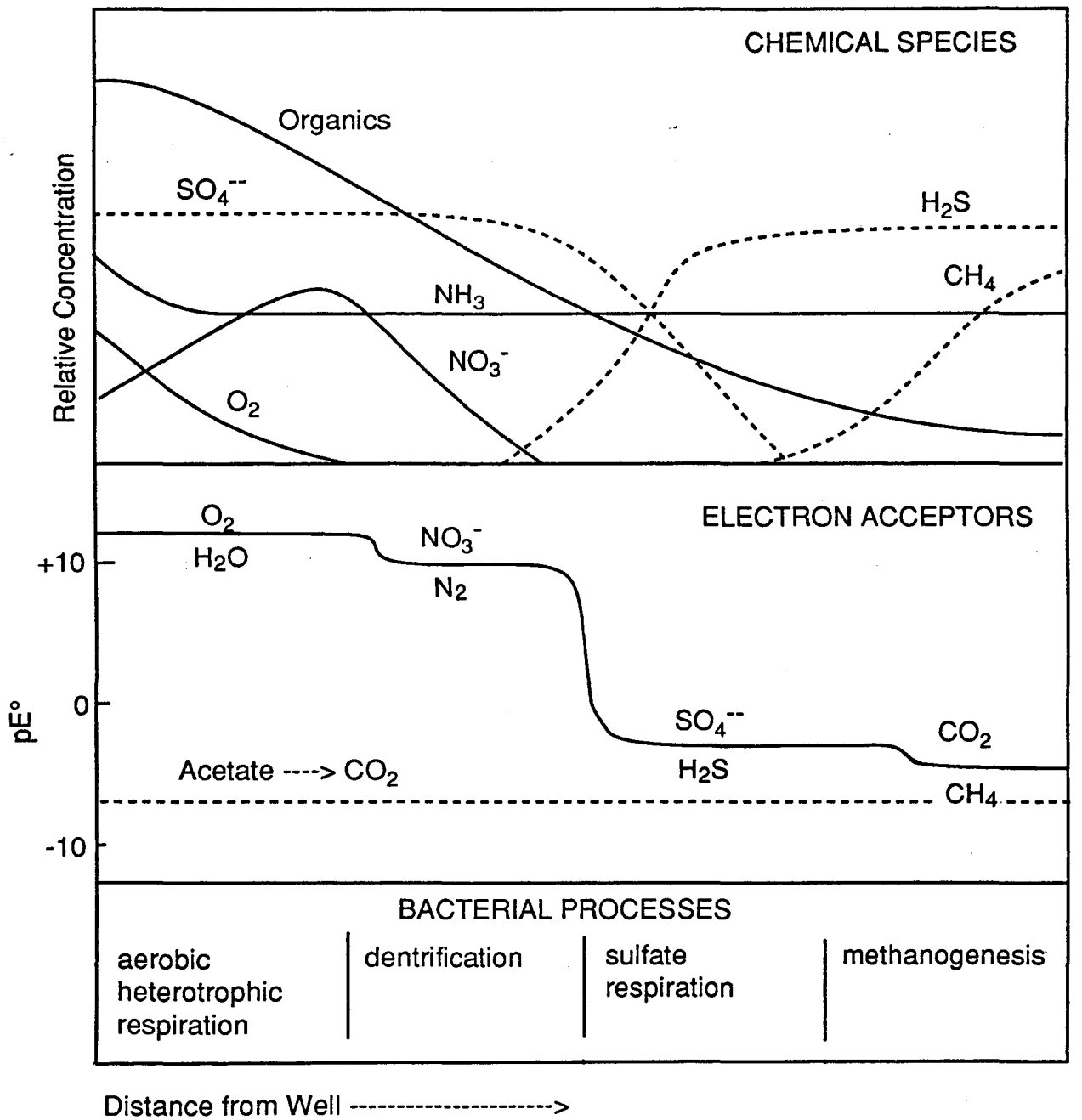


Figure 5.2. Hypothetical Zonation of Bacterially Mediated Reactions in an Injection Zone, (after Bouwer and McCarty, 1984)

Bacteria can be motile, i.e. swim freely through the aqueous phase, or attach themselves to solid surfaces. In an injection zone, as in soils, bacteria are probably attached to mineral surfaces, forming a reactive biofilm. Rittman and McCarty (1981 a,b) have formulated and tested a model to describe steady-state substrate consumption rates by such a bacteria laden biofilm. This model could be applied to predict hazardous waste consumption in injection zones. The model assumes diffusive transport of substrates into the biofilm from the aqueous phase, where they support bacterial metabolic processes according to a model for substrate utilization by bacteria that was proposed by Monod (1949). It is further assumed that the biofilm has attained secular equilibrium, there being no net loss or gain of biofilm mass. The use of the steady-state biofilm model has successfully explained the destruction of chlorinated hydrocarbons as secondary substrates by aerobic, denitrifying and methanogenic bacteria. Chlorinated aromatics, however, could be decomposed effectively only under aerobic conditions.

Bacterial decomposition of secondary substrates is in most cases, relatively rapid once a bacterial culture has acclimated to the secondary substrate. Depending on the porosity of the formation, substrate concentration, and biofilm area, the substrate decomposition half life may be only days to a few weeks. Under such conditions, bacterial consumption will take place primarily adjacent to the well bore in the injection zone. If, however, the bacterial population is low, and methanogenic conditions prevail, the decomposition half life could extend to several years. Bouwer and McCarty (1984) point out, that under such conditions, diffusive transport is not layer rate controlling, and a much simpler model using first-order decomposition kinetics is all that is required. The rate of change of substrate concentration with time may be defined as:

$$\frac{dC_i}{dt} = \frac{-kX}{K_s} Ci \qquad (5\text{-}5)$$

where k is the maximum specific rate of substrate utilization by the bacteria, $K_s$ is the Monod half-maximum-rate concentration of the substrate, and X is the average concentration of organisms capable of degrading the hazardous substrate in the injection zone. This simple differential equation may readily be incorporated in a transport equation of the type illustrated by equation (3-41). The needed parameters, k, X and $K_s$ should be determined from batch experiments, preferably using intact reservoir rocks as the material upon which the biofilm coating forms, and at the temperature and pressure of the injection zone.

## 5.4 Homogeneous Reactions in the Aqueous Phase

Comprehension of homogeneous reactions in the aqueous phase is somewhat better than what is known about heterogeneous reactions. Fortunately, the mounting concern regarding the toxicity of pesticides, industrial solvents and potential carcinogens, such as the halogenated dioxins, has stimulated a significant interest in degradation mechanisms. For example, an extensive review of hydrolysis rates of organic compounds was conducted by Mabey and Mill (1978). In this study, the authors showed that hydrolysis involves the participation of either $H^+$, $OH^-$, or water itself. The hydrolysis rate over a wide range of pH may therefore be pH dependent. The overall hydrolysis rate is the sum of the three mechanisms, thus:

$$k_L = k_B[OH^-] + k_a[H^+] + k_N \tag{5-6}$$

The (pseudo) first order hydrolysis constants for organic compounds vary widely, from $10^{-2}$ to $10^{-13}$ $s^{-1}$. A broad range falls into the region of concern indicated in the introduction to this section, i.e. $k = 10^{-6}$ to $10^{-11}$ $s^{-1}$.

Mill (1991) points out that hydrolysis reactions can be categorized both by the molecular structure of the chemical compound and the catalytic features of the host rock matrix. He notes that important classes of organic compounds that hydrolyse readily under injection zone conditions include esters, amides, alkyl and acyl halides, phosphate esters, epoxides, nitriles, acetals and ketals. Aromatic halides, ethers and sulfides are much more resistant to hydrolysis. Rate constants for many hydrolysis reactions can be predicted from structure activity relationships.

Section 6

# COMPUTER CODES

## 6.1 Introduction

This section is devoted to a discussion of various classes of computer codes that facilitate thermodynamic model calculations and permit simulations of reactive chemical transport. No attempt has been made to provide the names and addresses from which the codes may be obtained. The latest information regarding availability can be obtained by contacting the authors of the cited references. Many of the codes have been developed and applied in an academic environment, where the user is presumed to possess fairly extensive knowledge of the subject at hand. Consequently, the documentation may be too concise for some potential users. Most of the codes cited have been tested extensively and are considered to be reasonably robust. A few of the codes are proprietary, and there may be restrictions on their use. Mention of the names of computer codes, trade names, products, or services does not convey, and should not be interpreted as conveying official EPA approval, endorsement or recommendation.

Few, if any, of the cited codes were written with the understanding that they might be used to deal with deep well injection problems. Yet all may be adapted to meet such needs with varying levels of effort. The injection of a particular waste stream usually presents problems, or requires solutions, specific to that waste stream. Both the range of possible hazardous waste injectants, and mechanisms governing their mobility or destruction in the subsurface environment are extensive.

The purpose of modeling the chemistry of waste injection is to provide answers to such questions as:

- What will precipitate or be adsorbed and how much from a solution of a given composition?
- What will be the saturation concentration of a hazardous constituent in equilibrium with a phase containing that constituent as a major component?
- What will be the effect of dissolved constituents on the saturation concentration of a hazardous constituent?
- How will the concentration of a hazardous waste in solution be affected by reaction of the waste stream with ground water or host rocks?
- Are there any unforeseen chemical consequences of injecting a waste stream?

- How fast will a given substance precipitate or be adsorbed from solution?

Extant geochemical modeling codes are able to provide partial or complete answers to many of these questions provided sufficient and accurate thermodynamic data relating to the participating species and phases are available.

Computer codes greatly facilitate the elucidation of complex chemical processes, and have supplanted traditional methods of hand calculation using an array of ingeneous approximations and graphical techniques. No computer code is a panacea for dealing with the prediction of waste migration in subsurface aquifers. The current state of the art is such that, for all but extremely simple systems, waste migration predictions must be accomplished using several techniques, where computer codes only facilitate the calculations. Computer codes relevant to the problem at hand may be used to:

(1) Reduce and evaluate experimental data.

(2) Calculate the thermodynamic properties of phases or species at temperatures and pressures other than at standard state conditions (using thermodynamic models).

(3) Determine the distribution of species at equilibrium, given the principal extensive and intensive parameters in the system (using distribution of species codes).

(4) Predict the evolution of a chemical system, either as a function of reaction progress, i.e. the amount of material reacted, or as a function of time, (using mass transfer codes). (Such codes do not account for the spatial distribution of reactants or products.)

(5) Predict the chemical evolution of a system in which both chemical reactions and transport proceed simultaneously (using chemical transport codes).

These categories are discussed in turn.

### 6.2 Calculation of Thermodynamic Data

As is noted elsewhere in this report, the calculation of thermodynamic data is normally the preserve of specialists who have written their own codes to assist them in this arduous activity. Furthermore, the sources of raw data, from which thermodynamic parameters might be recovered for modeling purposes is so diverse that computer codes

must be frequently applied to suit the problem at hand, rather than in any systematic manner. One particular code, SUPCRT92 (Johnson et al., 1992) includes the revised HKF EoS (Tanger and Helgeson, 1988) for the computation of the partial molal properties of ionic and molecular species and is particularly valuable for extracting the 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 e.g. see Shock and Helgeson (1988,1990), partial molal properties of ions or molecular species from raw data can be calculated for insertion in the SUPCRT92 data base. SUPCRT92 can then be used to calculate dissolution reaction constants at any specified temperature and pressure between 0 - 800°C and 1 - 5.5 kbar, respectively. Such information is necessary for all distribution of species codes using the equilibrium constant approach, (see section 6.3). SUPCRT is a useful tool for computing equilibrium constants, whenever temperatures in an injection zone differ significantly from 25°C. Its systematic use would facilitate standardization of the treatment of data, and ensure greater accuracy than other methods of extrapolating dissociation constants or solubility products to higher temperatures, e.g. the Criss and Cobble approach, (Criss and Cobble, 1964; Cobble et al., 1982). If the petitioner is contemplating injection of fluid at temperatures greater than 200°C or is considering wet combustion at elevated temperature and pressure, such as proposed by Smith and Raptis (1986), then the use of the modified HKF model and the SUPCRT code is as noted in Section 3.4.1, the most convenient means of obtaining accurate partial molal properties of aqueous species above that temperature.

### 6.3 Distribution of Species

The distribution of species problem entails finding how the concentrations of various elements or constituents measured analytically in solution may be distributed among the ionic or molecular species in solution. It involves determination of the species distribution that represents the most stable configuration for the system. In thermodynamic terms, this constitutes finding the minimum Gibbs free energy of the system at a given temperature and pressure. Two quite different approaches to finding a solution to this problem have evolved with the expanded use of digital computers, known respectively as the "equilibrium constant approach" and the "Gibbs free energy minimization method". As pointed out by Zeleznik and Gordon (1968), both methods employ formulations of equations having a common origin and their content is the same. Thus the selection of method becomes one of convenience and traditional usage.

With the exception of SOLGASWATER (Eriksson, 1979), which uses a Gibbs free energy minimization routine, geochemical distribution of species codes employ the equilibrium constant approach, ostensibly because equilibrium constants relating aqueous species are directly determined and better known than the underlying thermodynamic properties of the participating species (Nordstrom et al., 1979). Codes using this approach, include ECHEM (Morrey, 1988), EQUILIB (Shannon et al., 1977; Morrey, 1981; Morrey and Shannon, 1981), EQ3/EQ6 (Wolery, 1983; Wolery et al., 1985, Wolery et al., 1990), GEOCHEM and REDEQL (Morel and Morgan, 1972; McDuff and Morel, 1978; Sposito and Mattigod, 1980) and its successor, SOILCHEM (Sposito and Coves, 1988), MINEQL (Westall et al., 1976; Ball et al. 1981; James and Parks, 1976), MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985) PHREEQE (Parkhurst et al., 1980, 1990; Plummer and Parkhurst, 1985, 1990), MIX2 (Plummer et al., 1975), SOL-MINEQ.88 (Kharaka et al., 1988; Perkins et al., 1990), SOLVEQ (Reed, 1982; Spycher and Reed, 1989), and WATEQ and related codes (Truesdell and Jones, 1973, 1974; Plummer et al., 1976; Ball et al., 1981; Krupka and Jenne, 1982). However the approach possesses several serious disadvantages when complex multicomponent systems are evaluated.

- 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, normally differs from the temperature and pressure at which the equilibrium constant was measured. This necessitates recalculation of the equilibrium constant using some thermodynamic model to interpolate between experimental values, or for purposes of extrapolation.
- The chemical reactions needed to define the equilibrium constants are usually arbitrary, and can often be represented in different ways without affecting the final results. There is therefore little uniformity in usage between code developers.
- Most equilibrium constants, especially those for solid phases, are not obtained by direct measurement, necessitating their calculation from $\Delta G_f^o$ data after specification of the reaction equation.
- Because equilibrium constants are usually computed, via the route described above, any change in the thermodynamic properties of a given species will necessitate recomputation of the equilibrium constants of all those reactions in which that species participates.

- Equilibrium constants must be calculated for a range of pressures and temperatures, and stored in an "equilibrium constant" data base. The P-T range covered may not be appropriate for the user.

It would be more convenient for the user, if the thermodynamic data for a given mineral or aqueous species were stored in a data base, and the standard state Gibbs free energies of the participating species were calculated at a given pressure and temperature for entry into a distribution of species code using the Gibbs free energy minimization method. In this way, the flexibility of the distribution-of-species code would be enhanced, and continuing improvements in the thermodynamic properties of participating species could be incorporated with minimum effort. Regrettably, such a convenient integrated computing capability is generally unavailable, although current developments suggest that it will eventually come about.

The equilibrium constant method entails the solution of a set of non linear mass action equations and linear mass balance equations, including the charge balance constraint, if so desired. The mass action equations for aqueous species and for solids are usually written as dissociation or dissolution equations, each breaking down into its "basis" or component species. Basis species are usually the simple charged ionic species of an element, such as $Na^+$, $Mg^{++}$, $Al^{+++}$, $Cl^-$, or commonly occurring simple molecular or ionic species such as $SiO_2(aq)$, $SO_4^{--}$, $CO_3^{--}$ or $NO_3^-$.

The equations required to solve the distribution of species problem is best described by means of a simple example, rather than through the use of abstract mathematical formulations. Consider the example of a carbon dioxide charged water in equilibrium with calcite.

In this simple case, the following aqueous species may be found in solution:–

<u>Cations</u> $H^+$, $Ca^{++}$, $Ca(OH)^+$, $CaHCO_3^+$

<u>Anions</u> $OH^-$, $CO_3^{--}$, $HCO_3^-$

<u>Neutral Species</u> $H_2CO_3(aq)$, $Ca(OH)_2(aq)$

The following solid phases may form in this system:–

$$Ca(OH)_2,\ CaCO_3(\text{calcite})$$

The basis species represented in this system are:–

$$H^+,\ Ca^{++},\ CO_3^{--},\ H_2O$$

all mass action equations are written in terms of these species, thus:–

$$OH^- + H^+ = H_2O \tag{6-1}$$

$$Ca(OH)^+ + H^+ = Ca^{++} + H_2O \tag{6-2}$$

$$H_2CO_3(aq) = 2H^+ + CO_3^{--} \tag{6-3}$$

$$\text{Calcite} = Ca^{++} + CO_3^{--} \tag{6-4}$$

etc.

where

$$K(OH^-) = \frac{[H_2O]}{[OH^-]\,[H^+]} \tag{6-5}$$

$$K(Ca(OH)^+) = \frac{[Ca^{++}]\,[H_2O]}{[Ca(OH)^+]\,[H^+]} \tag{6-6}$$

$$K(\text{calcite}) = \frac{[Ca^{++}]\,[CO_3^{--}]}{[\text{Calcite}]} \tag{6-7}$$

etc.

where [ ] denote activities

To the mass action equations must be added those involving mass balance of the components in solution, thus

$$\text{Total calcium, } \sum(Ca)\text{, in solution} = (Ca^{++}) + (Ca(OH)^+) + (CaHCO_3^+) \tag{6-8}$$

$$\text{Total carbonate, } \sum(CO_3^{--}) = (H_2CO_3) + (HCO_3^-) + (CO_3^{--}) + (CaHCO_3^+) \tag{6-9}$$

$$\text{Total hydrogen, } \sum(H_2) = (H_2O) + 0.5(H^+) + 0.5(OH^-) + (H_2CO_3) + 0.5(HCO_3^-) + 0.5(Ca(OH)^+) + 0.5(CaHCO_3^+) \tag{6-10}$$

$$\text{Total oxygen, } \sum(O_2) = 0.5(H_2O) + 0.5(OH^-) + 0.5(Ca(OH)^+) + 1.5(CaHCO_3^+) + 1.5(H_2CO_3) + 1.5(HCO_3^-) + 1.5(CO_3^{--}) \tag{6-11}$$

where ( ) denote concentrations.

Finally, electrical neutrality must be considered.

$$(H^+) + (Ca(OH)^+) + (CaHCO_3^+) = (OH^-) + (HCO_3^-) + 2(CO_3^{--}) \qquad (6\text{-}12)$$

The problem to be solved involves finding the concentrations of the individual ionic and molecular species, given the mass action equations such as (6-5) -(6-7), the mass balance equations (6-8) - (6-9), and the electrical neutrality constraint (6-12) given the relationship between the activity of a species and its concentration, e.g. Eqns (3-20)–(3-11), and where the total number of unknowns equal the number of equations.

The Debye-Hückel equation or some empirical or semi empirical extension is always used to calculate the activity coefficient, $\gamma_i$ of charged species (see section 3.4.2). For neutral species, the activity coefficients, $\gamma_i$, are sometimes determined by empirical correlation of the activity of carbon dioxide in a solution of corresponding ionic strength. To calculate the activity of water, various equations are used, e.g. Wolery (1983), p. 22. Ideally the Gibbs-Duhem relation between the solvent and solute species should be used to calculate the activity of water, but is not usually implemented, e.g. see Wolery (1983).

For solutions with many components and many species and complexes in solution, the number of equations, linear and non linear, can often exceed 100. The mathematical technique used to solve the set of linear mass balance and non linear mass action equations incorporating algorithms for calculating the activity coefficient is to convert the non linear equation to an infinite sequence of linear equations and solve iteratively. It is beyond the scope of this guide to discuss the various methods. Excellent reviews are given by Zeleznik and Gordon (1968) and by Van Zeggeren and Story (1970). The Newton-Raphson method is most often employed in such schemes. Various techniques are used to ensure rapid convergence. Although not always essential, it is also desirable to ensure that the system is electrically neutral. Chemical analyses always contain some analytical error, which for quality analyses is less than 5 weight percent of the total charge. This may be closed entirely by ''balancing'' on a predominant species in solution, such as $Cl^-$ or $Na^+$. The choice of species should be such that the addition or subtraction of a small quantity of balancing element, does not significantly affect the thermodynamic properties of the system.

From the practical viewpoint, it suffices to mention that not all iterative methods will converge for all types of problem. The tendency for some codes to ''hang-up'' or ''crash'' for no apparent reason, and the subsequent strategies or subterfuges necessary to modify the input to get a solution are inconveniences that should be avoided. It should also be noted that it is easy for the tyro to specify a problem that defies solution. In this

case, it is an asset if the code writer has incorporated diagnostic statements identifying the potential problem. Wolery (1983) and Morrey (1988) have made particular efforts in this direction with respectively the EQ3/6 and ECHEM codes.

The input required by distribution of species codes is usually that of a typical chemical analysis, i.e. the concentrations of various elements or species. Other inputs such as alkalinity, pH, oxidation state (Eh), temperature and solution density may also be required as well as specification of the aqueous species to be used to balance the charge and ensure electrical neutrality. Some codes also allow other features such as permitting saturation with respect to a particular mineral or group of minerals, control on the partial pressure of a gas phase, specification of oxidation state in terms of various redox pairs, e.g. $H_2S(aq)/SO_4^{--}$, $CH_4(aq)/CO_2(aq)$, $NH_4^+/NO_3^-$ etc. Of particular value is the ability to specify exactly the temperature of the sample, rather than approximating it to 25°C or some other temperature increment. Several distribution of species codes also incorporate models describing adsorption or ion exchange. These codes, among which can be cited MINEQL, MINTEQ, SOILCHEM and ECHEM, are for the most part oriented toward the interpretation of soil chemistry.

The output of a computer code can be just as varied. In addition to the species distribution, usually listed in order of abundance, and specifying the concentrations, activities and logarithms of activities, the output may show the relative abundance of species containing a particular element, calculated saturation indices with respect to minerals and gases, or even give results of a "mass transfer" calculation to show what and how much material must precipitate to prevent supersaturation in solution.

Periodically, comparative reviews regarding the features of various distribution of species computer codes are made. Those of particular interest to petitioners might include Nordstrom et al. (1979), Jenne (1981), Kincaid and Morrey (1984), Carnahan (1987b) and Mangold and Tsang (1987). Comparative assessments of computer codes for specific applications such as radioactive waste containment (Intera, 1983) and have also been made. Such studies sometimes highlight particular features of codes that may be useful or even essential to a specific problem being addressed by the petitioner. The choice of a distribution-of-species code depends on the use to which it will be put. The petitioner should review the features of each code carefully before making a selection. He can be aided by the above cited review papers.

The above discussion addresses distribution of species codes that describe species in terms of individual ions and complexes in solution where the activity coefficients are calculated using various forms of the Debye-Hückel equation such as Eqns. (3-20)–(3-22). The increasing use of the Pitzer interaction model for describing mixed electrolytes has

lead to the development of codes in which neutral salts rather than ionic species are represented in solution with the corresponding use of mean activity coefficients. Five computer codes, the latest version of EQ3/6 (Jackson and Wolery, 1985), TRANSCHEM (Scrivner et al., 1986), PHRQPITZ (Plummer et al., 1988), SOLMINEQ-88 (Kharaka et al., (1988) and a brine model developed by Professor John H. Weare and his colleagues at U.C.S.D. (Møller et al., 1991) incorporate the Pitzer interaction parameter electrolyte model. Such codes are of value to the petitioner confronted with highly saline waste streams or ground waters, and who wishes a higher level of accuracy than can be achieved using the distribution of species codes in which activity coefficients are computed using the limited and extended forms of the Debye-Hückel equation.

### 6.4 Reaction Progress and Kinetics

Reaction progress codes represent an evolutionary step from distribution-of-species codes. For whereas distribution-of-species codes consider the thermodynamic relations of a static system, reaction progress codes examine the consequence of an evolving system in which various phases in a system react with each other.

The original concept of reaction progress, developed by deDonder (1920) and deDonder and Van Rysselburghe (1936), and subsequently adopted by Helgeson et al. (1969) in their formulation of the PATH 1 code was an imaginitive advance in simulating complex geochemical systems. The essential premise of the model by Helgeson et al. (1969) is that 1 kg of water plus the dissolved species is 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 reacted, or $\xi$, (Xi), the reaction progress variable that is usually expressed in terms of gram moles of the normalized stoichiometry of the reactant assemblage.

In its simplest form, the model assumes that:–

- 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. However, they break down when applied to problems involving relatively slow reactions such as occur during deep well disposal of hazardous wastes at relatively low temperatures. Such systems are rarely if ever in either heterogeneous or even homogeneous equilibrium. Indeed, there is even evidence that natural low temperature systems, such as brines in Gulf Coast sediments, are also out of internal equilibrium with respect to oxidation state, even though the brines may be hundreds of thousands or even millions of years old, (Shock 1988). Lindberg and Runnels (1984), in discussing the oxidation state of ground waters, have also called into question the meaningfulness of redox pairs as a guide to predicting system Eh, since coexisting aqueous redox species are often not in equilibrium and yield differing Eh values. They estimate that homogeneous equilibrium with respect to Eh in ground waters may be achieved only after many thousands of years. Other investigators e.g. Palciauskas and Domenico (1976) and James and Rubin (1979) have also questioned the validity of the assumption of local equilibrium with respect to sorption or ion exchange reactions, and attempts to model chemical transport systems in which local equilibrium with respect to adsorption is assumed have demonstrated that kinetic factors must play a role, e.g. see Van Genuchten et al. (1974) and Vallette-Silver et al. (1981).

One reason why Helgeson et al. (1969) applied the reaction progress variable to monitor the course of geochemical reactions, was to avoid the explicit use of chemical kinetics, because so little is known regarding the dissolution and precipitation kinetics of minerals in aqueous solution. For example, Lasaga (1981a) in which he summarizes investigations of the kinetics of only 14 minerals. Only a few more mineral dissolution studies have been accomplished since that time. The initially promising approach advanced by Wood and Walther (1983) that the 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 square centimeter, is questioned by Helgeson and Murphy (1984) and Murphy and Helgeson (1987). Therefore, no unifying method is presently available that permits even a semiquantitative prediction of mineral dissolution kinetics.

In general, reaction progress codes cannot be used to model the evolution of injection zone chemistry during the period when waste is being injected, because the waste stream will be penetrating the host rock matrix at a rate that initially would exceed several meters per year and attainment of local equilibrium would be very unlikely. An exception would be when the waste stream is initially close to equilibrium with respect to the matrix minerals, and the principal reactions of interest involve ion exchange or adsorption. If it can be shown that both reactions achieve reversible equilibrium within a

period of 10–20 days, i.e., the time to equilibrate is short compared with the duration of injection and the distance travelled by the waste in that time is less than 1 meter, then application of a reaction progress code to study the chemical evolution of waste at points along the injected waste stream may be suitable.

After ceasing injection of the waste stream, the waste will move only at the same rate as the regional ground water movement prior to injection. In general, this rate is slow, of the order of 0.1–1.0 m/yr. Under such circumstances, a reasonably close attainment to reversible equilibrium may be achieved and reaction progress codes may supply useful semi-quantitative, if not quantitative information, regarding the fate of many inorganic components in the waste stream during the 10,000 year containment period.

Reaction progress codes can incorporate the net enthalpy generated by the chemical reactions being simulated. For simple adiabatic systems, they 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 it would permit estimates to be made of the maximum anticipated temperature excursion expected in chemically complex systems.

Despite their lack of applicability for systems in which reactions are slow in relation to ground water movement, reaction progress simulations have sometimes provided useful insights into the processes occurring in natural hydrochemical systems. Thus Plummer et al. (1983) investigated the evolution of ground water in the Floridian aquifer between Polk City and Wachula in Florida. These authors were able to reconcile the evolution of the ground water with the mineralogy of the limestone and dolomite aquifer between these two cites using the reaction transport code PHREEQE. Solomon (1986) has demonstrated very convincingly, that EQ3/6 simulations of the evolution of ground waters in basalts, correspond quite well to what is actually observed in the Grande Ronde formation of Washington State. Kerrisk (1983) has simulated the evolution of ground water chemistry and mineral formation at Rainier Mesa, Nevada using EQ6. Reaction progress codes have also been applied to the interpretation of laboratory experimental studies, e.g. see Knauss et al. (1984). Apart from these examples, few other reaction progress simulations have been rigorously correlated with field or laboratory observation, and to the writer's knowledge, none have been applied to model the evolution of a hazardous waste plume in a injection zone.

Reaction progress codes for geochemical simulations are readily modified to incorporate chemical kinetics. The relation between reaction progress and the kinetics of a process is defined by;

$$\frac{d\xi}{dt} = V \tag{6-13}$$

where V is the reaction velocity (Aargaard and Helgeson, 1982). The EQ6 code already possesses the capability of simulating reaction kinetics, (Delany et al. 1986), and its application can provide valuable insight into the evolution of systems where several heterogeneous reactions are competing, e.g. see Helgeson and Murphy (1983).

Few computer codes have been written to simulate reaction progress. The best known and documented are EQ3/6, (Wolery, 1983), PHREEQE, (Parkhurst et al., 1980,1990), and CHILLER (Reed and Spycher, 1989). Others, cited in the literature include the now obsolete PATH1 (Helgeson et al., 1969; Helgeson et al., 1970). FAST-PATH (Schlitt and Jackson) 1981, and SOLGASWATER (Eriksson, 1979). REDEQL (Morel and Morgan, 1972; McDuff and Morel, 1973) and MINEQL (Westall et al., 1976) have options for reaction progress like simulations, but are very limited in scope compared with EQ3/6, PHREEQE, and CHILLER. EQ3/6 also has quality assurance documentation (Wolery, 1986), which could be of benefit to petitioners in their applications to EPA.

### 6.5. Reactive Chemical Transport

Reactive chemical transport modeling should represent the ultimate level of sophistication in predicting the fate of hazardous wastes in the subsurface environment. Unfortunately, the complexity of models incorporating both hydrologic transport processes and chemical reactions is such that few codes have been developed with the level of sophistication desired.

There are currently two approaches to modeling chemical transport. In the first, all mass, momentum and energy transfer equations, including those in which chemical reactions participate, are solved for simultaneously, for each time step in the evolution of the system. In the second, two linked but separate subroutines are used. The first solves for mass, momentum and energy balance for the fluid at each time step. Then the chemistry is reequilibrated through a distribution of species code. The integrated or one step approach has been applied for a number of years, and includes studies by Lai and Jurinak (1972), Rubin and James (1973), Valocchi et al. (1981a,b), Jennings et al. (1982), Miller and Benson (1983), Noorishad and Carnahan (1985), Carnahan (1986), Willis and Rubin (1987) Noorishad et al. (1987), Merino et al. (1986), and Carnahan (1987a). In most early studies, relatively primitive isothermal systems were investigated, usually involving simple ion exchange formulations, sometimes including complexation, and where the pH of the system was assumed to remain constant. Under such conditions, even the ion

activity coefficients change little, and can be ignored without major error.

Many reactions controlling ground water composition are slow in relation to ground water movement, as noted in section 6.4. Therefore the condition 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. (1981a,b), Jennings et al. (1982), cannot be applied universally, thereby necessitating the introduction of chemical kinetics. A recent development of this kind is in 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. Such a code cannot be used without specialized expertise in its use. Furthermore, it is computationally intensive, and has not been tested with complex multicomponent systems.

The second approach appears to have been first utilized by Grove and Wood (1979). It was subsequently adopted by Reardon (1981) and by Walsh et al. (1982) using a distribution of species code developed by Morel and Morgan (1972). The same approach was also used by Cederberg et al. (1985) in which the distribution of species code MICROQL* was incorporated in a transport code TRANQL (Cederberg, 1985), and by Theis et al. (1984) and Kirkner et al. (1984, 1985) using the FIESTA code. The Electric Power Research Institute (EPRI) sponsored development of FASTCHEM, which is a combination of the transport code SATURN (Huyakorn et al., 1983) with MINTEQ (Felmy et al., 1984; Krupka and Morrey, 1985). The FASTCHEM code is extensively documented in a series of EPRI reports (Geotrans Inc., 1988; Hostetler and Erikson, 1989; Hostetler et al., 1989; Kincaid, 1988; Krupka et al., 1988; Morrey, 1988). Morrey and Hostetler (1985) also developed the code CTM1D, which also incorporates MINTEQ. Narasimhan et al. (1986), Liu (1988), and Liu and Narasimhan (1989a,b) describe use of the code DYNAMIX in which Narasimhan et al. (1986) united TRUMP (Edwards, 1972), a three dimensional transport model with PHREEQE (Parkhurst et al. 1980, 1990). The most recent version of DYNAMIX (Liu and Narasimhan 1988a) is capable of handling the thermodynamics of hydrolysis, aqueous complexation, redox reactions

*MICROQL is stated by Cederberg et al. (1985) to be a scaled down version of MINEQL (Westall et al. 1976).

and precipitation/dissolution as well as the kinetics of mineral dissolution. It has the capability of modeling systems in three dimensions and accommodating large arrays of both solid and aqueous species. An earlier version successfully modeled the behavior of ground water contamination from an abandoned uranium mill tailings dam (White et al., 1984). Yeh and Tripathi (1990,1991) have recently developed a reactive chemical transport code, HYDROGEOCHEM, capable of modeling saturated and unsaturated media. Apart from the usual chemical processes such as complexation, dissolution and precipitation, it also includes adsorption-desorption, ion exchange, redox and acid-base reactions. In this respect, its capabilities are similar to FASTCHEM, which also incorporates adsorption-desorption and ion exchange reactions, although FASTCHEM is limited in its ability to simulate redox reactions. Another reactive transport code, PHREEQM, using PHREEQE as the distribution of species code, has recently been developed by the USGS (Glynn et al., 1991).

The petitioner would undoubtedly be interested in deciding whether the one step or two step approach is more satisfactory for his purposes. At least two direct comparisons have been made modeling identical problems with both approaches. In the first Cederberg et al. (1985) modeled the one dimensional Palo Alto Baylands ground water transport with ion exchange reactions using TRANQL, and compared the results with the earlier one-step analysis by Valocchi et al. (1981a,b). Cederberg et al. (loc. cit) found that their results were the same as those by Valocchi et al. (1981a), but that their execution times were some 30 percent faster. In the second example, Liu and Narasimhan (1988a) compared DYNAMIX with THCC (Carnahan, 1986). THCC is similar to CHEMTRNS (Noorishod et al., 1987). In this study, the one dimensional transport of uranium in the presence of redox reactions was simulated in a hypothetical 3 m column. Local equilibrium was assumed, and no kinetically controlled reactions were included. The resulting output from both simulations were similar. The DYNAMIX code took only 2 minutes to run a $10^6$ second simulation on a CRAY XMP/14 machine. The THCC simulation was run on a DEC VAX 8500 machine, but the time of execution was not reported.

In general, the direct incorporation of chemical reactions in transport equations causes the resulting equations to be very non linear and difficult to solve numerically. This usually results in slower execution times. However, the execution time differential does not necessarily merit the selection of a two-step code over one-step code. Different programmers may select more computationally efficient algorithms for the solution of a problem. The question also arises as to which codes are more adaptable to underground injection problems. There is no clear answer at this time. Finally, it should be noted,

that although Cederberg et al. (1985), and Liu and Narasimhan (1988b) demonstrate that the two methods yield similar results, the fundamental differences in method used may lead to quite different results for certain problems. The petitioner should be careful, when selecting a code for his use, that he determine whether the model employed and the algorithms used are appropriate for the problem he wishes to simulate. For example, if the code is of the two step type, does it adequately handle rapid precipitation or dissolution while still maintaining mass balance? The method of solution may employ linearized ordinary differential equations that approximate the non linear differential equations. This can sometimes result in ''drift'' with respect to the mass balance of elements present in the system being modeled.

Section 7

# CHEMICAL MODELING TO PREDICT THE FATE OF HAZARDOUS WASTE AFTER DEEP WELL INJECTION

## 7.1 Relationship between Chemical Modeling and Laboratory or Field Studies

This section is devoted to a discussion of the ways in which geochemical modeling might be applied in the development of a petition. In the following paragraphs a hypothetical series of steps necessary to predict the long term behavior of a hazardous waste stream in the injection zone of a Class 1 well, is considered.

**Step 1: Basic Information**

Acquire the following chemical, mineralogic and hydrochemical information:

- Composition of the waste stream
- Groundwater composition, mineralogy, and chemical composition of the injection and confining zones.
- Hydrologic parameters of the injection zone and confining zones.

No geochemical modeling codes are required for this step.

**Step 2: Identification of Chemical Interactions**

Identify decomposition mechanisms of the hazardous waste, e.g.

- Hydrolysis
- Oxidation/reduction
- Bacterial decomposition
- Decarboxylation etc.

Identify mechanisms causing immobilization, e.g.

- Adsorption
- Ion exchange
- Precipitation/coprecipitation
- Oxidation/reduction

All thermodynamic and kinetic information relating to the above mechanisms should be evaluated from published and unpublished sources. Appropriate thermodynamic data and rate constants should be computed. Use can be made of distribution of

species codes to interpret data, and calculate solubility products, dissociation constants, surface complexation constants, exchange constants or sorption coefficients, where necessary. If the ionic strength of the participating solutions or brines exceeds 0.5, it might be necessary to use a code incorporating the Pitzer interaction model.

**Step 3: Thermodynamic and Kinetic Data**

Conduct laboratory experiments to measure rates and equilibrium states for those reactions cited in Step 2, above, which are deemed to exert a significant control on the migration of a hazardous constituent, either through decomposition or immobilization.

It is assumed that information in the literature is insufficient for predictive purposes. Batch or flow-through column tests can be used, as noted elsewhere. If tests are designed also to simulate the subsurface environment, care should be taken to ensure that the experiments either replicate the subsurface environment, or that the results can be confidently extrapolated to subsurface conditions.

For batch reactor studies, distribution of species and reaction progress codes can be used with advantage to interpret both the thermodynamic and the kinetics of the system. For flow through column reactor studies, one dimensional transport codes incorporating sorption, ion exchange, hydrolysis, etc. should be used to calibrate the observed results. Both batch reactor and column tests should be designed so that only a small number of parameters need to be quantified; all others should be fixed, known, or directly calculatable without calibration procedures.

Because laboratory studies are of relatively short duration, i.e. of the order of weeks to months, they do not normally identify slow reactions taking place over tens to thousands of years. If slow reactions are critical to the containment demonstration, then the experimental design should be carefully considered in order that the reaction rates are determined with the desired accuracy.

**Step 4: Predictions of the Fate of Hazardous Wastes**

Conduct a series of simulations of waste migration and decomposition/or immobilization over a period of up to 10,000 years.

These simulations must be conducted using a transport code that can accommodate the kinetics and thermodynamics of the decomposition/immobilization reactions defined as being appropriate for the conditions expected. One, two or three dimensional models can be used. Since, the hydrologic aspects of containment in the injection zone are of major interest, it might be necessary to conduct three dimensional non isothermal

simulations to model the geometry of the injection and confining zones. However, if conservative calculations demonstrate effective containment using one-dimensional models, then more elaborate simulations would be unnecessary.

The predictive simulations will be based on mechanisms quantified by measurements conducted during relatively short-term laboratory experiments. In these experiments, most observable reactions will be those that proceed relatively rapidly and attain completion within the 10,000 year time period. Such simulations will inevitably be conservative.

## 7.2 Criteria for Acceptability of the Petition

### 7.2.1 General

The review and approval of petitions to the EPA would be greatly facilitated if certain guidelines were followed in the layout and presentation of supporting information. In the discussion which follows, suggestions are given regarding the presentation of evidence concerning the chemical fate of hazardous wastes in the injection zone.

Information should be presented in the following sequence;

1. **Description of the injection environment.**
   A comprehensive description of the injection environment should be provided. The description is needed, not only to permit the development of an appropriate hydrologic model of the injection zone and confining horizons, but also to understand the nature of waste stream reactions with the rock matrix and develop an appropriate geochemical model. The description should include an account of the identity, distribution and heterogeneity and petrofabic of rocks in the injection zone and confining horizons, how they formed, their depositional environment, their physical properties, i.e. permeability, porosity, grain size and internal surface area, their mineralogy i.e. the identity and concentrations of mineral species composing the rock, and their chemical properties, i.e. chemical composition, and if necessary, parameters that characterize the reactive surface properties of the rock, e.g. organic content, hydroxylamine hydrochloride extractable iron and cation exchange capacity, (CEC).
   Of equal importance to the actual determination of the physical, mineralogical and chemical parameters characterizing the injection zone and confining horizon is the potential spread of values. Physical and chemical characterization studies are usually made on samples of core or drill chips. Such small samples

are unlikely to be representative of the injection zone as a whole. The petitioner should therefore determine the destribution of values expected, either from the characterization of multiple samples, or by comparison with samples taken from other locations in the same or similar geologic formations:

2. **Characterization of the waste stream(s).**
   Complete chemical analyses should be given and all hazardous waste constituents identified together with EPA concentration limits in drinking water or current analytical detection limits, if no EPA standards exist. RCRA waste codes should be given. The expected variation in concentrations of the hazardous constituents should also be given. The expected range of injection rates should be specified as well as the maximum permitted by EPA. Other physical properties of the waste stream, if they are used in subsequent modeling, e.g. density, temperature, viscosity, electrical conductivity, etc., should also be tabulated.

3. **Mechanisms of decomposition or immobilization of the hazardous wastes identified.**
   The mechanisms by which the hazardous waste is immobilized should be identified and all quantitative data used in subsequent models and pertinent to the mechanism tabulated, i.e. rate constants, equilibrium constants, etc. Literature from which the information is derived should be referenced. Specific studies conducted to acquire needed thermodynamic or kinetic information should be described fully in supporting appendices, and the results and conclusions summarized in the body of the petition text.

4. **Modeling studies**
   The modeling studies should include a complete description of the model used, and how the mechanisms identified in (2) above were incorporated in the model. Any code or simulator used should be identified, indicating who was responsible for its development, the version used, and if appropriate, the thermodynamic data employed in the simulation. If the code is non proprietary and has been verified and validated, references should be cited describing such tests, and a justification provided that the verification and validation studies are relevant to the conditions under which the computations were performed. If the code is proprietary, verification and validation demonstrations should be incorporated in supporting appendices, unless they are published elsewhere. If

the code has been verified or validated only to a limited extent, justification should be provided that the documentation provided is sufficient for the computation(s) given in the petition.

All assumptions, boundary conditions, initial parameters, etc. should be identified and described. Quantitative values should be given, specifying the ranges used for critical parameters, and sources of the data and supporting evidence. If calibration studies are conducted, then a description of these should be given in supporting appendices and the results summarized quantitatively in the petition text. The results of the modeling studies should be presented in readily understood graphical or tabular format, with appropriate textual amplification. The results in relation to EPA technical requirements should be clearly spelled out. A sensitivity analysis should be conducted to account for the known uncertainties in given parameters, and the impact on model predictions demonstrated.

**4. Conclusions**

The findings and conclusions regarding the chemical fate of each hazardous waste constituent in the injection zone should be given in summary form at the end of the pertinent section of the petition.

It is particularly important to note that all assumptions, parameter values and ranges used in predictive modeling of the fate of the hazardous wastes be included in the body of the text, and not buried in appendices. All tables and figures should be positioned in the petition immediately following their first reference in the text. They should not be positioned at the end of the text as if the petition were to be submitted for publication.

### 7.2.2 Quality Assurance

The EPA expects that all supporting experimental work and chemical analyses be conducted under approved quality assurance protocols. Measuring instruments should be periodically calibrated with standards, traceable to NIST, or other industrial standards of appropriate quality and chemical analyses should be conducted using EPA approved methods. Deviations from acceptable EPA procedures must be fully documented, with demonstrations that alternative procedures yield the same or better quality results than those currently accepted by EPA.

Many of the geochemical computer codes, described in this report, have been developed by several investigators over periods of ten years or more. The development of such codes is rarely supported with the level of funding necessary to generate the stingent quality assurance documentation necessary to meet federal government standards. An exception is EQ3 (Wolery, 1986) which is supported by the U.S. Department of Energy to provide the quality assurance documentation required by the U.S. Nuclear Regulatory Commission. It is therefore extremely important that the petitioner provides, documentation that the computer simulations are of the necessary quality and reliability when such documentation is not readily available from other sources. One benefit that does accrue from quality assurance documentation for computer codes is the traceability of sources of information from which the computer code or its associated thermodynamic data base is derived, such as that provided for EQ3 or ECHEM (Krupka et al., 1988) This greatly facilitates the checking of original source material and forming a judgment of the reliability of the package for an intended application.

If the petitioner is obliged to derive some of his own thermodynamic and kinetic data in order to conduct the predictive simulations necessary for the submission to EPA, then all such derivations should be completely documented, and the basis for all calculations described.

### 7.2.3 Suitability of a Computer Code for a Given Application

Although a few petitioners might find the time and resources to develop their own conceptional and mathematical models, most will find it necessary or desirable to utilize existing computer codes and data bases. A petitioner must then consider whether a particular code embodies a model that realistically represents injection zone conditions. It is essential that the user understands thoroughly the scientific basis of the algorithms employed in a selected code. Many models are satisfactory for certain limited applications, but give distorted or meaningless results in others. The writers of many of the codes had in mind only specific applications at the time they were written, and rarely is any attempt made to endow them with universal applicability. Thus, the user may find that a code may not function reliably when provided with parameters typical of injection zone conditions, when it was originally conceived to solve problems relating to soil chemistry, for example. The thermodynamic constants used in the model could be applicable only at different temperatures, pressures or supporting electrolyte compositions, or the aqueous electrolyte model could be restricted to a range of ionic strengths outside that observed in an injection zone containing a saline oil-field brine.

Another problem with the use of available codes is that they are often very complex. It is not surprising that unanticipated bugs lurk within them, only to surface inconveniently after elaborate preparations have been made to simulate a particular problem. The originators of the codes often are in no position to trouble-shoot for the inexperienced user, although they may welcome information that helps them locate and eliminate bugs.

Most codes are supported on an *ad hoc* rather than a continuing basis, a notable exception being the EQ3/EQ6 package developed by T. J. Wolery at the LLNL under DOE sponsorship. OLI Systems Inc. also maintains proprietary software for chemical modeling. The lack of continuing support is not necessarily a major problem. A code that has not been actively supported for several years, however, could have been written for a computer with an obsolete configuration and operating system. The code might not run with a present day machine even though written in FORTRAN, and could require considerable effort to make it operational. Documentation provided with geochemical computer codes is variable in quality and comprehensiveness, ranging from very complete, with numerous worked examples, such as is provided with the EQ3, ECHEM, and PHREEQE packages, to very superficial. Code documentation usually presupposes a familiarity with geochemical principles.

### 7.2.4 Verification and Validation of Models

Another aspect of quality assurance is the "verification" "calibration" and "validation" of computer codes. Before these terms can be described, a discussion is required to clarify the meaning and scope of computer simulations of geochemistry and geochemical transport modeling. The petitioner desires to simulate quantitatively the chemical transport processes relevant to hazardous waste containment. This initially involves the creation of a conceptional model of the injection zone and the waste stream invading the rock pores and fractures. The model is formalized as a mathematical representation of the physical and chemical processes and the spatial structure in which hazardous waste transport occurs. To simulate the behavior of the system in response to various perturbations over time, the petitioner normally requires a method of representing this response in numerical form. Usually this involves writing algorithms representing the temporal evolution of the system. The algorithms are represented in coded form as a set of instructions to permit a computer to perform the necessary digital calculations.

Potential errors can creep in it all stages of the modeling and simulation process.

1. The conceptional model must be a realistic interpretation of the anticipated processes that would actually occur, and the spatial representation must be consistent with the injection zone and confining beds.
2. The physical and chemical conditions and processes must be correctly identified in order to create a realistic mathematical model.
3. Even though the physical and chemical conditions may be correctly identified, they must be formulated in the correct mathematical form.
4. The mathematical model must be represented by algorithms acceptable for digital computation, and the correct boundary conditions must be identified.
5. The algorithms must be correctly coded for use by a digital computer.
6. In conducting a computer simulation, the correct initial and boundary conditions and choice of parameter values must be made.
7. Laboratory or field data must be correctly measured or analyzed.
8. A predictive simulation must be made over a time span where the model assumptions and parameters are valid.

The problems associated with the conceptualization and implementation of models to simulate transport processes in the natural environment have received increasing attention in recent years, largely in response to radioactive waste isolation programs in various nations (Tsang, 1987, 1991). The isolation of both radioactive and liquid chemical wastes deep underground must be assured over very long time periods through the use of predictive models.

The large number of potential uncertainties involved in such predictions, and rigorous isolation requirements, have stimulated a reapprasial of model validation concepts. While it is beyond the scope of this report to discuss these concepts at length, some aspects require further amplification. Quality assurance with respect to computer codes has lead to general usage of the terms "verification," "calibration" and "validation." The meaning of these terms are discussed in the following paragraphs.

"Verification" refers to the testing of the code to ensure that the coding yields a correct or nearly correct answer with specified input data. Verification is usually achieved through either the comparison of numerical with analytical solutions, through back-calculation of a result to ensure that it is consistent with the algorithm and input data used, or through direct comparison with the results of another code that is capable of solving the same problem. In most cases the verification of geochemical codes is relatively straight forward and is usually not a pressing problem. Tsang (1991) refers to a

code that is properly verified and documented, as "certified," i.e. it is "mathematically correct in the formulation and solutions, and properly documented on its purpose, accuracy, required discretization and range of applicability." Certification is a desirable goal, but as yet there appears to be no formally established certification procedure.

Several verification studies have been conducted by comparing the output of one code against another, where the same problem was initially proposed for solution. They include the study by Nordstrom et al. (1979) on 14 distribution of species codes, a comparison of EQ3/6 with PHREEQE (Intera Environmental Consultants, 1983) the study by Kincaid and Morrey (1984), and a comparison of EQ3/6, PHREEQE and SOLGASWATER by Puigdomenech and Emren (1990). Verification studies involving chemical transport codes include those by Miller and Benson (1983), Cederberg et al. (1985), and Liu and Narasimhan (1988b) and Narasimhan et al. (1992).

"Calibration" is a term usually applied to the use of transport or chemical transport codes in which not all of the parameters employed have been assigned correct values initially. Correct values are estimated by comparing the computer simulation to observed field data and 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 calculation process is usually employed where certain parameters cannot be measured directly, either in the laboratory or in the field.

"Validation" of a code is in reality confirmation of the validity of the model upon which the code is based. It logically follows that validation can be accomplished only under those same conditions and constraints that were presumed when initially formulating the model. Furthermore, a single validation demonstrates only that the model yields the correct answer(s) for the conditions of the validation. In principle, observations would have to be conducted many times over the full range of parameter variations permitted by the model in order to prove the model's validity.

As models become more complex, and the time periods required to predict model parameters extend beyond those that are practical for conducting tests, the difficulty in providing a meaningful validation increases substantially. Under such circumstances it becomes practical only to conduct partial validations of component parts of the model. Thus, a complex reactive chemical transport model might be sub-divided into individual processes, such as equilibrium chemistry (homogeneous equilibrium in the aqueous phase, heterogeneous equilibrium, ion exchange, adsorption, etc.) chemical kinetics, (hydrolysis, decomposition precipitate sorption, etc.), and transport processes (fluid flow, diffusion, dispersion etc.). The component describing the spatial geometry of the injection zone is a special problem in that it is site specific. Validation could be accomplished

by well testing at the site using primary injection, backup, or monitor wells.

For simple distribution of species problems, attempts at validation often reveal serious discrepancies between the real and simulated worlds. The discrepancies are traceable to three sources, (1) Utilization of an inappropriate model for the problem, i.e. error type 1, p. 109, (2) Errors in the thermodynamic or kinetic data, or other parameter values, i.e. error type 5, p. 109, or (3) Misinterpretation of laboratory or field data, i.e. error type 6, p. 109.

In many cases, the lack of agreement between observation and simulation stems from a combination of all three sources, but it is usually not readily apparent which is the principal contributor. Thus it is essential, when attempting validation studies, to ensure that the chemical system under scrutiny is completely and unambiguously characterized. The need for validating geochemical models and identifying sources of error in thermodynamic data has been recognized, and some progress has been made under the Chemval Project (Broyd et al., 1990).

Validation of more elaborate geochemical codes, such as those simulating reaction progress, $\xi$, is even less secure. Yet initial studies, cited in section 6.4, suggest that their use should be expanded, as they sometimes permit calibration of the temporal evolution of a chemical system during advective transport in ground water systems.

Validation studies employing chemical transport codes have for the most part been restricted to simple or partial systems, sometimes only qualitative validation was achieved, i.e. the results of a simulation correlated well regarding the gross features of the chemical response of the system, 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. (1981b), Miller and Benson (1983), and Cederberg et al. (1985) using the same data from the Palo Alto Baylands project. In these simulations, simple reversible ion exchange processes on alluvium were assumed, and good agreement was obtained with the response of a sedimentary aquifer to injected fluid of different composition from the preexisting ground water. A slightly more complex system involving the dissolution of gypsum and ion exchange was studied by Grove and Wood (1979) and compared with data obtained from a laboratory experiment, and a shallow test aquifer at Lubbock, Texas. Agreement with field observations was reasonably good.

The time and effort spent on the development and verification of computer codes in geochemistry currently has outstripped corresponding efforts at validation. Apart from a few simple validation cases cited above, the literature describing geochemical validations is insufficient to judge the reliability of the thermodynamic data, and the current

comprehension of geochemical processes occurring in the field. The correlation of predicted mineral stabilities with those actually observed in a particular geochemical environment, is encouraging, but does not necessarily demonstrate the correctness of the simulation unless repeated demonstrations provide the necessary corroborating evidence.

### 7.2.5 Use of Conservative Values

In many cases, so little may be known about the potential fate of a hazardous waste in the subsurface environment, that recourse must to be made to empirical studies to estimate and the magnitude of sorption, precipitation or decomposition. Such experimentation should always be performed with the objective of separating variables. Because transient effects of considerable importance to retardation over periods in excess of 10,000 years, may not be observable in a laboratory experiment of a few week's or month's duration, laboratory experiments will normally provide data only to compute conservative limits on migration rates. The use of "overtest" conditions to accelerate chemical reactions, either through increasing the temperature, by raising the concentration of the hazardous constituent, or by increasing the concentration or reactivity of the sorbent should be applied with caution because such deviations have the potential for misleading or incorrect interpretations when extrapolated to field conditions. The petitioner therefore should consider very carefully whether his experimental results can justifiably be extrapolated, and if so what arguments can be used to support his claims.

Finally, it should be emphasized that the petitioner is given the task of demonstrating containment of a hazardous waste under the conditions specified by EPA. The petitioner must show the validity of the containment mechanisms of a given hazardous substance. Thereafter, he must show that all parameters used are unequivocally conservative in computing whether or not containment will be achieved. So long as this is done to the satisfaction of EPA, all other arguments are secondary. EPA is concerned less with the precision of predictions of the fate of the waste, than with their being conservative.

The petitioner may question why he should be concerned with the precision and accuracy of geochemical models used to justify the containment of hazardous wastes in the injection zone if EPA requires only that the predictions be conservative. The response is that the petitioner must provide the needed assurance that his predictions are indeed conservative and that the arguments be uses in justification for the selection of model parameters are meaningful and readily understood. As is elaborated upon in the following section, EPA also requires that an uncertainty analysis be conducted. In order to do this, the expected variation in parameter values must be known for the injection zone environment and waste stream composition. Because geochemical models often

contain very many parameters, it is important to identify those that may influence the final result greatly from those that do not. The sensitivity of a given parameter in affecting the final result may depend on an accurate determination of another parameter, e.g. the solubility of certain precipitates containing hazardous metals or hydrolysis by hazardous organic compounds may be pH dependent.

The level of accuracy required of a given model depends on the nature of the problem at hand. For simple mechanisms of decomposition or immobilization involving few parameters, and a large margin of error in proving containment, high levels of accuracy are not required, and excessively conservative assumptions may be used without adverse effect on the petition demonstration. However, as the question of containment becomes more uncertain, so will the need for greater precision and accuracy increase in the models used. If the geochemical model must be also complex in order to accommodate all the chemical processes affecting the fate of the hazardous constituents of the injected waste, then the cumulative effect of parameter uncertainty may be so great as to render model prediction meaningless. In this report, the writer has emphasized the highest level of accuracy in all parameters consistent with the current state of the art, even though it is conceded that such accuracy may not be necessary for all petitions. In many cases, it is better to err on the side of unnecessary accuracy in parameter determination to avoid jeopardizing the validity of model predictions, or repeating the calculations if insufficient accuracy was used initially.

### 7.2.6 Uncertainty Analysis

Parameters that require consideration in hazardous waste transport modeling include thermodynamic properties of participating species and phases, rate constants, sorption and exchange coefficients, the accessible surface area, organic content, hydroxylamine hydrochloride extractable iron, or specific sorption site density, complexing effects, hydrodynamic parameters such as hydraulic dispersion, and the microstructural environment, i.e. heterogeneities in porosity, permeability, sorption capacity, mineralogy, matrix block diffusion, etc. A waste stream containing several hazardous constituents may interact with the injection zone host rock in ways which, if not unpredictable, are at least complex and difficult to quantify. A typically complex hydrochemical system may involve perhaps a hundred or more parameters, many of which may be poorly determined or unknown. In some scenarios, it may be necessary not only to identify all of the critical

parameters to predict containment, but to quantify the significance that uncertainties have on the final analysis. An ad-hoc variation of selected parameters would not normally be adequate as otherwise unidentified complex interactions between parameters may be missed.

Many parameters used in geochemical calculations are based on the findings of single investigations, and no corroborating evidence may be forthcoming. It is dangerous to proceed on the assumption that such information is always correct. For important parameters, and particularly those whose correctness may not be intuitively evident, corroboration is extremely desirable. This may be provided from independent studies, or through a demonstration of internal consistency with independent data.

In view of the fact that the predictive analysis must be conservative, an evaluation of the probability of each parameter causing EPA technical requirements for each hazardous waste to be exceeded, should be estimated, and the overall probability calculated for containment not being achieved. The evaluation of statistical uncertainty and sensitivity analysis in complex geochemical models has received increased attention during the past decade, primarily because of the stimulus provided by the need for more precise estimates of uncertainty attached to models predicting radionuclide migration from high level nuclear waste repositories.

Because of the large number of variables in geochemical models, and the computer intensive requirements for their solution, the issue is to find a method whereby the effect of uncertainties in the input parameters on the output can be determined in an efficient and cost effective manner. Iman and Helton, (1985, 1988) investigated three techniques, response surface methodology based on input from a factorial design, Latin Hypercube Sampling (LHS) with and without regression analysis, and differential analysis. These techniques were tested on three complex computer models, two of which concerned chemical processes and one concerned primarily with physical processes. They found that the LHS to be the preferred method.

The LHS method is a modified form of Monte Carlo sampling, which permits a reduced number of samples to be made in order to obtain a required degree of confidence. Because straight forward Monte Carlo sampling techniques are computer intensive when applied to geochemical problems e.g. see Merino (1979), the LHS approach appears to represent a practical advance. Fortran 77 computer codes have been written by Iman and Shortencarier (1984) and Iman et al. (1985) to facilitate the use of LHS and interpretation of results when conducting sensitivity analyses of complex computer models.

While such sophisticated techniques may not soon be implemented routinely in models predicting the fate of hazardous wastes, their use may encourage a more systematic approach to sensitivity analyses and increase both the confidence in chemical fate predictions and help identify those critical parameters needing greater care in their measurement and characterization.

Section 8

## CONCLUSIONS

The review of geochemical modeling capabilities and the underlying chemical and physical principles upon which the models are based leads to a series of conclusions regarding the state of knowledge in this area, and implications for predicting hazardous waste behavior in deep saline aquifers. They are as follows:–

1. Geochemical modeling of the fate of hazardous waste in saline aquifers in deep sedimentary formations is at a preliminary state of development, and has not been adequately tested in the field or the laboratory to show that it can be used for quantitative predictions under all conditions.
2. Many diverse mechanisms affect the fate of hazardous waste constituents in deep aquifers. No single computer code is presently capable of modeling all processes. Available computer codes must be selected on the basis of what they can best do for a particular application.
3. The state-of-the-art in many areas of geochemical research is embryonic. Examples include the accurate determination of activity coefficients of ions in strong mixed electrolytes (i.e. brines), the thermodynamic properties of clays, and the thermodynamics of adsorption. Thermodynamic data for many minerals and organic aqueous species are unavailable. Therefore, much initial preparatory research must be done by the petitioner before he can conduct suitable simulations. Existing thermodynamic data bases used with geochemical modeling codes will require close scrutiny before they are used.
4. Although the literature describing the adsorption of inorganic and organic species on clays is substantial, no integrated compilation of data is available for practical applications. Suitable adsorption or ion exchange models, which can be utilized for the diverse range of conditions expected in deep well injection, have not been tested sufficiently under those conditions to establish their utility.
5. Information on the kinetics of both heterogeneous and homogeneous reactions of relevance to the fate of hazardous compounds is fragmentary. The petitioner will frequently have to resort to his own evaluations of literature data or conduct his own experiments to acquire the needed data.
6. A substantial number of computer codes are available to let the petitioner conduct evaluations of distribution of species in solutions. Computer codes to

model mass transfer or mass transport with simultaneous chemical reactions, are presently of limited availability or scope. The petitioner must be cautious in the selection of codes, and should ensure that a chosen code will permit the simulations he desires.

7. Distribution of species codes are of two-types; the "equilibrium constant" type, and the "Gibbs free energy minimization" type. Both are mathematically equivalent, but the latter is in principle more flexible and easy to use. Most available codes are of the former type. Additional work is often required to modify any of them for use in deep well injection studies.

8. Chemical transport codes fall into two categories, the "one step" or the "two step type". The former results in the need to solve highly non-linear equations and can therefore be computationally intensive. The latter may suffer from problems of drift, but tends to be more flexible in its ability to treat a diverse range of problems.

9. Some geochemical codes have been verified, but few have been used to test the validity of the underlying models. There is an urgent need for more field validation studies under any conditions, let alone those associated with deep disposal wells.

10. The development of methods to conduct systematic sensitivity studies using complex geochemical codes is urgently needed. Latin Hypercube Sampling methods for input parameter selection appears to be the most promising approach when using repeated computer runs to define the uncertainty of results.

## ACKNOWLEDGEMENTS

This work was supported by the Underground Injection Branch, Office of Drinking Water (WH-550), U.S. Environmental Protection Agency, through U.S. Department of Energy Contract No. DE-AC03-76SF00098.

The writer would like to take the opportunity to acknowledge his debt to Dr. George Birchard of the U.S. Nuclear Regulatory Commission, who sponsored research involving the validation of geochemical computer models through NRC FIN No. B 3040-6 under Interagency Agreement DOE-50-80-97, through U.S. Department of Energy Contract No. DE-AC03-76SF00098. The research conducted under the latter program over a five year period was the source of many fruitful ideas and concepts that are expressed in this report.

The writer would also like to express his appreciation for many informal discussions with his colleagues at the Lawrence Berkeley Laboratory, who provided lucid explanations of issues relating to chemical transport modeling. Among these, he would particularly like to thank Dr. Chalon L. Carnahan, Iraj Javandel, T. N. Narasimhan, and Jehan Noorishad. He would also like to thank the reviewers Dr. Regina M. Capuano, University of Texas at Austin, Dr. William R. Roy, Illinois State Geological Survey, and Mr. Robert E. Smith, of the U.S. Environmental Protection Agency for their many constructive comments and suggestions, which have been accounted for through improvements and modifications to the contents of this report. Discussions with scientists and engineers at the EPA regional offices and of companies who are responsible for the preparation of petitions have greatly assisted the author in putting into perspective the issues concerned with producing and evaluating petitions. The author would like to acknowledge their contributions in many of the topics discussed in the this report.

The state of the art in geochemical modeling would be nowhere near what it is today and this report would not be possible, if it had not been for the leadership of the late Professor R. M. Garrels, University of South Florida, and Professors H. C. Helgeson and K. S. Pitzer, University of California, Berkeley. The author is indebted to them for their vision and as a source of inspiration.

Finally, the writer would like to extend his thanks to Dr. Chin-Fu Tsang, of the Lawrence Berkeley Laboratory and Mr. David W. Morganwalp, formerly project officer of the Underground Injection Control Branch of the Office of Drinking Water, U.S. Enviromental Protection Agency, and Mr. Robert Smith, the current project officer, for their interest, support and patience during the preparation of this report.

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