DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

LBL--22719

DE87 006930

MODELING OF THERMODYNAMIC AND CHEMICAL CHANGES IN LOW-TEMPERATURE GEOTHERMAL SYSTEMS

Amanda L. Spencer

Earth Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

M.S. Thesis

December 1986

This work was supported by the Assistant Secretary for Energy Research, Office of Basic Energy Sciences, Division of Engineering and Geosciences, through the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

due

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Table of Contents

LIST OF FIGURES	i
LIST OF TABLES	v
NOMENCLATURE	vii
ACKNOWLEDGMENTS	x
1.0 INTRODUCTION	1
2.0 BACKGROUND	4
2.1 Literature Review	4
2.2 Chemistry of Low-Temperature Systems	14
3.0 DEVELOPMENT OF THE NUMERICAL CODE	26
3.1 Governing Equations	26
3.2 Numerical Formulation	30
3.3 Code Modification	35
3.4 Performance of the Code	37
4.0 APPLICATION OF THE CODE	43
4.1 Sensitivity Studies	43
4.1.1 Approach	43
4.1.2 Study of Kinetic Reactions	46
4.1.3 Study of Convective Transport	59
4.2 Non-Dimensional Study	66
4.3 Field Example	87
4.4 Theoretical Study	114
5.0 CONCLUSIONS	123
APPENDICES	128
Appendix A: Equation of State for Liquid Water	128

Appendix B: Subroutine incorporated into the code PTCC to calculate the kinetic reactions of oxygen-18.	132
---	------------

LIST OF FIGURES

Figure 1.	Chlorine concentration versus time from Selfoss, Iceland (Tomasson and Halldorsson, 1981).	11
Figure 2.	Chemical data from the Wairakei geothermal field in New Zealand (Henley and Stewart, 1984)	12
Figure 3.	Chemical data from the La Primavera geothermal field in Mexico (Domingues and Lippmann, 1983).	13
Figure 4.	Equilibrium curves for oxygen-18 for (a) quartz/water (Clayton et al., 1972); (b) basalt/water, felsic rock/water (after Cole et al., 1983) (c) dolomite/water (A), calcite/water (B); (Northrop and Clayton, 1966).	25
Figure 5.	Sketch showing region R, with subregion V, and unit normal $\hat{n}$ (after Lai, 1985).	27
Figure 6.	Sketch of mesh structure with node n connected to m surrounding nodes separated by a distances of $D_{n,m}$ and $D_{m,n}$, respectively, and interface area of A (Bodvarsson, 1982).	33
Figure 7.	Three node mesh used in testing transport of the non-reactive chemical components.	38
Figure 8.	Analytical and numerical solutions to kinetic transport problem for oxygen-18.	41
Figure 9.	Sketch of three-node mesh used in sensitivity studies.	45
Figure 10.	The influence of the rock/fluid system on the kinetic reactions of oxygen-18.	47
Figure 11.	Comparing the effects of δ_R^{18} on the kinetics of oxygen-18 in a dolomite/water system at a temperature of 125 °C.	50
Figure 12.	Significance of the average grain radius on the kinetic reactions of oxygen-18.	52
Figure 13.	Significance of porosity on kinetic reactions of oxygen-18.	53
Figure 14.	Significance of temperature on the kinetic reactions of oxygen-18.	55
Figure 15.	Significance of temperature on the kinetic reactions of silica. Initial silica is 25 ppm.	57
Figure 16.	Significance of temperature on the kinetic reactions of silica. Initial silica is 500 ppm.	58
Figure 17.	Significance of A/V on the kinetic reactions of silica.	60
Figure 18.	Significance of porosity on silica transport by convection only.	62

Figure 19.	Comparison between the convective transport of silica with and without kinetic reactions.	63
Figure 20.	Significance of volume on silica transport by convection only.	64
Figure 21.	Temperature versus time for various field volumes and flow rates.	68
Figure 22.	Fitting a linear temperature function to the kinetic rate constant for silica.	69
Figure 23.	Equilibrium solubilities for silica (from Robinson, 1982). A linear function of temperature is assumed over the temperature range 80 °C to 150 °C, for α -cristobolite.	70
Figure 24.	Fitting a linear temperature function to the kinetic rate constant for oxygen-18.	71
Figure 25.	Testing the uniqueness of the nondimensional parameters for, (a) silica and (b) oxygen-18.	75
Figure 26.	Type curves for different values of the dimensionless parameters, D_1 and D_2 , by varying q/x .	77
Figure 27.	Simple cross-sectional sketch of the Ellidaar geothermal system (Lai, 1985).	78
Figure 28.	Field data from the Ellidaar geothermal field (Hettling, 1984) for silica plotted non-dimensionally against dimensionless time.	79
Figure 29.	Type curves of range in dimensionless parameter D_3 , showing effect of relative recharge in from the top and side. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100x \bar{\alpha} = \% \text{ flux from the top}$; $100x \bar{\beta} = \% \text{ flux from the side}$).	80
Figure 30.	Type curves of range in dimensionless parameter D_3 . Porosity has been raised to from 5% to 10%. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100x \bar{\alpha} = \% \text{ flux from the top}$; $100x \bar{\beta} = \% \text{ flux from the side}$).	82
Figure 31.	Type curves of range in dimensionless parameter D_3 . The q/x has been decreased by an order of magnitude. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100x \bar{\alpha} = \% \text{ flux from the top}$; $100x \bar{\beta} = \% \text{ flux from the side}$).	83
Figure 32.	Type curves of range in dimensionless parameter D_3 . The q/x has been increased by an order of magnitude. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100x \bar{\alpha} = \% \text{ flux from the top}$; $100x \bar{\beta} = \% \text{ flux from the side}$).	84

Figure 33.	Type curves of range in dimensionless parameter D_3 . The value of A/V has been increased from 5.5 to 25.0. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).	85
Figure 34.	Plot of temperature versus time showing match between numerical model and field data from the Ellidaar field.	88
Figure 35.	Plot of fluoride versus time showing the match between the numerical model and field data from the Ellidaar field.	89
Figure 36.	Plot of sodium versus time showing the match between the numerical model and field data from the Ellidaar field.	90
Figure 37.	Plot of silica versus time showing the match between the numerical model and field data from the Ellidaar field.	93
Figure 38.	Plot of oxygen-18 versus time showing the match between the numerical model and field data from the Ellidaar field.	94
Figure 39.	Map of Seltjarnarnes geothermal field, Iceland showing layout of wells and main production area (Kristmannsdottir, 1986).	96
Figure 40.	Two-layer mesh used to model the Seltjarnarnes geothermal area Iceland, including the initial conditions and values of field parameters.	97
Figure 41.	Plot of silica versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.	99
Figure 42.	Plot of chloride versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.	100
Figure 43.	Plot of sodium versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.	101
Figure 44.	Plot of oxygen-18 versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.	102
Figure 45.	Plot of temperature versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal field, Iceland.	103
Figure 46.	Silica versus time with and without kinetic transport using the best model for Seltjarnarnes.	104
Figure 47.	The central section of the two-dimensional mesh designed to model the Seltjarnarnes geothermal field, Iceland (Tulinius et al., 1987). Small dots mark the well sites.	106

Figure 48.	The chlorine transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.	108
Figure 49.	The sodium transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.	109
Figure 50.	The silica transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.	110
Figure 51.	The oxygen-18 transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.	111
Figure 52.	Sketch showing the suggested boundary between seawater and meteoric water at the Seltjarnarnes geothermal field, Iceland.	112
Figure 53.	A simple hypothetical model of a typical geothermal system.	115
Figure 54.	Temperature contours for the system evolving under the influence of a heat source for 100,000 years. Contour units are in °C.	117
Figure 55.	The pattern of fluid flow and of the silica precipitation/dissolution for the system evolving under the influence of a heat source. The relative sizes of the arrows corresponds to the amount of fluid flow. The light shading represents the area of precipitation; the dark shading corresponds to the area of dissolution.	118
Figure 56.	Oxygen-18 contours for the evolving system after 100,000 of heating. Contour units are in per mil.	121

LIST OF TABLES

TABLE 1.	Equations describing the equilibrium constant for each form of silica	18
TABLE 2.	Temperature dependent functions for the rate and equilibrium constants of oxygen-18 for each rock/fluid system.	21
TABLE 3.	Oxygen-18 contents of the rock types included in the present work. (Source: Henley, Truesdell and Barton, 1984)	23
TABLE 4.	Performance test of conservative species transport using the code PTCC.	39
TABLE 5.	Performance test on the kinetic reactions of oxygen-18 using the code PTCC.	40
TABLE 6.	Comparison of the times to reach chemical equilibrium at various temperatures obtained by the code PTCC and those obtained using the analytical solution developed by Cole (1983).	42
TABLE 7.	(a) Values of the parameters used in the single element model for the sensitivity studies of the kinetic reactions. (b) Values of the parameters used in the model for the convective sensitivity studies.	45
TABLE 8.	Comparison of the equilibrium and rate constants between rock/fluid systems at 125 °C.	48
TABLE 9.	Values of the dimensionless parameters held constant in Figures 29 through 33.	81

TABLE 10. **Values for the concentrations of the chemical species for** **107**
the different fluids used in modeling the Seltjarnarnes
Geothermal field.

NOMENCLATURE

A	Area [m^2]
A/V	Surface area of silica per volume [m^{-1}]
C	Concentration of silica [ppm]
C*	Dimensionless concentration
CS	Concentration of chemical species [ppm]
c	Heat capacity [$\text{J/kg} \cdot ^\circ\text{C}$]
D	Coefficient of dispersion
E	Total energy [J]
G_f	Mass source/sink [$\text{kg/m}^3 \cdot \text{s}$]
G_H	Heat source/sink [$\text{J/m}^3 \cdot \text{s}$]
g	Acceleration of gravity [m/S^2]
K_t	Effective thermal conductivity [$\text{kgm}^2 / ^\circ\text{C}(\text{s}^2)$]
k	Absolute permeability [m^2]
k_1	Rate constant for kinetic reactions of silica [m/s]
M	Mass [kg]
$\hat{n}$	Direction cosine
^{16}O	Oxygen-16
^{18}O	Oxygen-18
P	Pressure
q	Flow rate [kg/s]
r_1	Rate constant for kinetic reactions of oxygen-18 [$\text{mol/m}^2 \cdot \text{s}^1$]
S	Moles of oxygen in solid
SA	Surface area [m^2]

T	Temperature [$^{\circ}\text{C}$]
t	Time [s]
V	Volume [m^3]
v_d	Darcy velocity [m/s]
W	Moles of oxygen in fluid
X	Mole fraction [mols/kg]
α	Fractionation factor for oxygen-18
β	Compressibility [pa^{-1}]
δ^{18}	Del value for oxygen-18 content [per mil]
γ	Expansivity [$^{\circ}\text{C}^{-1}$]
μ	Dynamic viscosity [$\text{kg/m}\cdot\text{s}$]
ω	Average grain radius [m]
ϕ	Porosity
ρ	Density [kg/m^3]
τ	Dimensionless time

Subscripts

f	Fluid
H	Heat
m	Mass
o	Initial value
R	Rock/solid
RW	Rock-water
s	Source/sink
t	Thermal

Superscripts

eq **Equilibrium value**

f **Final**

i **Initial**

ACKNOWLEDGEMENTS

First, I would like to thank Dr. P.A. Witherspoon for his support and guidance during my work on this thesis. His critical review of this work, as well as his encouragement and enthusiasm, were most appreciated. I would also like to express my deepest gratitude to Dr. G.S. Bodvarsson. His helpful suggestions contributed significantly to this project. He has greatly aided in my technical writing skills and has provided me with many fundamental techniques in approaching numerical modeling.

I would like to thank Dr. K.S. Udell for his helpful discussions and critical review of my thesis work. Very special thanks are due to Mary Bodvarsson. Without her help in typing and editing, this thesis would have been greatly delayed.

Finally, without the encouragement and support of Robert Prucha this work might not have been completed. His help and patience were greatly appreciated.

1.0 INTRODUCTION

In recent years, study of geothermal systems as a means for energy production has significantly increased. However, the majority of this research has focused on high temperature systems, while exploration and study of low-temperature systems for direct use has received much less attention in the United States. Use of low-temperature systems for direct use is common in many other countries, including the Soviet Union, Japan, China, and Iceland. These countries provide good examples of the benefits of utilizing low-temperature geothermal systems as an alternate means of energy.

A potential problem with the development of low-temperature geothermal systems is the risk of a rapid decline in the temperature of the system as a result of exploitation. This cooling directly affects the economic viabilities of a geothermal project and it is of great importance to be able to determine the cold water recharge zones and predict the long term rate of the temperature decline. Most previous studies of geothermal systems have consisted of developing a hydrological model of the region from existing geological and geophysical data. Mass and heat transport equations are then employed to estimate the permeability of the field, and the field volume. The role of geochemistry has been predominantly qualitative, for tracing the paths of fluid flow with tracers or indicate the temperature of the system using empirical relations between the chemical component and temperature (geothermometry).

In the present work, a method is developed to incorporate the transport of several chemical components into a model of the transport of fluid mass and heat within a geothermal system. Utilizing as much data from the geothermal system as possible would permit a more detailed understanding of the geothermal system under investigation. By incorporating the chemical transport into a mass/heat transport model, more of the available data on the geothermal field would be employed and consequently more information can be extracted from the analysis. It will be demonstrated that the use of coupled hydrological, thermal and chemical data will allow for the determination of field porosities, amounts and regions of cool recharge into the system as well as field

permeabilities and the hot reservoir volume. With the additional information a reliable prediction of the long-term cooling rate can be made. The economical potential of a geothermal project can then be forecasted in the early stages of the project.

OBJECTIVE AND ORGANIZATION OF PRESENT WORK

The objective of the present study is to develop a method of modeling the chemistry of low-temperature systems to aid in determining the zones and amounts of cool recharge into a system, and in estimating the properties of a system. The study is presented in three main parts:

- (1) A background on topics pertinent to the present work;
- (2) Development of a numerical code incorporating chemical transport.
- (3) Applications of the modified code to both theoretical and field examples.

The first part includes a literature review covering different methods of modeling geothermal systems and previous work done using these methods. Following the literature review, a short chapter is given on the behavior of chemical components common to low-temperature geothermal systems. Several chemical components are chosen as strong candidates to be included in a modeling scheme and are discussed in more detail.

The second part involves a review of the governing equations for mass, heat and chemical transport. The numerical code, PT (Bodvarsson, 1982), capable of modeling pressure and temperature, is then described. Next, modifications to PT to incorporate silica transport, performed previous to the present work by Lai (1985), are discussed. The modifications to incorporate multi-component chemical transport into the existing code are developed, and the performance of the new code tested.

In the third part of this work, the code is applied to test the sensitivity of the chemical transport to various field parameters. The chemical transport equation is non-dimensionalized, and sensitivity studies applied to dimensionless groups that are

introduced. Next, the code is applied to two field examples, utilizing pressure, temperature and chemical data from the Ellidaar and Seltjarnarnes geothermal areas in Iceland. And a theoretical study of the evolution of low-temperature systems in terms of a circulation that is influenced by a heat source at depth and cool rainwater infiltrating at the surface is presented.

Before developing a background on the methods of modeling geothermal systems, it is helpful to define the characteristics common to the systems. Geothermal systems are classified as either high-temperature or low-temperature. High-temperature fields are above 150°C , and are usually two phase, consisting of liquid water and steam. Low temperature fields have fluid temperatures less than 150°C and the fluid is entirely in the liquid phase.

The majority of geothermal systems are comprised of a heat source at depth, overlain by a permeable zone saturated with fluids and recharged from waters infiltrating from the surface. Warm surface springs are common to many systems, providing a conduit for fluid to escape as the pressure within the system rises due to the incoming heat. Also, many low-temperature fields may develop due to high local thermal gradients (e.g. the Laugarnes field in Iceland). The present work is focussed on low-temperature fields and studies of both types of systems: those which developed due to a high thermal gradient and those which developed due to a heat source at depth are presented.

2.0 BACKGROUND

2.1 LITERATURE REVIEW

Developing potentially economic geothermal systems for direct use and for electrical power generation where possible will ease the dependance on oil and coal in the future. Creating methods to reliably study a system will help to promote the development of low-temperature systems. According to a world survey of low-temperature geothermal utilization taken in 1980, 44 countries have low-temperature geothermal resources. Of these countries, 24 are involved in exploration, 12 are utilizing the low-temperature geothermal energy and 9 countries have conducted appraisals of the energy potentials for possible exploitation (Gudmundsson and Palmason, 1982). A report by Howard (1975a) indicates that by 1975, 400 MW-thermal were being used for residential and commercial applications, 5500 MW-thermal were being used for agriculture and 200 MW-thermal were being used for industrial applications (most of the latter from high temperature fields).

Residential and commercial applications consist primarily of space heating. Gertsch and Juncal (1984), have reviewed four case histories of direct use space heating projects currently in progress in Northern California at Wendel in Lassen County, Greenville in Plumas County, Big Bend in Shasta County, and Cederville in Modoc County. Space heating by these thermal systems has significantly lowered the consumption of oil and natural gas generally required for these heating purposes. Eighty percent of the homes and commercial buildings in Iceland utilize low-temperature geothermal energy for space heating. A survey by Hettling (1984) documents over a decade of field data making up detailed case studies for three low-temperature fields near Reykjavik. Tomasson (1966) and Tomasson and Halldorsson (1981) reviewed the history of the Selfoss low-temperature geothermal area in Iceland, a field which has been used for domestic heating since 1948. These examples demonstrate that utilizing low temperature thermal energy can indeed lower a region's oil dependance on

electrical power.

Another important use of low temperature thermal energy for the future is in agriculture. The Soviet Union has made extensive use of low-temperature geothermal energy in large acreage green houses in areas not normally considered farmable. (The stated amount of use of 5500 MW-thermal by Howard (1975a) may be too high according to Gudmundsson and Palmason (1981)).

There are a number of ways to model geothermal systems. These methods can be split into four basic groups: (a) hydrological methods, (b) geochemical methods, (c) numerical methods involving pressure and temperature data, and (d) integrated pressure-temperature-chemistry numerical methods. The method developed in this paper falls in the last category. However, before describing this code, it is helpful to review the previous work done within all of the above mentioned categories.

Hydrological methods utilize all the available data on the geology of the region, well-test analysis, and geophysical and lithological well logs, to piece together a hydrological model of the given system. Hydrological methods have been practiced longer than any of the other methods, and numerous examples of its application are available. A few examples of various ways to use this type of modeling on liquid dominated fields are described.

Halfman et al (1982) developed a model for the fluid flow path of the liquid-dominated geothermal system at Cerro Prieto based on geophysical and lithological data, well completion data and downhole temperatures. Zais and Bodvarsson (1980) analyzed pressure and production data from geothermal systems at Wairakei, the Geysers, Larderello, and Cerro Prieto using the exponential and hyperbolic production decline type curves developed by Arp (1945,1956), along with the historical data from the fields, to model the production decline of each system. Hulen and Nielson (1982) utilized surface and borehole drilling data to formulate a reservoir model of distinct thin stratigraphic aquifers in the Baca Geothermal area. With the aid of this model, stratigraphic permeability was estimated, and thermal fluid flow paths traced. Benson (1982) analyzed well production data from a well near Wendel, California to establish a

model in which fractures provide the main component of the reservoir permeability. Hydrological methods can be very useful, but extensive data about the field, often not available, is necessary to develop an accurate model. available is necessary.

The second method of developing a reservoir model consists of utilizing the chemical data on a geothermal system. Several approaches have been taken to analyze the geochemical data. One approach is using the documented chemical concentrations as geothermometers, by applying empirical equations to describe the given chemical species concentration as a function of temperature. Several authors (Fournier, 1977; Fouillac and Michard, 1981; Fournier and Truesdell, 1973; Fournier and Potter, 1982) have described experimentally developed empirical equations for quartz, alpha-cristobalite, beta-cristobalite, chalcedony, (Na/K), Na-K-Ca, Na/Li, and oxygen-18. Most often, geothermometry is combined with chemical analyses to determine chemical characteristic of certain locations and to describe flow paths as well as subsurface temperatures. Thompson, Grunder and Hildreth (1983) used Na-K-Cl, Na-Li relations to estimate the near-surface and deeper reservoir temperatures combined with a detailed water chemistry analysis to determine the probable fluid flow paths and sources of recharge in the liquid-dominated Calabozos Caldera Field in Central Chile. Capuano (1981) used this approach to estimate the subsurface temperatures at a low-temperature system near Artesian City Area, Idaho, and to predict the flow paths and recharge zones of the system. recharge zones of the system.

The fluid chemistry of the Wendel-Amedee geothermal system in Northern California was analyzed using the above approach and the economic potential of the system for electrical and/or direct use was estimated by studying projected temperatures and cool recharge zones (Adams, 1984). Na-K, Ca-Na, Ca-K and silica geothermometers were used in Nicaragua on a number of sites to select the most probable economically exploitable region (Tonani and Teilman, 1980). Hilfiker et al. (1980) compared silica geothermometers with temperature gradients in the central Western region of New York State to detect areas of elevated temperature, helpful in locating potential geothermally active regions. Michels (1977) developed a similar approach to geothermometry in which he applies an empirically derived equation relating salt

concentrations to saturation pressures and temperatures to describe the thermodynamic behavior of low-temperature geothermal brines.

Another approach to utilizing geochemical data for reservoir modeling is to develop ways to trace the transport of a chemical species. Konikow (1977) developed a solute-transport model to predict the movement of dissolved chloride from industrial wastes discharged into unlined ponds. He combined a finite-difference solution to the fluid flow equation with the method-of-characteristics solution to the solute-transport equation (both methods are described in detail in his paper). Many studies have utilized the concentration of the stable isotope oxygen-18, which often is characteristic to a specific region, to study the flow patterns of the fluid in a system (e.g. Giggenbach et al., 1983; Payne and Yurtsever, 1974; Panichi et al., 1974; Stahl and Aust, 1974).

Other studies have concentrated on the effects of heat on the precipitation/dissolution of a chemical species within a geothermal system. Kandarpa and Vetter (1981) developed a semi-empirical model which can predict sulfate precipitation due to injection of cool water into a geothermal system. Several studies which used simulated experimental models coupling transient flow behavior and kinetic reactions discuss the effects of silica precipitation and permeability reduction (Keith et al., 1983; Moore et al., 1981; Itoi et al., 1984). Itoi et al. (1985) developed a mathematical model of permeability reduction due to exploitation of a geothermal system using fluid flow equations, silica concentrations and equations for the kinetic reactions of silica, combined with the Kozeny-Stein equation (Camp, 1964) for permeability.

The third approach to studying and modeling geothermal systems is by numerical solutions to fluid and heat flow equations, enabling the pressure and temperature to be documented as functions of time. Most commonly a hydrological model of the system being studied is developed by utilizing available geological and geophysical data. Boundary conditions, discretization schemes and initial input parameters are determined from the hydrological model and applied to the numerical code. Several numerical codes have been developed in the past decade, and used to predict geothermal reservoir behavior under various types of conditions. Sorey (1975) developed a three-

dimensional single-phase finite-difference code for fluid and heat transport; he applied this to the Long Valley, California geothermal region to study the natural convection within the system. Mercer et al. (1975) developed a single-phase finite-element code which was then applied to the Wairakei, New Zealand geothermal region and a match between field data and the calculated data achieved. Bodvarsson (1982) developed a single phase, integrated finite-difference method to solve the heat and mass transport equations, including the pressure and temperature dependency of density and the temperature dependency of viscosity, expansivity and compressibility. He applied the code to the geothermal system at Krafla, Iceland by simulating individual wells to find a match with the well-test data. Lippman and Bodvarsson (1985) combined a detailed hydrological review, a numerical model of the natural state of the system and numerical solutions to various production states using the code described above to develop a comprehensive model of the Heber geothermal system in Southern California. Several studies have utilized single-phase numerical codes to study free convection in geothermal systems (Cheng, Yeung and Lu, 1976; Elder, 1966; Rana, Horne and Cheng, 1978). Numerical simulators for two-phase flow in high-temperature, vapor dominated systems have also been developed (eg: Coats, 1977; Toronyi and Farouq Ali, 1975; Faust and Mercer, 1979; Garg et al., 1975; Lamster et al., 1975; Pruess, 1979). These simulators have been used to model the behavior of two-phase and vapor dominated fields (eg. Moench, 1976) as well as to predict the convective heat transfer near plutons (Kang and Ahern, 1984; Cathles 1977; Norton and Knight, 1977). These will not be reviewed in detail, as the present work is mostly interested with single-phase systems.

The fourth approach to modeling the behavior of geothermal systems combines all three of the above approaches, utilizing every aspect of systems modeling to achieve the most comprehensive representation of the system as is possible. This involves developing a detailed hydrological model of a system from all available geological, geophysical and lithological data. Numerical solutions to the heat and mass transport equations, as well as solute transport equations are developed. Boundary conditions for the chemical species, pressure and temperature are set by the conceptual model. The behavior of the geothermal system is modeled by matching well-test data,

downhole temperatures and pressures. The reservoir volume, permeability and possibly the amount and zones of recharge can then be established. As numerical codes have become more complex and solution techniques upgraded, the integrated hydrological-pressure-temperature-chemistry approach has become more credible and probably the most reliable method for assessing the potential of geothermal systems. accurate solutions to geothermal models is logical.

Although not as common, a few studies have been completed utilizing an integrated pressure-temperature-chemistry approach to modeling hydrological systems. Norton and Taylor (1979) combined chemical and isotopic transport equations with mass and heat transport in a finite difference code. Pressure and temperature were solved as the dependent variables and were used in turn, to solve the oxygen-18 variations in plagioclase. The density was also calculated as a function of temperature and pressure. They applied the model to the Skaergaard intrusion after developing an extensive geological and geophysical background from which the initial and boundary conditions were formulated. The calculated oxygen-18 and the measured oxygen-18 were in excellent agreement for all three of the major rock units. Li et al. (1982) developed a mathematical model which describes the behavior of a hot water geothermal system accompanied by dissolution/precipitation of silica. The fluid flow, thermal energy and solute transport equations were solved using a Galerkin finite-element method for spacial derivatives and implicit finite difference method is used for the time derivatives. Parmentier (1981) developed a finite-difference code solving mass, heat and oxygen-18 transport in a porous medium. Density was treated as a function of temperature and pressure. Oxygen-18 transport included convective transport as well as kinetic reactions between the rock and water, and oxygen diffusivity in feldspars. Parmentier used the model to study oxygen-18 depletion near igneous intrusions being cooled by groundwater convection.

Until recently, a large problem with integrated solute transport equations was the numerical diffusion introduced in the first order finite-difference modeling. Higher order modeling would reduce the error but could also cause large oscillations near fronts. Lai (1985) developed an integrated method which utilizes a second order Godunov scheme

with monotonized upwind central differencing and operator splitting. By use of operator splitting, the convection terms are solved by an explicit upwind central difference method modeled after Van Leer (1977) and the diffusion terms are solved by an implicit central difference method. Lai reports negligible numerical diffusion nor oscillations, and obtained an excellent match between calculated and observed data for field data from Ellidaar, Iceland.

Of all the work reviewed, silica and oxygen-18 were the only chemical components included in an integrated pressure-temperature-chemical numerical model. But for many geothermal systems being studied, data is also available on several other chemical components. For example, chloride concentrations were recorded at the Selfoss geothermal area from 1965 to 1980 (Figure 1). At the Laugarnes geothermal area in Iceland, silica, chloride, sulfates, fluoride, carbon dioxide, and total dissolved solids were recorded over a period of ten years (Hettling, 1984). Chloride concentrations from the Wairekei geothermal field in New Zealand have been recorded (Figure 2). At the La Primavera geothermal field, in Mexico, a chemical history of the fluids including the silica, boron, and sulfate concentrations, were recorded from 1980 through 1982 (Figure 3). To best utilize all the available data on a geothermal system, an integrated hydrological-pressure-temperature-chemistry numerical code which can handle several different chemical species needs to be developed. As a first step towards this goal, a review on the chemistry of pure liquid geothermal systems is necessary.

Figure 1. Chlorine concentration versus time from Selfoss, Iceland (Tomasson and Halldorsson, 1981).

Figure 2. Chemical data from the Wairakei geothermal field in New Zealand (Henley and Stewart, 1984)

Figure 3. Chemical data from the La Primavera geothermal field in Mexico (Domingues and Lippmann, 1983).

2.2 CHEMISTRY OF LOW-TEMPERATURE GEOTHERMAL SYSTEMS

The main purpose of a review of the chemistry of liquid geothermal systems is to gain insight into the best chemical species to include in a modeling scheme. For best results a background on the behavior of the common chemical species found in liquid-dominated fields is necessary before choosing which species to model. Once the chemical species are chosen, an indepth review of their behavior is essential.

Due to the different geologic settings of geothermal systems, each system will have an assemblage of chemical components unique to its history and setting. Some systems contain only groundwaters of meteoric origin, while others near the coast may be fed by seawater or a mixture of meteoric water and seawater. Still other systems may contain connate water (fossil marine water). The heat source, if magmatic, can add fluids containing a wide assortment of chemical components. The hot geothermal waters may react with their host rocks, dissolving components such as silica and altering primary minerals to form new mineral suites.

Although the range of chemical components in a fluid may be very complex, certain components are common to most systems. These include oxygen-18, silica, chloride, deuterium, calcium and sodium; less abundant but still common to many systems are potassium, magnesium, boron, fluoride carbonates, and sulfate. Kinetic reactions and rate constants as functions of temperature and pressure are not well-known for any of the components listed above, except for silica and oxygen-18. This makes it difficult to determine whether or not a component is in chemical equilibrium. However, if the solubilities of the minerals containing a chemical component are low and equilibrium rates are very slow, the kinetic reactions of the species will not be significant over small time ranges (i.e. < 100 yrs). Also, if the species is not chemically active with other chemical components in solution or in the surrounding rock, and the oxidation/reduction reactions in a medium range of pH (4.0 - 9.0) are not strong, the component may be considered "non-reactive" or conservative. For the purposes of modeling the behavior of these components, kinetic/diffusion effects can be ignored. A

mixing model to simulate the non-reactive chemical components can be assumed, accounting for convective transport only.

Hem (1970) reviews the behavior of all the chemical components characteristic to natural waters. From this review it was possible to choose which components could be considered non-reactive, and included in a mixing model scheme. The stable isotope deuterium, when in solution, does not interact significantly with the surrounding country rock and is chemically stable in solution at low temperatures ($< 200^{\circ}\text{C}$). With these characteristics, it is a good candidate for a conservative model. Chloride ions do not enter significantly into oxidation/reduction reactions; they also do not form important solute complexes with other ions and are not significantly adsorbed onto mineral surfaces. Circulation of chloride ions is largely through physical processes, making it an excellent choice for a mixing model scheme. Boron and sulfate are slightly more chemically active but also appear to be good candidates for a mixing model. Sulfate ions require specific biological factors to be present before entering into oxidation/reduction reactions and are chemically stable in aerated water. Boron is generally found in minerals resistant to chemical attack and is chemically stable in natural waters. Fluoride is generally stable in natural waters, but can form strong solute complexes with many ionic and is contained by some very soluble minerals. Some error might incur if it is assumed a conservative species, but the error is likely to be insignificant.

The cations of calcium (Ca^{2+}), magnesium (Mg^{2+}), and sodium (Na^{+}) are all subject to cation-exchange (calcium the most, magnesium the least), which can have considerable affect on the concentration of the species in water. Calcium is very pH sensitive, precipitating as CaCO_3 readily at higher values of pH. Magnesium is much less likely to precipitate out of solution, and sodium will only precipitate at very high concentrations ($> 100,000$ ppm). Therefore, although not completely conservative, the cations Mg^{2+} and Na^{+} can be modeled in a non-reactive scheme, given the possibility that slight error may result. Calcium is likely not to be a dependable choice for a conservative species since it is so chemically active. Potassium ions are also not a good candidate for a conservative model, as they are difficult to liberate from silicate

minerals, and are readily re-adsorbed. Also, the narrow range in concentration of potassium found in natural systems suggests a significant chemical control mechanism, but not enough is known for any calculations to be made.

The kinetic and diffusion reactions for oxygen-18 between water and host rock have been studied by several authors. Oxygen-18 exchange between feldspar and water was analyzed by Yund and Anderson (1974, 1979), and O'Neil and Taylor (1967). O'Neil et al. (1969), and Northrop and Clayton (1966) have studied fractionation of oxygen-18 in carbonate-water systems. O'Neil and Taylor, (1969) covered kinetic exchange between muscovite and water; O'Neil and Kharaka (1976) studied exchange between clays and water. Oxygen-18 exchange in quartz-water systems has been studied by Clayton et al. (1972). Gilletti et al. (1978) and Gilletti and Anderson (1975) studied oxygen-18 diffusion in feldspar/water and mica/water systems. In most of the studies mentioned above the authors have developed temperature and/or pressure dependent equations to describe the kinetic and diffusive reactions from the experimental results.

Kinetic and diffusive reactions have also been studied for silica. Rimstidt and Barnes (1980) and Bohlman et al. (1980) have studied the kinetics of silica-water reactions and developed temperature/pressure dependent relationships to describe the results. Fournier and Potter (1982) and Fournier et al. (1982) studied the solubility of quartz in water and sodium chloride solutions. Robinson (1982) has reviewed both the kinetic and diffusive behavior of silica, as well as providing a detailed overview of similar studies.

Due to the availability of information on silica and oxygen-18 it is possible to design a more detailed model to simulate their behavior in a geothermal system. The model could include transport due to convection, dispersion, kinetic reactions and sources/sinks. To pave the way for the development of this model, an in depth review of the behavior of silica and oxygen-18 are provided.

Behavior of Silica

Silicon (Si) is the second most abundant element in the earth's crust. It is the primary building unit for most of the minerals comprising igneous and metamorphic rocks. It is present in almost all rocks and most natural waters. Silica is primarily deposited in four different forms: quartz (crystalline silica), α -cristobalite, β -cristobalite, and amorphous or microcrystalline silica (eg., chert, flint, chalcedony, jasper). Quartz is the primary form found in igneous rocks and usually constitutes the majority of the grains in most sandstones. It is the most resistant form of silica, crystallizes at lower temperatures and remains stable through a wider temperature and pressure range. The cristobalites and microcrystalline forms are less stable and more soluble in water.

The rate law describing the deposition/dissolution of silica is dependent on which form of silica is deposited/dissolved. It is a function of temperature and pressure, but according to Fournier and Potter (1982), the pressure effects are small relative to the temperature effects and may be neglected without significantly affecting the results. Therefore, the rate law describing the kinetic reactions of silica may be written (Robinson, 1982):

$$\frac{dC}{dt} = k_1 \left[\frac{A}{V} \right] (C^{eq} - C) \quad (1)$$

where C is the silica concentration, k_1 is the rate constant, and A/V is the surface area open to reaction per volume of system. The rate constant, k_1 , is a function of temperature and can be written (Rimstidt and Barnes, 1982):

$$k_1 = \exp \left[\frac{-\bar{A}}{T} + \bar{B} \right] \quad (2)$$

where $\bar{A} = 9410.7$, $\bar{B} = 0.90261$, and T is the temperature in $^{\circ}\text{K}$.

The equilibrium constant, C^{eq} , for silica is predominantly a function of temperature, slightly of pressure (which, as discussed above, will be neglected). Fournier and Potter (1982) developed a series of equations for the equilibrium silica concentration

over a wide range of temperatures and pressures based on experimental data. The equations descriptive for the temperature range of 25° to 300° C (liquid-fluid systems) are listed for each form of silica in Table 1.

TABLE 1. Equations describing the equilibrium constant for each form of silica (Temperature, T, is in degrees Kelvin).

Form of silica	Equation for C^{eq}
Amorphous silica	$6 \times 10^4 \left(\frac{10^{(0.238 - 7.884 \times 10^{-4} T - 840.1/T)}}{\rho_f} \right)$
Quartz	$6 \times 10^4 \left(\frac{10^{(1.881 - 2.028 \times 10^{-4} T - 1500.0/T)}}{\rho_f} \right)$
α -cristobolite	$6 \times 10^4 \left(\frac{10^{(-0.0321 - 988.2/T)}}{\rho_f} \right)$
β -cristobolite	$6 \times 10^4 \left(\frac{10^{(-0.258 - 793.6/T)}}{\rho_f} \right)$

Silica transport may also occur by chemical diffusion, described by:

$$\frac{dC}{dt} = \rho_f D \nabla^2 C \quad (3)$$

where D is the coefficient of dispersion and ρ_f is the density of the fluid.

Behavior of Oxygen-18

Oxygen-18 (^{18}O) and oxygen-16 (^{16}O) are both isotopes of oxygen; ^{16}O is much more common, constituting approximately 99.76% of all oxygen. Craig (1963) noted that the ratio of $^{18}\text{O}/^{16}\text{O}$ of the water in a system is dependent on many factors, including fluid phase (gaseous, liquid or solid), latitude and elevation, showing a trend of progressive depletion of the heavy isotope (^{18}O) with distance from the tropical seas. These dependencies are primarily due to the temperature and pressure effects on the fractionation of the isotopes. The heavy isotope will preferentially enter into the condensed forms of water (rain and snow) with enrichment of ^{16}O in the remaining vapor. Thus, as water is evaporated from the sea and moves inland, it becomes steadily enriched in ^{16}O as the ^{18}O leaves with the precipitation. Because of this, a fluid's oxygen-18 content will be characteristic of its source and may be useful in determining flow paths within a system.

Oxygen-18 is usually measured in terms of its "delta value," defined by:

$$\delta^{18}\text{O}_f = \left[\frac{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{meas}} - \left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SMOW}}}{\left(\frac{^{18}\text{O}}{^{16}\text{O}} \right)_{\text{SMOW}}} \right] \times 10^3 \text{ ‰ (permil)} \quad (4)$$

where $(^{18}\text{O}/^{16}\text{O})_{\text{meas}}$ is the measured value, and $(^{18}\text{O}/^{16}\text{O})_{\text{SMOW}}$ is the value for standard mean ocean water. The SMOW standard is based on a hypothetical water sample with an isotopic ratio of oxygen similar to an average sample of ocean water with a value of 0.0 per mil. Thus, the per mil value of the oxygen-18 becomes more negative with distance inland from the sea and ranges between -7.0 and -11.0 in most regions.

Like silica, oxygen-18 within the fluid will react with the oxygen of the host rock by intersurface reactions. The rate law for the interface reactions is predominantly dependent upon temperature (A.H. Truesdell, personal communication, March 1986). It also depends upon the crystallinity of the system, the rock type, and the average grain size of the rocks. Thus, an understanding of the lithology of the system is necessary to describe the rate of kinetic reactions. According to Cole (1983), the rate law

for the kinetic reactions of oxygen-18 in water may be written:

$$\frac{dW_2}{dt} = \left(-\frac{A}{SW}\right)r_1(W_2^{eq} - W_2)(W_1 + \alpha S_1) \quad (5)$$

where r_1 is the rate constant, W is moles of oxygen in water, S is moles of oxygen in solid, A is the total surface area of reaction, α is the fractionation factor, subscript 1 is oxygen-16, subscript 2 is oxygen 18, and superscript eq is the equilibrium value. Finally, since oxygen-18 makes up a very small part of the total amount of oxygen in the fluid and α is generally near unity, the following approximation will be used in the present study:

$$(W_1 + \alpha S_1) \approx (W + S) = \text{total moles of oxygen in the system.}$$

As mentioned earlier, oxygen-18 is most often measured as a δ value; therefore, it would most useful to get the rate law in the " δ " form. In terms of the parameters W, S, S_1, W_1, W_2, S_2 ; the δ value is:

$$\delta^{18}O_f = \left[\frac{\left(\frac{W_2}{W_1}\right)_{\text{meas}} - \left(\frac{W_2}{W_1}\right)_{\text{SMOW}}}{\left(\frac{W_2}{W_1}\right)_{\text{SMOW}}} \right] \times 10^3 \text{ ‰} \quad (6)$$

Therefore,

$$W_2 = \left[\left(\frac{(\delta^{18}O_f)}{10^3 \text{ ‰}} + 1 \right) \left(\frac{W_2}{W_1} \right)_{\text{SMOW}} \right] \cdot W_1 \quad (7a)$$

$$W_2^{eq} = \left[\left(\frac{(\delta^{18}O_f^{eq})}{10^3 \text{ ‰}} + 1 \right) \left(\frac{W_2}{W_1} \right)_{\text{SMOW}} \right] \cdot W_1 \quad (7b)$$

and

$$\frac{dW_2}{dt} = \left(\frac{W_1}{10^3 \text{ ‰}} \right) \left(\frac{W_2}{W_1} \right)_{\text{SMOW}} \cdot \left(\frac{d\delta^{18}O_f}{dt} \right) \quad (8)$$

We also have

$$\frac{d\delta^{18}\text{O}_f}{dt} = \left(\frac{S + W}{SW} \right) A \cdot r_1 \left(\delta^{18}\text{O}_f^{\text{eq}} - \delta^{18}\text{O}_f \right) \quad (9)$$

The rate constant is defined by (Cole et al., 1985):

$$r_1 = \exp \left[\frac{-A'}{T} + B' \right] \quad (10)$$

where A' and B' are constants dependent on the type of rock/fluid system (see Table 2 for the values of the constants for each rock/fluid system included in the present study).

TABLE 2. Temperature dependant functions for the rate and equilibrium constants of oxygen-18 of each rock/fluid system.

Rock	$\log r_1$ (T in K)	Source	Δ_{RW}^{eq} (T in °C)	Source
Basalt/seawater	-2520/T - 4.80	1	-0.01463T + 7.85	1
Basalt/water	-2520/T - 4.80	2	-0.052T + 15.2	2
Granite/seawater	-2000/T - 4.15	2	-0.075T + 23.5	2
Granite/water	-1300/T - 5.73	2	-0.070T + 23.5	2
Quartz/water	-1250/T - 6.55	2	-0.05T + 22.0	3
Calcite/water	-2250/T - 3.35	2	-0.038T + 18.1	4
Dolomite/water	-2500/T - 2.75	2	-0.046T + 21.4	5

Sources

- (1) Cole et al., 1986
- (2) Cole, 1983
- (3) Clayton et al., 1972
- (4) O'Neil, 1963
- (5) Northrop and Clayton, 1975

The total surface area of reaction, A , varies slightly between rock types due to the different grain geometries characteristic of the rock type. According to Cole et al. (1983), for rock types with predominantly spherical grains (basalts, granites, quartz), the surface area of reaction is (in meters):

$$A = 4\pi\omega^2 \left[\frac{M_R}{\rho_R 1.33\pi\omega^3} \right] = \frac{3V(1-\phi)}{\omega}; \quad (11a)$$

and for carbonates:

$$A = (bh) \left[\frac{M_R}{\rho_R bh(2\omega)} \right] = \frac{3V(1-\phi)}{\omega}; \quad (11b)$$

where M^R is the mass of the solid, ρ^R is the density of the solid, V is the total volume of the sample, and ω is the average grain radius (or one half the average grain width in the case of the carbonates).

The equilibrium value can be expressed by

$$\delta^{18}O_r^{eq} = \frac{\left(\delta^{18}O_R^i - \Delta_R^{eq} + \frac{W}{S} \cdot \delta^{18}O_f^i \right)}{1 + \frac{W}{S}} \quad (12a)$$

where Δ_R^{eq} is the equilibrium isotopic fractionation value, $\delta^{18}O_R^i$ is the initial oxygen-18 measurement in rock, and $\delta^{18}O_f^i$ is the initial oxygen-18 measurement of the fluid.

In a most geothermal system, the value for W/S is less than 0.1 and equation 12a may be simplified to:

$$\delta^{18}\text{O}_f^{\text{eq}} = \delta^{18}\text{O}_R^{\text{i}} - \Delta_{\text{RW}}^{\text{eq}} \quad (12\text{b})$$

without significant error. From equation 12b, the importance of the amount of oxygen-18 within the rock on the equilibrium oxygen-18 content is apparent. The $\delta^{18}\text{O}_R$ content varies greatly between different rock types. Table 3 lists the typical range of $\delta^{18}\text{O}_R$ for each rock type included in the presented study.

TABLE 3. Oxygen-18 contents of the rock types included in the present work.
(Source: Henley, Truesdell and Barton, 1984)

Rock Type	Oxygen-18 (per mil)
Granite	10 - 25
Carbonates	10 - 20
Basalts	5 - 10
Quartz	10 - 25

The equilibrium rock/fluid fractionation value is a function of temperature and is dependent upon the rock/fluid system. In most studies on oxygen-18 fractionation, the results are not expressed in terms of the Δ_{RW} value, but as the isotopic fractionation factor. The "per mil" fractionation, or $10^3 \ln \alpha$, is often a linear or approximate linear function of temperature over small temperature ranges. According to Friedman and O'Neil (1977), the "per mil" fractionation can be approximated by the rock/fluid fractionation:

$$10^3 \ln \alpha \approx \Delta_{\text{RW}}$$

or

$$10^3 \ln \alpha^{\text{eq}} \approx \Delta_{\text{RW}}^{\text{eq}} \quad (13)$$

Therefore, the results of studies on the equilibrium curves between the "per mil" fractionation value and temperature were used in this study to express the equilibrium rock/fluid fractionation value as a linear function of temperature. Figure 4 shows the equilibrium curve for each rock/fluid system and, referring back to Table 2, the linear temperature functions assumed in this study are listed. Inspecting the curves in Figure 4, indicates that the use of a linear temperature function over small temperature ranges should not introduce a significant amount of error. However, most of the studies on the fractionation of oxygen were performed at high temperatures; it is assumed in the present work that the curves can be extrapolated to lower temperatures. Also, due to the lack of information available on several of the rock/fluid systems, some approximations were necessary. Specifically, for basalt/water the temperature function of the kinetic rate constant was not available, therefore the same function as for the basalt/seawater rate constant was assumed. Information on the equilibrium rock/water fractionation value, $\Delta_{R/W}^{18}$, for a granite/seawater system was not available. As a substitute, the function for a felsic rock/water system was incorporated into the kinetic transport equations. As a result of these approximations, modeling the kinetic transport within a basalt/water or granite/seawater system will not be as accurate as in the other rock/fluid systems.

Figure 4. Equilibrium curves for oxygen-18 for (a) quartz/water (Clayton et al., 1972); (b) basalt/water, felsic rock/water (after Cole et al., 1983) (c) dolomite/water (A), calcite/water (B) (Northrop and Clayton, 1966).

3.0 DEVELOPMENT OF NUMERICAL CODE

To develop the numerical method used in this paper, the code PTC (Lai, 1985) was expanded to include transport modeling of non-reactive chemical components and the transport of oxygen-18. PTC is an integrated pressure-temperature-chemistry numerical code capable of modeling two-dimensional fluid, heat and silica transport in fractured porous media. A combination of the second order Godunov method and operator splitting is utilized to solve the convection-diffusion-type equations. The code PTC was originally developed from PT (Bodvarsson, 1982), a numerical code for modeling three-dimensional transport of fluid and heat.

The newly expanded code PTCC utilizes the method developed by Lai to simulate the transport of oxygen-18 and the non-reactive species. To describe the development of PTCC, the governing equations for fluid, heat, and chemical transport are presented. A review of the numerical formulation of the governing equations for fluid and heat transport used in PT, and the modifications of PT introduced by Lai (1985) in developing PTC follow. Finally, a section on the additions made to PTC in developing PTCC, as well as an account of the performance of the expanded code are presented.

3.1 GOVERNING EQUATIONS

To model the heat, fluid and chemical transport for a single-phase geothermal system, the basic laws of conservation need to be introduced.

Conservation of Mass

Consider a region, R , of a geologic formation, saturated with a liquid fluid and containing a fixed subregion, V (Figure 5). The rate of change of the mass of fluid within V can be expressed as

$$\frac{dM_f}{dt} = \int_V \frac{\delta(\phi \rho_f)}{\delta t} dV + \int_V G_f dV \quad (14)$$

Figure 5. Sketch showing region R , with subregion V , and unit normal $\hat{n}$ (after Lai, 1985).

where M is the total mass of fluid within V , ϕ is the porosity, G_f is the mass generation rate per unit volume within V and t is time. The left hand term in Eq. 14 is the total mass flow rate across the boundaries of V and can be expressed as a surface integral by

$$\frac{dM_f}{dt} = \int_A \rho_f \vec{v}_d \cdot \hat{n} dA \quad (15)$$

where $\hat{n}$ is the outward unit normal vector, dA is the elemental surface area and $\vec{v}_d$ is the fluid velocity. The fluid velocity can be calculated by Darcy's Law:

$$\vec{v}_d = \frac{-k}{\mu} (\nabla P + \rho_f \vec{g}) \quad (16)$$

where k is the intrinsic permeability, μ is the dynamic viscosity, P is the pressure and $\vec{g}$ is the acceleration due to gravity. Substituting (15) into Eq. 14 and rearranging, we have

$$\int_V \frac{\delta(\phi \rho_f)}{\delta t} dV = - \int_A \rho_f \vec{v}_d \cdot \hat{n} dA + \int_V G_f dV \quad (17)$$

According to the divergence theorem, the first term on the right-hand side may be written as

$$\int_A \rho_f \vec{v}_d \cdot \hat{n} dA = \int_V \nabla \cdot \rho_f \vec{v}_d dV \quad (18)$$

Substituting this back into (17), we have the integral form of the continuity equation:

$$\int_V \frac{\delta(\phi \rho_f)}{\delta t} dV = - \int_V \nabla \cdot \rho_f \vec{v}_d dV + \int_V G_f dV \quad (19)$$

Conservation of Energy

Considering the same region R , with subregion, V , the rate of change of energy within V may be written as

$$\frac{dE}{dt} = \int_V \left[\frac{\delta(\phi \rho_f c_f)}{\delta t} + \frac{\delta((1-\phi) \rho_r c_r)}{\delta t} \right] T dV + \int_V G_H dV \quad (20)$$

where subscripts f and r refer to fluid and rock respectively, c is the specific heat, T is the temperature and E is the total amount of energy within subregion V. The total energy flow rate, (dE/dt), across the boundaries of V, is composed of the heat flux due to convection and the heat flux due to conduction. By Fourier's Law for heat flow, the conductive flux term can be described by

$$\vec{q}_{\text{cond}} = -K_t \nabla T \quad (21)$$

where K_t is the effective thermal conductivity of the subregion V. The convective flux is described by

$$\vec{q}_{\text{conv}} = \rho_f \vec{v}_d c_f T \quad (22)$$

Substituting (21) and (22) into Eq. 20 gives

$$\begin{aligned} & - \int_A K_t \nabla T \cdot \hat{n} dA + \int_A \rho_f \vec{v}_d c_f T \cdot \hat{n} dA \\ & = \int_V \left[\frac{\delta(\phi \rho_f c_f)}{\delta t} + \frac{\delta((1-\phi) \rho_r c_r)}{\delta t} \right] \cdot T dV + \int_V G_H dV \end{aligned} \quad (23)$$

Once again, the divergence theorem may be used to transform the surface integrals into volume integrals. Applying the theorem and rearranging terms gives the energy equation in integral form:

$$\begin{aligned} & \int_V \left[\frac{\delta(\phi \rho_f c_f)}{\delta t} + \frac{\delta((1-\phi) \rho_r c_r)}{\delta t} \right] T dV \\ & = - \int_V \nabla \cdot K_t \nabla T dV + \int_V \nabla \cdot \rho_f \vec{v}_d c_f T dV + \int_V G_H dV \end{aligned} \quad (24)$$

Conservation of Chemical Species

To develop the solute equation, a similar method as was taken for the mass and energy equation can be applied. A mass balance of the chemical species over subregion V can be expressed as

$$\frac{dCS}{dt} = \int_V \frac{\delta(\phi \rho_f CS)}{\delta t} dV + \int_V G_r CS_r dV \quad (25)$$

where CS is the concentration of the solute, CS_f is the concentration of the solute within the fluid being generated. The rate of change in concentration of the chemical species, (dCS/dt) , consists of chemical flux due to dispersion and flux due to convection. These may be expressed as

$$\vec{q}_{disp} = \rho_f D \nabla CS \quad (26a)$$

and

$$q_{conv} = - \rho_f \vec{v}_d CS \quad (26b)$$

where D is the coefficient of dispersion.

As was done for the energy equation, we first take the total flux across the boundaries of V, and apply the divergence theorem to transform the surface integrals into volume integrals. After substituting these back into the original equation, we have the integral form of the solute transport equation:

$$\int_V \frac{\delta(\phi \rho_f CS)}{\delta t} dV = \int_V (\nabla \cdot \rho_f D_{ij} \nabla CS) dV - \int_V (\nabla \cdot \rho_f \vec{v}_d CS) dV + \int_V G_f CS_f dV \quad (27)$$

where D_{ij} is the dispersion tensor necessary for the two-dimensional system.

3.2 NUMERICAL FORMULATION

Well-test data on geothermal systems usually provide the temperature, pressure and chemical concentrations within the system. In the governing equations developed above, these will be considered the primary dependant variables. In developing PT, Bodvarsson (1982) took into account the temperature and/or pressure dependance of the density, viscosity, compressibility and expansivity. These are considered the secondary dependant variables and are calculated after the temperature and pressure have been solved for, using the equations of state for water and rock. The equations of state may be written:

For the fluid,

$$\beta_f = \left. \frac{1}{\rho_f} \frac{\delta \rho_f}{\delta P} \right|_T \quad (28a)$$

$$\gamma_f = \left. \frac{1}{\rho_f} \frac{\delta \rho_f}{\delta T} \right|_P$$

For the rock,

$$\beta_r = \left. \frac{1}{\phi} \frac{\delta \phi}{\delta P} \right|_T \quad (28b)$$

$$\gamma = \left. \frac{1}{\phi} \frac{\delta \phi}{\delta T} \right|_P$$

where β = compressibility, and γ = expansivity.

The density of the fluid is dependant on temperature and pressure and is calculated by (Buscheck, 1980; Bodvarsson, 1982):

$$\rho_f = A(T) + B(T) \cdot C(P) \quad (29)$$

The functions $A(T)$, $B(T)$, and $C(P)$ are given in Appendix A.

Viscosity is considered only a function of temperature, and the pressure effects are neglected. The equation for the viscosity of the fluid is written (Bodvarsson, 1982):

$$\mu = a_1 10.0 \left[\frac{a_2}{T + a_3} \right] \quad (30)$$

where $a_1 = 2.414 \times 10^{-5}$, $a_2 = 247.8$, and $a_3 = 133.15$.

The specific heats for the fluid and the rock are considered constant, as is the effective thermal conductivity. For the three-dimensional code PT, Bodvarsson (1982) transformed the integral form of the governing equations for fluid and heat into numerical notation and used the integrated finite difference method (Edwards, 1972; Sorey, 1975; Narasimhan and Witherspoon, 1976), for their solution.

In numerical notation the mass equation becomes

$$(V\phi\rho_f)_n \left[\beta_t \frac{\Delta P_n}{\Delta t} - \gamma_t \frac{\Delta T_n}{\Delta t} \right] \quad (31)$$

$$= \sum_m \left(\frac{k\rho A}{\mu} \right)_{n,m} \left[\frac{P_m - P_n}{D_{n,m} + D_{m,n}} - \hat{n}_s \rho_s \vec{g} \right] + (G_r V)_n$$

and the energy equation becomes

$$\begin{aligned} \left[(\rho c)_m V \right]_n \frac{\Delta T_n}{\Delta t} = \sum_m \left[\frac{(K_t A)_{n,m}}{D_{n,m} + D_{m,n}} (T_m - T_n) \right. \\ \left. + \left(\frac{\rho c_r A k}{\mu} \right)_{n,m} (T_{m,n} - T_n) \left[\frac{P_m - P_n}{D_{n,m} + D_{m,n}} - \hat{n}_s \rho_s \vec{g} \right] \right] + (G_h V) \end{aligned} \quad (32)$$

β_t and γ_t are the total compressibility and total thermal expansivity, respectively, and are written as

$$\beta_t = \beta_r + \beta_f \quad (33a)$$

$$\gamma_t = \gamma_r + \gamma_f \quad (33b)$$

The equations are solved for a node, n , connected to an arbitrary number of nodes, m . $D_{n,m}$ and $D_{m,n}$ represent the distance from nodes n and m to the interface between the two nodes (Figure 6).

The code utilizes an upstream weighting technique for the interface temperatures. The implicit formulation used incorporates an option to use a fully implicit, fully explicit or intermediary scheme by specifying the weighting factor, a_p , as a value between 0 and 1:

$$a_p = 0 \quad \text{fully explicit}$$

$$a_p = 1 \quad \text{fully implicit}$$

$$a_p = 0.5 \quad \text{Crank-Nicholson}$$

The spacial gradients are estimated by a linear approximation. The permeability and thermal conductivity of the matrix are calculated using a harmonic mean to ensure continuity of flux at the interface. For a more detailed description of the code see Bodvarsson (1982).

Figure 6. Sketch of mesh structure with node n connected to m surrounding nodes separated by a distances of $D_{n,m}$ and $D_{m,n}$, respectively, and interface area of A (Bodvarsson, 1982).

To solve the mass and heat equations (31 and 32, respectively), they are combined and solved simultaneously in a single matrix equation of the form

$$[A] \{x\} = b \quad (34)$$

The vector $\{x\}$ contains the unknowns ∇P and ∇T ; the vector $\{b\}$ contains the known explicit quantities. The matrix $[A]$ contains the coefficients, which in general are functions of temperature and pressure, hence making the equations non-linear. The sets of equations are solved using an efficient direct solver (Duff, 1977) and an iterative scheme for the non-linear coefficients.

In modifying PT and adding silica transport to the code, Lai (1985) utilized an operator splitting technique to enable the governing equations for chemical and heat transport to be solved in two fractional steps. As seen by (29) and (27) the equations for heat and chemical transport are of identical form and can be solved by the same method. Before these equations are solved, the equations for Darcy velocity (Eq. 16) and continuity (Eq. 19) are combined to calculate the pressure field, using the integrated finite difference method of the original code PT.

Then, the energy and chemical transport convection-diffusion type equations are solved in two steps. The first step neglects the diffusion and source terms, and leaves for the energy and chemical species equations, respectively:

$$\int_V \sigma_T \frac{\nabla T}{\nabla t} dV + \int_A \nabla_T T \cdot \hat{n} dA - \int_V T \nabla \cdot \nabla_T dV = 0 \quad (35a)$$

and

$$\int_V \sigma_c \frac{\delta CS}{\delta t} dV + \int_A \nabla_c CS \cdot \hat{n} dA - \int_V CS \nabla \cdot \nabla_c dV = 0 \quad (35b)$$

where

$$\sigma_T = \phi \rho_f c_f + (1 - \phi) \rho_r c_r$$

$$\sigma_c = \phi \rho_f$$

$$\nabla_T = \nabla_d \rho_f c_f$$

$$\nabla_c = \nabla_d \rho_f$$

These equations are solved by the explicit, monotonized, upwind/central differencing method developed by Van Leer (1977) and expanded by Colella (1984). [See Lai (1985) for a description of this method.]

The second step solves the diffusion and source terms, neglecting the convection term. For the energy and chemical species, the diffusion/ source equations to be solved are

$$\int_V \sigma_T \frac{\delta T}{\delta t} dV = \int_V \nabla \cdot K_t \nabla T dV + \int_V q_m c_f (T_s - T) dV \quad (36a)$$

and

$$\int_V \sigma_c \frac{\delta CS}{\delta t} dV = \int_V (\nabla \cdot \rho_f D_{ij} \nabla CS) dV + \int_V q_m (CS_s - CS) dV \quad (36b)$$

These equations are solved by the integrated finite difference method. When the pressure, temperature and chemistry have been calculated, the water and rock properties are updated. This procedure is repeated until the solution converges. The convergence criteria is set by

$$\left[\frac{\lambda_{\text{new}} - \lambda_{\text{old}}}{\lambda_{\text{old}}} \right]_{\text{max}} \leq \tau_\lambda \quad (37)$$

where λ refers to P, T, or C; τ_λ is the specified residue constant, and "max" refers to the maximum value over the entire mesh.

3.3 CODE MODIFICATION

In the present study, the code PTC was expanded to include transport of "non-reactive" chemical components and the stable isotope oxygen-18. Diffusion transport is assumed negligible, and the kinetic reactions for the non-reactive species are not significant within the temperature range of interest in this study. Therefore, the governing equation describing this behavior can be written

$$\int_V \frac{\delta(\phi \rho_r CS)}{\delta t} dV = - \int_A \rho_r \vec{v}_d CS \cdot \hat{n} dV + \int_V G_r CS_r dV \quad (38)$$

The convection term (first term on right-hand side), is solved by the explicit, monotonized, upwind/central differencing method as developed by Lai (1985). The source term is solved by implicit central differencing.

Included in the source term for the oxygen-18 transport is the exchange due to the kinetic reactions between the rock and water for oxygen-18. After the pressure, temperature and oxygen-18 transport due to convection are calculated, and the equation of state parameters are updated, a subroutine is called to calculate the change in oxygen-18 in the water due to kinetic reactions, over one time step. The oxygen-18 value is then updated, and the solutions for all the primary dependant variables are checked for convergence before initiating the next time step.

The subroutine incorporates the option to evaluate oxygen-18 transport for several rock/water systems. These include basalt/seawater, basalt/water, granite/seawater, granite/water, clay/water and quartz sandstone/water. The equations for oxygen-18 transport described in the section on the chemistry of low-temperature fields must be transformed into a numerical form for evaluation in the subroutine as follows:

$$\begin{aligned} \delta_r^{n+1} &= \delta_r^n - \left(\frac{W}{S} \right) \cdot \Delta \delta_r^n \\ \delta_r^{eq^{n+1}} &= \frac{\left(\delta_R^{n+1} - \nabla_{RW}^{eq} + \left(\frac{W}{S} \right) \delta_r^n \right)}{\left(1 + \frac{W}{S} \right)} \\ \Delta \delta_r^{n+1} &= \left(\frac{W + S}{WS} \right) A_{r1} (\delta_r^{eq^{n+1}} - \delta_r^n) \cdot \Delta t \\ \delta_r^{n+1} &= \Delta \delta_r^{n+1} + \delta_r^n \end{aligned} \quad (39)$$

where δ is an abbreviated form used for $\delta^{18}\text{O}$. At the beginning of each call, W , S , A , r_1 , and ∇_{RW}^{eq} are updated using the most recent temperature, porosity and density data.

A listing of the subroutine is given in Appendix B, along with a description of the input parameters and variables.

3.4 PERFORMANCE OF THE CODE

To evaluate the performance of the code, simple transport problems are simulated, and the results compared with known analytical solutions. Performance tests for silica transport have already been completed by Lai (1985). To test the non-reactive species transport, a three-node, one-dimensional problem is selected (Figure 7). The volumes of the two outer nodes are very large, holding the pressure, temperature and chemical concentrations of these nodes constant. A pressure gradient is induced between the nodes by assigning a pressure of 40 bars to node 1 and 20 bars to node 3. The concentration in the second node is initially zero; the concentration in the first node is $C_1 = 1.0$. The analytical solution describing the concentration within node 2 (C_2) as a function of time is written:

$$C_2 = D_1 \left[1 - e^{-\left(\frac{V_1 A}{V_2 \phi t} \right) t} \right] \quad (40)$$

where subscripts 1 and 2 refer to nodes one and two. Table 4 contains the solutions for a specific time for both the analytical and numerical methods; the results show an excellent match.

Figure 7. Three node mesh used in testing transport of the non-reactive chemical components.

TABLE 4. Performance test of conservative species transport using the code PTCC.

Time (year)	Analytical Solution	Numerical Solution
0.1893	0.7648	0.7650
0.3431	0.9279	0.9280
0.5184	0.9811	0.9813
1.4371	0.9999	0.9999

To test the performance of the code for the kinetic reactions of oxygen-18, a single element model is selected, eliminating convection. Temperature and pressure are assumed constant. The rate and equilibrium constants are both functions of temperature and will remain constant for a constant temperature. The total moles of oxygen-18 in the fluid, W , the total moles of oxygen-18 in the solid, S , for the systems, and the total surface area of the grains, A , are all dependent on the densities of water and rock, porosity, and the volume of the system. These parameters do not vary throughout the problem, therefore W , S , A will also remain constant. The analytical solution is linear and solved in one step:

$$\delta(t)_f = \delta_f^{eq} - (\delta_f^{eq} - \delta_f^i) e^{-(Y A_r)_k t} \quad (41)$$

where $Y = (W + S)/WS$.

In Eq. 41, the initial δ_R^{18} and δ_f^{18} remain constant. In the numerical method, the initial δ_R^{18} and δ_f^{18} are updated after each time step. Although this method is more consistent with the kinetic reactions of oxygen-18 in an actual system, it is not consistent with the analytical solution. To achieve a match with the analytical solution, the initial δ_R^{18} and δ_f^{18} must be held constant in the numerical method. The results of this procedure, presented in Table 5, show an excellent match with the results of the analytical method.

TABLE 5. Performance test on the kinetic reaction of oxygen-18 using the code PTCC.

Time (years)	Analytical Solution	Linearized Numerical Solution
6.3	-6.754	-6.755
25.4	-4.024	-4.022
31.9	-3.376	-3.374
178.0	0.001	0.003
3171.0	0.070	0.070

It is also interesting to examine how much of a difference updating the initial δ_R^{18} and δ_f^{18} can make on the system. Figure 8 shows a comparison between the results of the analytical solution and the numerical solution (updating δ_R^{18} and δ_f^{18}). Measurements taken on a geothermal system of the oxygen-18 in the fluid are recorded with one decimal place accuracy or better, so the difference shown in the figure could introduce a substantial amount of error into a numerical modeling scheme.

As a second test on the performance of the numerical code in modeling the kinetic oxygen-18 transport, the time for a non-convecting, non-conducting system to reach equilibrium was examined. The numerical results for several temperatures were compared with the results obtained when using the equation given by Cole, (1983):

$$t(\text{sec}) = \frac{-\ln(1-\alpha)(W/S)(\omega\rho X_f)}{3(1+(W/S))r_1(10^{-4})} \quad (42)$$

to estimate the equilibrium time by hand calculation. (All parameters are as previously defined.) Determining the exact equilibrium time from the numerical results was difficult, as the change in δ^{18} remains very small for many years before attaining equilibrium. To maintain a systematic approach, 10^{-4} was chosen as the limit for the amount of change per time step. When the change per timestep became smaller than

Figure 8. Analytical and numerical solutions to kinetic transport problem for oxygen-18.

this value, the system was considered in isotopic equilibrium. Table 6 lists the results of each method; the comparison between the two methods of solution is quite good.

TABLE 6. Comparison of the times to reach chemical equilibrium at various temperatures between the results obtained by the code PTCC and those obtained using the analytical equation developed by Cole (1983), for the time to reach chemical equilibrium at various temperatures.

Temperature (° C)	Rate constant (mols/m ² ·s)	Time: analytical (sec)	Time: PTCC (sec)
50	2.501×10^{-13}	1.46×10^{13}	0.43×10^{13}
100	2.780×10^{-12}	1.32×10^{12}	0.5×10^{12}
150	1.750×10^{-11}	2.10×10^{11}	2.0×10^{11}
200	7.453×10^{-11}	4.90×10^{10}	4.7×10^{10}

4.0 APPLICATIONS OF THE CODE

4.1 SENSITIVITY STUDIES

Before attempting to model a complex geothermal system, or applying the code to a field problem, it is very useful to perform a series of sensitivity studies to determine how certain parameters can affect chemical transport. The kinetic reactions of oxygen-18 and silica in a porous media were examined first. The study included the influence of the type of rock/fluid system on oxygen-18 transport and the significance of the the average grain radius (or A/V in the case of silica), the porosity, the temperature and the volume of a geothermal system on the kinetic reactions of both the oxygen-18 and silica. Second, the convective transport of a conservative chemical species was examined. The study used silica as the component, but since the kinetic reactions of silica were not considered in this part of the study, the results apply equally to any conservative component. The study included the significance of the porosity and volume on convective chemical transport. The method used in the sensitivity studies involved systematically varying each of these parameters while holding all other parameters constant and noting the effects on the oxygen-18/silica transport.

4.1.1 Approach

To examine the transport of oxygen-18 and silica by kinetic reactions, a simple, single element model was developed, eliminating convective transport. The values for the field properties of the model, listed in Table 7a, are comparable to actual field properties of many geothermal systems. The value for the average grain is characteristic of a fine-grain porous medium. Each parameter remains constant unless it is the one being studied. A basalt/water system was used in all the studies (excluding the rock/fluid study), because the field examples reviewed later in the present work involve basalt/water systems. For the same reason, alpha-cristobalite was selected as the type of silica in the model. The initial oxygen-18 and silica in the fluid are not in chemical

equilibrium at the given temperature of the model (see Table 7a). Thus, at the start of the problem, the components begin to shift towards equilibrium, and the effects of the field parameters on this shift can be examined.

The model developed to study convective transport of a chemical component in a porous media included a warm region (the field area) with cool recharge coming in from the top and side. Fluid is produced out of the warm region at 100 kg/s; the recharge amounts coming in from the top and side are equal (50 kg/s from each region). Table 7b lists the values for the field properties assumed in the study. Once again, each parameter remains constant unless it is being studied. Alpha-cristobalite was used for the form of silica in the system. Figure 9 shows a sketch of the system. Although it is very simple, many low-temperature geothermal systems have similar patterns of recharge and field property values.

TABLE 7a. Values of the parameters used in the single element model for the sensitivity studies of the kinetic reactions.

Parameter	Value
Volume	$1 \times 10^9 \text{ m}^3$
Porosity	10%
Permeability	$1 \times 10^{-14} \text{ m}^2$
Temperature	125 °C
δ_r^{18} (initial)	-8.0 per mil
Silica (initial)	25 ppm
ω	0.0×10^{-4}
A/V	10.0

Figure 9.

Sketch of three-node mesh used in sensitivity studies.

TABLE 7b. Values of the parameters used in the model for the convective sensitivity studies.

Parameter	Value
Volume (field)	$1 \times 10^9 \text{ m}^3$
Porosity	10%
Temperature	
(field)	125 °C
(top)	50 °C
(side)	75 °C
Silica	
(field)	184 ppm
(top)	50 ppm
(side)	84 ppm

4.1.2 Study of kinetic reactions

Oxygen-18

The influence of the rock/fluid system on the oxygen-18 transport was studied using the single element model described above. The oxygen-18 content is plotted against time for each rock/fluid system in Figure 10. The same initial oxygen-18 content in the rock (5.6 per mil) was used for all rock/fluid systems to more clearly see the differences in the kinetic transport between each system. A noticeable aspect of Figure 10 is the different shape of the curves between the rock/fluid systems. The shapes of the curves are governed primarily by the kinetic rate constant and slightly by the value of the equilibrium constant.

Figure 10. The influence of the rock/fluid system on the kinetic reactions of oxygen-18.

The curves for the basalt/fluid systems are linear, while the curves for the dolomite/water and quartz/water show a steady curving drop before flattening out towards the end of the thirty year period. This can be most clearly understood by referring to Table 8, which lists the values for the rate constant (as $\log r_1$) and the δ_f^{eq} at 150 °C, for each rock/fluid system. The rate constants of the dolomite/water and quartz/water systems are much higher at this temperature than the basalt/fluid systems. Thus, the basalt systems move much more slowly towards equilibrium.

TABLE 8. Comparison of the equilibrium and rate constants between rock/fluid systems at 125 °C.

Rock/fluid system	δ_f^{eq} (per mil)	$\log r_1$
Granite/seawater	-8.53	-9.15
Granite/water	-8.53	-10.62
Calcite/water	-7.75	-8.98
Dolomite/water	-10.05	-9.00
Basalt/seawater	-0.43	-11.10
Basalt/water	-3.35	-11.10

The granite/seawater and calcite/water systems also have relatively high rate constants, but do not show the curvature of the dolomite/ and quartz/water systems. This can be explained by the equilibrium constants of the different systems. The granite systems and calcite/water system are very near their δ_f^{eq} values at the start of the problem. The high rate constants for the granite/seawater and calcite/water systems allow them to shift quickly towards equilibrium, causing the curves to almost immediately flatten out. In the case of granite/water, the proximity of the initial oxygen-18 content of the system to the δ_f^{eq} at the start of the problem allows the system to shift rapidly to the equilibrium value, even though the value of the rate constant is very low at 125 °C.

Another interesting aspect of Figure 10 is the affect of seawater versus pure water in the basalt and granite systems. According to the results, seawater in place of pure water has a significant effect on a basalt system but not on a granite system. This is most likely not true. As was discussed in section 2.2, the temperature function of the kinetic rate constant for a basalt/water system and of the equilibrium rock-water fractionation (Δ_{RW}^{eq}) for a granite/seawater system are not available. Therefore, the same rate constant for basalt/seawater was assumed for basalt/water, and the same Δ_{RW}^{eq} function for granite/water was assumed for granite/seawater.

The values of δ_f^{eq} for the two basalt systems are significantly different. This is logical considering the much higher content of oxygen-18 found in seawater than meteoric waters. However, inspecting the rate constants for the granite systems at 125 °C (see Table 8) also indicates a significant difference between the rate constants for systems of the same rock type but containing differing water types. This suggests that seawater in place of water affects the rate at which a system shifts toward equilibrium as well as the equilibrium value. Therefore, assumptions made in section 2.2 and mentioned above, could introduce errors when calculating the δ_f^{18} transport.

Before concluding the rock/fluid study it is necessary to point out the effect of the choice of δ_R^{18i} , the initial oxygen-18 content of the rock. As was mentioned above, the δ_R^{18i} was held constant between runs. However, actual oxygen-18 contents can differ greatly between rock types (see Table 3 for a list of the range in δ_R^{18} for the rock types used in the present work). The initial value of δ_R^{18} significantly influences the δ_f^{eq} of a system (see equation 12). Figure 11 compares the transport of oxygen-18 in a dolomite/water system with a δ_R^{18i} of 5.6 per mil to that of the same system with a δ_R^{18i} of 15.0. The rate at which the two systems reach equilibrium is approximately the same, being governed by the rate constant, but the oxygen-18 content in the second system is now increasing. The figure helps to clarify that in most real systems, interactions between the rock and water will tend to increase the oxygen-18 content.

Following the rock/fluid study, the effects of varying the average grain radius on the kinetic reactions of oxygen-18 were investigated. Figure 12 shows the effects of

Figure 11. Comparing the effects of δ_R^{18l} on the kinetics of oxygen-18 in a dolomite/water system at a temperature of 125° C.

varying the average grain size, ω , on the oxygen-18 equilibrium. As the surface area depends on $(1/\omega)$ (see Eq. 11a), the rate of change of oxygen-18 is inversely proportional to the average grain size. Therefore, as the average grain size is decreased from 10^{-2}m to 10^{-6}m , the rate of change of oxygen-18 increases rapidly. The ultimate effect of this increase is for the system to achieve equilibrium much more quickly. Since the model was held at the same temperature for all the runs, the value of δ^{eq} is also the same. Thus, when $\omega=10^{-6}\text{m}$, the system reaches chemical equilibrium within 12 years, while for the larger grain sizes, the shift towards equilibrium has barely begun after 12 years.

For this study to be most useful, an understanding of actual grain sizes found in rock systems is essential. In fine-grained, highly consolidated materials, fluid flow will be dominantly through fractures. Thus, the effective ω could be quite large ($> 0.01\text{ m}$). While in loosely consolidated, very fine-grained systems, ω would range between $10^{-5} - 10^{-6}$. Moderately consolidated, medium grained systems would have an ω between the above extremes. This suggests that, while in loosely consolidated granular systems the kinetic reactions of oxygen-18 occur rapidly, the kinetic reactions of oxygen-18 in highly compacted, fractured systems could be negligible over short time spans (i.e. the approximate thirty years of productivity of a geothermal system under exploitation).

Next, the significance of the porosity of a geothermal system on the kinetic reactions of oxygen-18 transport were examined. From the results of the porosity study (plotted in Figure 13) it is clear that the kinetic reactions occur most quickly for systems with low porosities. This is due to the $(1 - \phi)/\phi$ dependence in the equation solving for the change in oxygen-18 with time. The two constants, surface area, A , and the term $(S+W)/SW$, when multiplied together become:

$$\frac{A(S+W)}{SW} = (3/\omega) \left[\frac{1}{\rho_f X_f} \left(\frac{1-\phi}{\phi} \right) + \frac{1}{\rho_R X_R} \right] \quad (43)$$

where the symbols are as previously described. When $\phi = 1\%$, the term $(1-\phi)/\phi$ is 99.0 and $A(S+W)/SW$ is about five times larger than when $\phi = 5\%$ and $(1-\phi)/\phi = 19$.

Figure 12. Significance of the average grain radius on the kinetic reactions of oxygen-18.

Figure 13. Significance of porosity on kinetic reactions of oxygen-18.

The equation for the change in oxygen-18 per time step (see Eq. 9), is directly proportional to $A(S+W)/SW$, which explains the large difference in the behavior of the oxygen-18 transport between $\phi = 1\%$ and $\phi = 5\%$. As ϕ increases, the change in $(1-\phi)/\phi$ (and therefore $A(S+W)/SW$) becomes much smaller, and the oxygen-18 curves will lie more closely together.

Also noticeable in Figure 13, is the increase in linearity with increasing porosity. Once again this is due to a dependence on $(1-\phi)/\phi$ in the term W/S , found in the equation for the equilibrium oxygen-18 content (see Eq. 12) for a basalt/water system where:

$$W/S = \left(\frac{\phi}{1-\phi} \right) \left(\frac{\rho_f X_f}{\rho_R X_R} \right) \quad (44)$$

The net effect with increasing porosity is a more negative equilibrium value, making the system closer to being in isotopic equilibrium at the initiation of the problem. Thus, as was seen in the study on the different rock/fluid systems, the curves become more linear when they are closer to equilibrium at the offset.

The effects of temperature on the kinetics of oxygen-18 in a basalt/water system were studied next. At the lower temperatures, Δ_{RW}^{18} is larger, making δ_r^{18} more negative and closer in absolute value to the initial oxygen-18 content of the fluid. Also at lower temperatures, the kinetic rate constant is much smaller. Both of these effects tend to make the curve more linear at lower temperatures and the small kinetic rate constant increases the amount of time necessary to reach equilibrium. These effects show up clearly on Figure 14 a plot of the oxygen-18 content versus time for various temperatures.

For completeness, the effects of volume on the kinetic reactions of oxygen-18 were examined. A review of the rate equation (see Eq. 9) indicates that the reservoir volume will not effect the kinetics of oxygen-18. Although surprising at first, when the term $A(S+W)/SW$ in the rate of change equation for δ^{18} is examined more closely it

Figure 14. Significance of temperature on the kinetic reactions of oxygen-18.

becomes:

$$\begin{aligned} A \frac{(S + W)}{SW} &= \frac{3V(1-\phi)}{\omega} \left[\left(\frac{1}{V\phi\rho_f X_f} \right) + \left(\frac{1}{V(1-\phi)\rho_R X_R} \right) \right] \\ &= 3 \frac{(1-\phi)}{\omega} \left[\frac{1}{\phi\rho_f X_f} + \frac{1}{(1-\phi)\rho_R X_R} \right] \end{aligned}$$

and it can be seen that the volume term drops out. Neither the kinetic rate equation nor the equilibrium fractionation value are dependent on the volume, thus the kinetic rate of change of oxygen-18 is completely independent of the volume size of the field if convection is neglected.

Silica

The effects of temperature, porosity and surface area per volume (A/V), on the kinetic reactions of silica in a porous medium were also studied using the single element model with the parameter values as listed in Table 6a. For the first study, temperature was varied from 50°C to 200°C, while holding all other parameters constant. The results, plotted in Figure 15, show a large jump in the effects of the kinetic reactions between 100°C and 200°C. However, this indicates only that the silica concentration in the 100°C system is closer to the equilibrium concentration at the start of the problem, than is the silica concentration in the 200°C system. To more clearly see the effects of temperature on the kinetic reactions of silica, a second case was run, again varying the temperature from 50°C to 200°C, but choosing an initial silica concentration of 500 ppm in the fluid. Thus, the system at 200°C was initially the closest to its equilibrium concentration of silica (477 ppm.), while the system at 50°C was the furthest from its equilibrium concentration of 51 ppm. Comparison of the results of the second case (Figure 16) to the results of the first, gives a better indication of the importance of temperature on the kinetic reactions. The shape of the curve will indicate how rapidly the system is moving towards equilibrium. In the first case, the

Figure 15. Significance of temperature on the kinetic reactions of silica. Initial silica is 25 ppm.

Figure 16. Significance of temperature on the kinetic reactions of silica. Initial silica is 500 ppm.

system at 200°C moves very rapidly toward equilibrium, as demonstrated by the step-like curve. The system at 50°C, in the second case moves much more slowly towards equilibrium as demonstrated by the nearly horizontal, linear curve. Comparison of the two plots suggest that below 150°C the kinetic effects on silica transport decrease significantly in importance.

Next, the significance of porosity on kinetic reactions of silica were examined. Reviewing the kinetic rate of change of silica (see Eq. 1), indicates that neither the volume nor the porosity of a system will affect the kinetic reactions. The A/V term is essentially empirical and is not calculated using the actual field volume. Therefore, the kinetic reactions of silica are independent of volume size and porosity.

Finally, the affect of the surface area open to reaction per volume of the system was studied. A/V was varied from 1. to 1000., the temperature was held at 125°C, and the initial silica concentration was 500 ppm. The results, plotted in Figure 17, demonstrate the importance of the A/V value on how rapidly a system moves towards equilibrium. The higher the A/V term, the more rapidly the silica concentration in a system will equilibrate, and the shape of the curve becomes increasingly more step-like. This may be understood more clearly by referring to the equation describing kinetic transport (see Eq. 1), which shows the rate of change of silica to be proportional to A/V . Thus, if A/V is varied, the rate of change of the silica concentration will vary accordingly.

4.1.3 Studies on convective chemical transport

Studies on the significance of porosity and field volume size on convective chemical transport were performed using the model with recharge in from the top and side described in the approach, and having the parameters of Table 7b. The results of the porosity study, plotted in Figure 18, indicate that systems with lower porosities will transport conservative components more quickly than those with higher porosities. This is due to the inverse proportionality in the transport equation between the rate of change in concentration and the mass of fluid in the system ($V\phi\rho_f$).

Figure 17. Significance of A/V on the kinetic reactions of silica.

The case above involved silica, but without the kinetic effects (ie: silica was assumed conservative). It is also of interest to examine how the kinetics might influence the transport of silica in a convective system. A moderate value of A/V was chosen ($A/V = 10.0 \text{ m}^{-1}$), and a case run using the same system as above with 10% porosity and including kinetic reactions. It is apparent that the two effects, convection and kinetic reactions, are opposing each other in this system (Figure 19). This is because the difference in temperatures between the separate recharge areas are not as large as the differences in the silica concentrations, thus the change in temperature in the warm region is not as rapid as that of the silica concentration. As the concentration of the silica is being lowered due to the convective transport, the kinetic reactions are causing the silica concentration to increase towards an equilibrium set by the temperature.

The results of the study on the volume, plotted in Figure 20, indicates a strong dependence between the volume and amount of chemical transport. This is due to the inverse proportionality between the volume and the rate of change of the chemical concentration. Therefore, if the volume is decreased by an order of magnitude, the rate of chemical changes will increase proportionally.

In summary, the sensitivity studies on the kinetic reactions of oxygen-18 and silica and the convective transport of chemical components are found to be helpful in determining which parameters have the most (or least) significant effects. Temperature and A/V determine the importance of the kinetic reactions of silica in a geothermal system. Due to the proportionality between the rate of change of silica and A/V , varying A/V appears to have the greatest effects on the shape of the silica versus time curve. Porosity and volume have no effect on the kinetic reactions of silica. Likewise, for oxygen-18 transport, the temperature and average grain radius played the most significant role in determining the importance of the kinetic reactions and the shape of the curve. However, unlike the kinetics of silica, the kinetic reactions of oxygen-18 are also significantly affected by the porosity, with the transport becoming much more rapid as the porosities decrease. In the study on convective transport, the volume significantly affected the transport of a chemical component, due to the inverse

Figure 18. Significance of porosity on silica transport by convection only.

Figure 19. Comparison between the convective transport of silica with and without kinetic reactions.

Figure 20. Significance of volume on silica transport by convection only.

proportionality with the rate of change of the concentration of the component. The porosity is also inversely proportional to the change in the concentration in the rate equation, but its effects are less pronounced because it was varied over a much smaller range.

4.2. NON-DIMENSIONAL STUDY

After studying the effects and significance of various parameters on silica and oxygen-18 transport, it is useful to perform a dimensional analysis on the governing equation for chemical transport. The goal in this exercise is to characterize the governing equation by dimensionless groups of parameters. If successful, the number of dimensionless parameters will be many less than the total number of parameters describing the system. Further sensitivity studies may then be performed by holding some of the dimensionless groups constant, while varying the values of those remaining. The results may be plotted in the form of type curves. Field data can then be matched with the type curves to get estimates of field parameters.

To non-dimensionalize the chemical transport equation, several simplifying assumptions must be made. First, the field is assumed to have only two zones of recharge, one from the top (noted by subscript a in this study), and one from the side (noted by subscript b). The amount of fluids coming in from the top and side is equal to the amount of fluid being produced (ie. mass is conserved; $q = q_a + q_b$); and both the flux from top or side is proportional to q ($q_a = \alpha q$; $q_b = \beta q$). Second, transport due to dispersion/diffusion is neglected. Third, temperature is assumed to be linear function of time such that,

$$T = \bar{a}t + \bar{b} \quad (45)$$

where

$$\bar{a} = \frac{q}{x} \left(\alpha T_a + \beta T_b - T_o \right) \left(\frac{c_f \rho_f}{c_R \rho_R} \right) \phi$$

$$\bar{b} = T_o$$

and

$$x = V \phi \rho_f$$

This assumption will always be approximately valid if the flow rates from the two recharge zones does not change significantly with time. This verified by Figure 21, a

plot of temperature versus time for various field volumes at production rates of 250 kg/s and 25 kg/s.

Fourth, the kinetic rate constant and equilibrium constant are both assumed to be linear functions of temperature. Over short temperature ranges (between 75°C - 150°C), this assumption is approximately valid for both silica and oxygen-18, as is shown in Figures 22, 23 and 24; for oxygen-18, the equilibrium constant actually is a linear function of temperature (see Eq. 12). From the figures, the temperature dependent functions are found to be:

For silica (α -cristobalite),

$$C^{\alpha} = a' T + b' \quad (46a)$$

$$k_1 = A' T + B'$$

where

$$a' = 5.091$$

$$b' = -123.64$$

$$A' = 2.0 \times 10^{-9}$$

$$B' = -178.9 \times 10^{-9}$$

For oxygen-18 in a basalt/seawater system,

$$\delta^{\alpha} = a' T + b' \quad (46b)$$

$$r_1 = A' T + B'$$

where

$$a' = \left[\frac{0.01463}{1 + \left(\frac{\phi}{1-\phi} \right) \left(\frac{\rho_f X_f}{\rho_R X_R} \right)} \right]$$

$$b' = \frac{\delta_R^i - 7.85 + \left(\frac{\phi}{1-\phi} \right) \left(\frac{\rho_f X_f}{\rho_R X_R} \right) C_o}{1 + \left(\frac{\phi}{1-\phi} \right) \left(\frac{\rho_f X_f}{\rho_R X_R} \right)}$$

Figure 21. Temperature versus time for various field volumes and flow rates.

Figure 22. Fitting a linear temperature function to the kinetic rate constant for silica.

Figure 23.

Equilibrium solubilities for silica (from Robinson, 1982). A linear function of temperature is assumed over the temperature range 80°C to 150°C, for α -cristobolite.

Figure 24. Fitting a linear temperature function to the kinetic rate constant for oxygen-18.

$$A' = 2.8 \times 10^{-13}$$

$$B' = -259.0 \times 10^{-13}$$

To non-dimensionalize the governing equation, a step-by-step inspectional analysis technique, described by Tillotson and Nielson (1983) was used. The technique consists of the following steps;

- (1) List the physical law and boundary conditions.

$$\frac{dC}{dt} = \left(\frac{Q}{x} + Yc_2\bar{B} \right) - \left[\frac{q}{x} + c_2Y \right] C - (Yc_1)tC + (Yc_1\bar{A})t^2 + (Y(c_1\bar{B} + c_2\bar{A}))t$$

and at $t = 0$, $C = C_0$. The constants $\bar{A}$, $\bar{B}$, c_1 and c_2 are defined:

$$\bar{A} = a' \bar{a}$$

$$\bar{B} = a' \bar{b} + b'$$

$$c_1 = A' \bar{a}$$

$$c_2 = A' \bar{b} + B'$$

The constant Y is defined differently for silica and oxygen-18. For silica:

$$Y = A/V;$$

and for oxygen-18:

$$Y = A \left(\frac{W + S}{SW} \right).$$

- (2) Put variables in dimensionless form.

$$C^* = \frac{C}{C_0}$$

$$\tau = \left(\frac{q}{x} \right) t$$

- (3) Substitute back into physical law.

$$\frac{C_0 q}{x} \frac{dC^*}{d\tau}$$

$$= \left(\frac{Q}{x} + Yc_2B \right) - \left[\frac{q}{x} + c_2Y \right] C_o C^* - (Yc_1) \frac{x}{q} C_o \tau C^* \\ + (Yc_1 \bar{A}) \left(\frac{x}{q} \right)^2 \tau^2 + Y(c_1 \bar{B} + c_2 \bar{A}) \frac{w}{q} \tau$$

(4) Divide equations by the leading coefficient of one term.

$$\frac{dC^*}{d\tau} = \left(\frac{Q}{x} + Yc_2B \right) \frac{x}{qC_o} - \left[\frac{q}{x} + c_2Y \right] \frac{x}{q} C^* - (Yc_1) \frac{x^2}{q^2} \tau C^* \\ + (Yc_1 \bar{A}) \left(\frac{x}{q} \right)^3 \frac{\tau^2}{C_o} + \frac{Y}{C_o} (c_1 \bar{B} + c_2 \bar{A}) \left(\frac{x}{q} \right)^2 \tau$$

(5) Determine the dimensionless groups by inspection.

$$D_1 = \frac{Yc_1 x^2}{q^2} \quad D_3 = \frac{Q}{\bar{A}x} \\ D_2 = \frac{Yc_2 x}{q} \quad D_4 = \frac{\bar{B}}{\bar{A}} \frac{q}{x} \\ D_5 = \frac{q}{x} \frac{C_o}{\bar{A}}$$

The equation can now be written in dimensionless form as:

$$\frac{dC^*}{d\tau} = \left(\frac{D_3 + D_2 D_4}{D_5} \right) - (1 + D_2) C^* - D_1 \tau C^* \\ + \left(\frac{D_1}{D_5} \right) \tau^2 + \left(\frac{D_2 + D_1 D_4}{D_5} \right) \tau \quad (47)$$

Equation 47 is nonlinear and cannot be readily solved analytically. Instead, the numerical code (PTCC) was used and the results are presented in terms of the dimensionless parameters. To test the uniqueness of the dimensionless parameters, the the overall group values are held constant, while parameters within the group are varied. For example, D_1 is held constant, but Y , c_1 , x , and q are varied such that when they are multiplied as $(Yc_1 x)/q^2$, the value remains constant. In order to do this for all five of the dimensionless parameters, the groups must be written in terms of the

fundamental parameters and set equal to the values of the first run. To find the values of the second run, one parameter is changed (such as porosity) and the equations are solved simultaneously for the new values of the remaining parameters. If the dimensionless groups are unique, the results of the two runs will match identically. The test runs used the following values for the dimensionless parameters, for silica;

$$D_1 = -18.8,$$

$$D_2 = 86.7,$$

$$D_3 = -1.5,$$

$$D_4 = -9.6,$$

$$D_5 = -0.5,$$

and for oxygen-18;

$$D_1 = 2.1,$$

$$D_2 = 22.4,$$

$$D_3 = 3.5,$$

$$D_4 = 44.8,$$

$$D_5 = -18.8.$$

The results are plotted in Figures 25a,b as dimensionless concentration versus dimensionless time for silica and oxygen-18, respectively. As is demonstrated in the figures, the runs match identically for both silica and oxygen-18.

After validating the dimensionless groups, it must be decided which of these groups will be most useful to study. Since the dimensionless parameters for silica and oxygen-18 are nearly identical, the studies could be performed equally on one or the other. To avoid repetition, studies on the dimensionless parameters were performed using silica transport only. As a first attempt, to study the effects of q/x , D_1 and D_2 were varied, (by varying q/x) and holding the other dimensionless groups constant. For the study, q/x was varied over several orders of magnitude and the results plotted as

Figure 25. Testing the uniqueness of the nondimensional parameters for, (a) silica and (b) oxygen-18.

type curves in Figure 26. In the figure, C^* is shown plotted against τD_2 . It is necessary to multiply τ by D_2 before plotting. Because τ varies proportionally with q/x , when q/x changes by an order of magnitude, the dimensionless time will as well. The range in values between type curves becomes very large and are cumbersome to plot. If τ is multiplied by D_2 , q/x will cancel out. As indicated in the figure, when the volume increases, and/or the production rate decreases, the change in chemical concentration become smaller and the curves flatten out. The larger the reservoir volume (or, equivalently, the larger the flow rate), the shorter the time for the inflow of lower concentration waters to have an effect.

As a second attempt, D_3 was varied by changing the amount of flow in from the top and sides (varying $\bar{\alpha}$ and $\bar{\beta}$). It is not strictly correct that the other dimensionless parameters remained constant, but D_3 is much more affected by a change in $\bar{\alpha}$ and $\bar{\beta}$; the amount of error assumed by regarding the other parameters as constant between runs is less than 10%.

To demonstrate the usefulness of type curves made from varying D_3 , field data from the Ellidaar field in Iceland was analyzed. The Ellidaar field is a low-temperature field located near the sea, in the southwestern part of the country, in predominantly fractured basalts. Figure 27 gives a simple conceptual model of the system. The field was modeled previously by Lai et al. (1985), using a similar model and they estimated the field parameters as:

$$V=2.5 \times 10^8 \text{ m}^3,$$

$$\phi=5\%,$$

$$A/V=5.5 \text{ m}^{-1},$$

$$\bar{\alpha}=0.9, \quad \bar{\beta}=0.1.$$

The high value of $\bar{\alpha}$ indicates large recharge from above.

The silica concentration data from the field was plotted non-dimensionally against time (Figure 28). A set of type curves were made (Figure 29), varying D_3 and using a simple three-element model, similar to the one shown in Figure 9, with the field

Figure 26. Type curves for different values of the dimensionless parameters, D_1 and D_2 , by varying q/x .

Figure 27. Simple cross-sectional sketch of the Ellidaar geothermal system (Lai, 1985).

Figure 28. Field data from the Ellidaar geothermal field (Hettling, 1984) for silica plotted non-dimensionally against dimensionless time.

Figure 29.

Type curves of range in dimensionless parameter D_3 , showing effect of relative recharge in from the top and side. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).

parameters of the Ellidaar field. In Figure 29, it was found to be more helpful to identify the curves by the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from top}$; $100 \times \bar{\beta} = \% \text{ flux from side}$), to indicate the changes in the amounts of recharge from the top and side associated with varying D_3 . The field data was then matched with the type curve. The curve fell between the 75:25 and 100:0 curves, which agrees with the estimates by Lai.

Several more sets of type curves were then generated by varying the field properties. Table 9 lists the values of the dimensionless parameters D_1 , D_2 , D_4 and D_5 , along with the number of the figure which shows a plot of the resulting type curves obtained by holding these values constant and varying D_3 . The first set of type curves was obtained by increasing the porosity to 10% (Figure 30); the second, by increasing q/x by an order of magnitude (Figure 31); the third, by decreasing q/x by an order of magnitude from the original value (Figure 32); and the fourth, by increasing A/V from 5.5 to 25.0 (Figure 33). Again, the field data was tested for a match. No match was found between the field data and the type curves of different porosity and q/x values, indicating the choice of porosity = 5% and $V = 2.5 \times 10^8$ are the most accurate estimates of the parameters. A match with the fourth type curve, with a larger A/V , was possible. However, in the second match, the field data curve also fell between the 75:25 and 100:0 curves, in agreement with the estimate by Lai.

TABLE 9. Values of the dimensionless parameters held constant in Figures 29 through 33.

Figure	D_1	D_2	D_4	D_5
29	18.8	86.7	9.60	-0.50
30	18.8	43.4	4.80	-0.25
31	1.88	8.67	9.60	-0.50
32	188.	867.	9.60	-0.50
33	94.0	434.	9.60	-0.50

Figure 30.

Type curves of range in dimensionless parameter D_3 . Porosity has been raised from 5% to 10%. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).

Figure 31.

Type curves of range in dimensionless parameter D_3 . The q/x has been decreased by an order of magnitude. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).

Figure 32.

Type curves of range in dimensionless parameter D_3 . The q/x has been increased by an order of magnitude. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).

Figure 33. Type curves of range in dimensionless parameter D_3 . The value of A/V has been increased from 5.5 to 25.0. The curves are identified in the legend by the variations made in the ratio of $\bar{\alpha}$ to $\bar{\beta}$ multiplied by 100 (where $100 \times \bar{\alpha} = \% \text{ flux from the top}$; $100 \times \bar{\beta} = \% \text{ flux from the side}$).

As seen from this field example, the type curves can be useful in giving approximate values for the amount of flux coming from the top and sides, the volume (from q/x), and the porosity, without lengthy trial and error matching of temperature, pressure and chemical concentration data. A simple mesh with "ballpark" estimates for the field parameters must be designed, and several sets of type curves developed as in the above example. Then, the best match of the field data with the type curves can be determined, and the field parameters estimated. However, it was also seen that an accurate estimate of the A/V value appears not to be possible from the type curve matches.

4.3 FIELD EXAMPLES

If a more accurate solution to the field parameters are necessary, a numerical model should be used to match the field data (pressure, temperature, and concentrations change with time). This technique was applied to the field data from two low-temperature fields. The first field example was the Ellidaar geothermal field, Iceland, described in the previous section. The second was the Seltjarnarnes field, also in Iceland.

Ellidaar field

The main purpose in modeling the Ellidaar field was to check the values of the parameters found in this study against those found by Lai. Also, to see if the additional chemical data utilized in this study actually helps define more unique parameters. As a first approximation, a very simple two layer system was designed, with recharge from the top at 60°C and from the sides at the same temperature as the hot reservoir (110°C). It should be noted that the actual field recharge patterns are probably much more complex, with perhaps considerable recharge from a deeper, cooler source. The model included fluoride, sodium, silica, and oxygen-18 transport. Concentrations from the upper recharge zones were estimated based on data from shallow wells in the region; the concentrations of the components coming from the side were assumed identical to the initial concentrations in the hot reservoir (refer to Figure 27 for sketch of system). By matching the temperature decline data and the change in fluoride and sodium data with time, the amount of fluid coming in from the top and sides could be estimated. Although the rate of change in concentration for two conservative species will be the same, both fluoride and sodium were modeled to get more reliable results. This study found that 85% of the recharge of the fluid came from the top, while 15% came from the side. Figures 34, 35 and 36 show how the field data for temperature, fluoride and sodium concentrations versus time, with the match of the numerical model. These values for the recharge are felt to be more unique and reliable than the results reported by Lai. In this study, three individual sets of data

Figure 34. Plot of temperature versus time showing match between numerical model and field data from the Ellidaar field.

Figure 35. Plot of fluoride versus time showing the match between the numerical model and field data from the Ellidaar field.

Figure 36. Plot of sodium versus time showing the match between the numerical model and field data from the Ellidaar field.

(temperature, fluoride, and sodium) had to be matched before the amount of recharge could be defined, while previously the recharge amounts were defined only by the temperature data.

Matching the silica and oxygen-18 data to define the porosity and volume of the field revealed some serious drawbacks in the trial and error technique. When matching the silica data, ignoring the oxygen-18 data, it was found that the data could be matched over a range in porosity from 2% to 15%, simply by varying the A/V term of the kinetic transport. Also, the oxygen-18 transport could be matched using a wide range in the average grain radius and the porosity. Thus, some method was required to determine the correct A/V or ω , before an accurate porosity could be defined. The empirical equation used to compute the A/V term by Rimstidt (1979) is written:

$$A/V = 8.55 \left(\frac{1}{r} \right) \quad (48)$$

where r is the average grain radius (not necessarily equal to ω).

If an average grain radius could be defined from field data, the A/V value can then be calculated, and the porosity uniquely determined. This was tested on the Ellidaar data, choosing an average grain radius of $0.1\text{mm} = 10^{-4}\text{ m}$ (reasonable for basalts), so A/V was equal to 8.55×10^4 . Unfortunately, when this value was used in the numerical model, the silica concentration curve was not even close to being a match to actual field data.

As a second attempt at defining A/V, it was noted that if a connection between ω and A/V could be found, then one of the two sets of chemical data could be used to define ω and A/V, while the other set could be used to define the porosity. As was seen in Section 2.2, the equation defined by Cole, et al., (1983) for the surface area of reaction is written:

$$SA = \frac{3V(1-\phi)}{\omega} \quad (49)$$

For silica transport, the 'A' in A/V is the surface area of quartz open for reaction. Therefore, it could be written in terms of SA by:

$$A = \bar{x}(SA) = \bar{x} \left[\frac{3V(1-\phi)}{\omega} \right] \quad (50)$$

where $\bar{x}$ is the fraction of quartz present in the rock. For example, if the rock was made up of 30% quartz, then $x=0.3$ and $A=0.3(SA)$.

A/V could then be found by:

$$A/V = \frac{3x(1-\phi)}{\omega} \quad (51)$$

If this theory is correct, a trial and error technique can be applied by varying ω (and therefore A/V) and the porosity until a match between the numerical model and field data is achieved by both silica and oxygen-18. This technique was applied successfully to the field data from Ellidaar, and a match was achieved for both oxygen-18 and silica using a porosity of 5% and average grain radius of 0.11m ($A/V = 10$). Figures 37 and 38 plot the field data for silica and oxygen-18 versus time, overlain with the best results achieved by the numerical model. The results indicate a connection between the average grain radius and A/V , but the values are not similar to those generally found for porous medium reservoirs. It is probable that the fractured nature of the Ellidaar system causes the large values in grain radius. In other ω is not the actual grain radius, but the effective radius of the average block size surrounded by fluid flow paths. suggesting that the two parameters are empirical.

It should be noted that the match with the oxygen-18 data is based upon very sketchy data. Oxygen-18 readings for the field have only been taken since 1980. Much of the information gained in concentration curves comes from the shape of the curve near the beginning of the production of the field, and to define a curve at all, an initial reservoir oxygen-18 value is necessary. Since this data was not available, deuterium data was used to calculate the oxygen-18 content of the surface waters using the relation (Henley, Truesdell, Barton; 1984):

$$D = 8\delta_r^{18} + 10 \quad (52)$$

The δ^{18} content of the surface waters was then used to calculate the equilibrium value of oxygen-18 in the reservoir assuming a temperature of 110°C by:

Figure 37. Plot of silica versus time showing the match between the numerical model and field data from the Ellidaar field.

Figure 38. Plot of oxygen-18 versus time showing the match between the numerical model and field data from the Ellidaar field.

$$\delta_f^{18\text{O}} = \frac{\delta_R^i - \Delta_{RW}^{eq} + (W/S)\delta_f^i}{1 + (W/S)} \quad (53)$$

where all parameters are as defined previously. A value of -4.5 was obtained and used as the initial oxygen-18 value in the hot reservoir.

Seltjarnarnes field

The second field chosen for study was the Seltjarnarnes geothermal field in southwestern Iceland. It is located on the outskirts of the capital, Reykjavik. Six wells have been drilled in the area: four production wells and two observation wells. The geological setting is similar to Ellidaar, except Seltjarnarnes is much closer to the sea (see Figure 39 for a map of the area). The reservoir rocks are predominantly basalt lavas and hyaloclastites. The water is of meteoric origin, but the produced fluids have become increasingly more saline in recent years. Production of the hot reservoir began in the mid-1960s at a rate of 3 l/s. In 1971, production was increased to 33 l/s and again increased in 1981 to 50 l/s. Although the salinity of the field has been increasing indicating an influx of seawater, the oxygen-18 content has decreased slightly. These two phenomena appear to contradict one another, as the very high oxygen-18 content of seawater relative to the local meteoric water should cause an increase in the oxygen-18 content of the hot reservoir. This suggests that the majority of the recharge comes from deeper, non-saline water.

Based upon the available data, a simple model of the field was developed. In the beginning, a simple two layer mesh was employed. The regions directly above and adjacent to the hot field were assumed to have fluid of nearly the same composition as that initially present in the geothermal reservoir (chloride = 500 ppm, sodium = 300 ppm). The silica concentrations in the top and side were the equilibrium values of each zone for the assumed temperatures and the oxygen-18 content was slightly more negative in the lower recharge zone. Figure 40 shows a sketch of the mesh and the initial concentrations and temperatures. The temperatures of the different zones were derived from well data.

XBL 8612 12845

Figure 40. Two-layer mesh used to model the Seltjarnarnes geothermal area Iceland, including the initial conditions and values of field parameters.

Using a trial and error procedure a match for the data obtained. Figures 41 - 45 show the field data plotted against time for silica, chloride, sodium, oxygen-18 and temperature, along with the computed results obtained from the numerical model. Due to the wide scatter of the field data, it was difficult to determine accurately the field parameters inferred from the match. The results obtained suggest a reservoir volume between $7.5 \times 10^8 \text{ m}^3$ and $1.0 \times 10^9 \text{ m}^3$ and a porosity between 2% and 5% was necessary to match the field data. The matches shown in the figures were obtained with a model having a reservoir volume of $7.5 \times 10^8 \text{ m}^3$, a porosity of 2%, and 82% of the recharge into the field coming from the less saline side region. This model was chosen as the best match as it was the only model, within the ranges of volume and porosities given above, to show a decrease in the oxygen-18 over time, as was documented in the field data. The lower porosity and smaller volume size required less recharge from the more saline top and more recharge from the side. The values for A/V and ω were found to be 1.0 and 0.35, respectively, in all the matches made with models having reservoir volumes and porosities within the ranges given. The low value for A/V (and therefore high value for ω) indicates that the kinetic reactions of silica and oxygen-18 play a relatively small role in this system. To illustrate this point, a plot (Figure 46) was made with silica concentration versus time for two cases: with kinetic reactions and without (convection only), using the "best match" model. It must be emphasized that due to the use of such a coarse mesh, these are only rough estimates of the field parameters and flow patterns. To determine the field parameters more uniquely, a finer mesh must be designed. This was the next step applied in modeling the Seltjarnarnes field.

Tulinius et al (1987) designed a two-dimensional, areal grid to model the pressure and temperature conditions of the Seltjarnarnes geothermal field. The central part of the grid is shown in Figure 47. The mesh contains 316 elements; small 50 meter square nodes surround the wells, with the nodes becoming progressively larger away from the well field region. To achieve a match with the pressure data, six zones with different permeabilities and porosities were necessary. The main geothermal field area was located in a high permeability zone ($k = 8.0 \times 10^{-14} \text{ m}^2$), incorporating wells SN-02.

Figure 41.

Plot of silica versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.

Figure 42. Plot of chloride versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.

Figure 44. Plot of oxygen-18 versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal area, Iceland.

Figure 45. Plot of temperature versus time showing the match between the numerical model and field data from the Seltjarnarnes geothermal field, Iceland.

Figure 46. Silica versus time with and without kinetic transport using the best model for Seltjarnarnes.

SN-06 (see Figure 39). Well SN-01, considered to be outside the main field area, was located in a low permeability, low porosity ($k = 1.0 \times 10^{-14}$; $\phi = .07\%$) region. Surrounding the near well region was a moderate permeability, moderate porosity ($k = 2.5 \times 10^{-14}$; $\phi = 4\%$) region covering an area of $4.1 \times 10^7 \text{ m}^2$. The outermost region represented by the large volume nodes was found to have a moderate permeability and high porosity ($k = 2.5 \times 10^{-14}$, $\phi = 15\%$). The volume and porosity of the main geothermal region were determined to be $8.3 \times 10^8 \text{ m}^3$ and 2%, respectively. The close agreement of the results for the field region gained by a pressure and temperature data match with the results of the simple two-layer model gained by the chemical transport match, lends support to the value of chemical transport modeling.

The finer mesh described above, along with the results of the temperature and pressure match, and available chemical field data were employed to further study the Seltjarnarnes field. The initial conditions for the chemistry of the fluid in the well field region were set by field data obtained at the initiation of field production. Two different fluid chemistries were incorporated in the model, representing seawater and meteoric water. Table 9 lists the concentrations used for each fluid type for the four chemical components modeled. Since the results of the two previous studies performed on the Seltjarnarnes geothermal field were in close agreement, the chemistry match in this study was not aimed towards verifying field parameters such as the permeabilities, porosities, and reservoir volume. Rather, the purpose of the study was to define the boundaries of the seawater adjacent to the well field.

XBL 8612-12839

Figure 47. The central section of the two-dimensional mesh designed to model the Seltjarnarnes geothermal field, Iceland (Tulinius et al., 1987). Small dots mark the well sites.

TABLE 10. Values for the concentrations of the chemical species for the different fluids used in modeling the Seltjarnarnes geothermal field (Oxygen-18 in per mil, all other components in ppm).

Component	Seawater	Meteoric Water
Chlorine	19,000	500
Sodium	10,500	300
Oxygen-18	0.001	-10.5
Silica	5	130.0 (at 110 ° C)
	5	80.0 (at 75 ° C)

The results of the chemistry match are plotted for each well, for each chemical component; chloride, sodium, silica and oxygen-18, respectively, in Figures 48 through 51. For the best match, the seawater boundary follows approximately to the land/sea boundary, surrounding the wells on three of four sides, and lying within 350 meters of wells SN-02 and SN-05 to the northeast. Figure 52 shows the suggested seawater/meteoric water boundary. The shaded region contains the meteoric water; the area outside this region contains seawater.

The results also raised several other points. The matches with the oxygen-18 data for the individual were not good; the numerical model showed a much more rapid increase in oxygen-18 than what the field data shows (see Figure 51). This infers that a three-dimensional model of the system is necessary, with fluid of a third chemical composition, of meteoric origin and containing a lower (< -10.5 per mil) oxygen-18 content, entering the system. The reviews by Hettling (1984) of other geothermal systems nearby to the Seltjarnarnes geothermal field suggest that a third type of fluid with a lower oxygen-18 content recharges these systems at depth from an inland source, while seawater intrudes the fields at the shallower depths.

The match with sodium data was also not very good, indicating that the sodium ions in the system sustain significant ionic-exchange reactions, and are not truly

Figure 48.

The chlorine transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.

Figure 49. The sodium transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.

Figure 50. The silica transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.

Figure 51.

The oxygen-18 transport match between the numerical model and field data for the Seltjarnarnes geothermal system for (a) well SN-01; (b) well SN-02; (c) well SN-03; (d) well SN-04; (e) well SN-05; (f) well SN-06.

XBL 8612-12846

Figure 52. Sketch showing the suggested boundary between seawater and meteoric water at the Seltjarnarnes geothermal field, Iceland.

conservative as assumed in the present model. The matches with the chloride are much better, as shown in Figure 48.

The results of the silica match suggest that kinetic reactions do play a role in the transport of silica in the Seltjarnarnes system, in opposition with the results obtained with the simple, two-layer chemistry match. Before the start of production, the silica concentration was approximately 130 ppm at a temperature of 110°C, in the well field region. Comparison of this concentration to equilibrium concentrations for each form of silica at 110°C (see Figure 23), indicates that the form of silica in the system is most likely α -cristobalite. However, at this temperature the true equilibrium value for α -cristobalite would be 150 ppm, indicating that there may also some β -cristobalite mixed with the α -cristobalite, lowering the equilibrium value.

To achieve the best match for silica, the A/V value was set at 25.0. Referring back to Figure 17 which shows the effect of A/V on the kinetic reactions of silica, it can be seen that a value of 25.0 indicates moderately rapid kinetic reactions. The silica match would probably improve if a three-dimensional model with a third type of fluid of meteoric origin is used as suggested by the oxygen-18 modeling.

Although the chemistry modeling has identified some shortcomings of the two-dimensional model, the model can be used to roughly predict the future influence of the seawater on the system. Thus, an estimate of the amount of influx of seawater into the field over the next fifteen or twenty years could be obtained. From this information, the potential corrosion problems in the future may be identified and the necessary steps taken to minimize or alleviate these problems.

4.4 THEORETICAL STUDY

As a final application of the multi-component, mass and heat transfer code, a theoretical study of an evolving geothermal system was performed. The system was modeled after the characterization given by White (1963) of a typical geothermal system. Geothermal systems, as described by White, consist of at least one permeable aquifer with a low-permeable cap, surface recharge and a heat source at depth. Warm surface springs often develop as the system heats and the expanding fluid flows out through fractures in the rock matrix. The hypothetical system developed in the present study includes two permeable aquifers separated by a three hundred meter layer of low-permeability rock. The shallow aquifer is overlain by a low-permeability rock layer one hundred meters thick, extending to the ground surface. Both of the low-permeability layers extend a distance of ten kilometers. Beyond the ten kilometers there is a ten kilometer stretch of a permeable rock spanning from the surface to the bottom of the system. The total depth of the system is 1800 meters; the upper aquifer is 400 meters thick, while the lower aquifer is 1000 meters thick. Cool rainwater (at 10° C) percolates in across the ten kilometers of permeable ground surface. A warm spring initiating from a fracture underlying the low-permeable cap layer results due to the warming. Figure 53 shows a sketch of the hypothetical model.

At the start of the problem, the system is in hydrostatic equilibrium and the temperature profile is governed by the local geothermal gradient. Both silica and oxygen-18 are in equilibrium with the temperature, throughout the system. A deep heat source begins to warm the system, releasing 1.3×10^{10} watts per square meter, across a distance of five kilometers, into the system at the depth of 1800 meters. The system is allowed to heat for 100,000 years before the heat plume dies out and the system begins to cool with rainwater continuing to percolate in at the surface.

After heating for 3,200 years, the portion of the system directly above the heat source begins to warm up, but the effects do not spread far. The temperatures of the right-hand side of the system still reflect the geothermal gradient. By 32,000 years,

Figure 53. A simple hypothetical model of a typical geothermal system.

the two influences on the system, the incoming heat and the infiltration of cool water, show up clearly on the temperature profile (Figure 54). Directly above the heat plume, exists an overall thermal gradient of approximately $130^{\circ}\text{C}/\text{km}$, while the right-hand side is influenced completely by the influx of cool rainwater and the geothermal gradient.

After 100,000 years of heating, the system has reached a quasi-steady condition between the influx of heat and cool water. The only region to be heated has remained the portion directly above the heat plume. The pattern of flow through the system indicates that most of the cool fluid mass descends quickly to the bottom of the system. As it moves horizontally across the bottom of the deep aquifer, the fluid is warmed and quickly begins to rise. The warming decreases away from the heat source. Below the lower cap layer, the warmed fluid mixes with cool fluid, as both are moving to exit the system from the spring conduit. This decreases the thermal gradient, keeping the majority of the temperature rise in the system confined to the lower depths. It is also evident from the mass flux (see Figure 55), that the heating of the system is due to conduction not convection, as the flux above the heat plume is nearly zero. This helps to explain why the system warms only above the heat plume.

The quasi-steady condition indicates that although the thermodynamic changes within the system are small, the balance of energy into the system and energy out of the system is not equal. Considering that the average temperature change over the last 70,000 years of heating was an increase of about 30°C in the warmed region, and the change necessary to reach equilibrium between the inflowing and outflowing heat needs to be about another 120°C , it will probably take the system an additional 600,000 years to reach a true steady state. For the purpose of this study, it is not necessary to continue heating until the system reaches steady state.

After the system has reached a quasi-steady condition, the heat plume "dies out" and the system is cooled by the infiltration of cool rainwater. The effects of the cooling are slow initially but after 32,000 years, the effect of the cool influx of water is felt over the entire system, lowering the temperature by over 100°C in the previously

Figure 54. Temperature contours for the system evolving under the influence of a heat source for 100,000 years. Contour units are in $^{\circ}\text{C}$.

Figure 55.

The pattern of fluid flow and of the silica precipitation/dissolution for the system evolving under the influence of a heat source. The relative sizes of the arrows corresponds to the amount of fluid flow. The light shading represents the area of precipitation; the dark shading corresponds to the area of dissolution.

The pattern of fluid flow and of the silica precipitation/dissolution for the system evolving under the influence of a heat source. The relative sizes of the arrows corresponds to the amount of fluid flow. The light shading represents the area of precipitation; the dark shading corresponds to the area of dissolution.

warm region. The temperature drop is enough to lower the pressure head under the lower cap and cause the warm spring to stop flowing. After the heat source has been extinct for 100,000 years, the system is entirely cooled and the temperature profile is once again governed by the geothermal gradient.

The influence of the heat plume on the silica concentration is primarily controlled by the kinetic transport. This is due to the fact that in the regions where the fluid is moving significantly, the temperature is low and nearly constant. Thus the amount of silica to be transported by the fluid is small. The dissolution and precipitation of silica directly follows the changes in temperature. During the first 3,200 years, silica is steadily dissolved from the country rock above the heat plume, rapidly increasing the porosity. No silica was precipitated out of the fluid in the outer regions during this time, due to the slow initial affect of the infiltration cool rainwater. When significant mixing of warm and cool waters begins to take place, precipitation of silica out of the fluid occurs beneath the lower cap layer (referring back to Figure 55, the areas of precipitation are shaded lightly, and the areas of dissolution are shaded more darkly), and the porosity of the under the lower cap is decreased.

Although the program does not calculate the change in permeabilities due to the dissolution/precipitation of silica, it is likely that the permeability above the heat plume is increased due to silica dissolution and decreased under the lower cap, due to silica precipitation. This should cause the flow patterns within the system to change continuously, moving more fluid through the areas of increased permeability and less fluid through the areas of decreased permeability. The pattern of the precipitation/dissolution within the system should remain approximately the same, but the amounts would likely be greater had the effects of the permeability change been accounted for. A greater amount of fluid would be flowing nearer to the plume to be heated. More silica would be dissolved from the lower portion of the system and consequently more silica would be re-precipitated under the cap.

The pattern of silica dissolution/precipitation during the 100,000 years of cooling is in reverse of the 100,000 years of heating. As the warm region cools, silica

precipitates out of the fluid. By the time the system has completely cooled, the previously dissolved silica has been re-precipitated. As mentioned above, the model cannot calculate the changes in the permeabilities of the system. Even though most of the dissolved silica has been re-deposited, the permeability of the system will not necessarily be the same for two reasons. First, the silica will not be re-deposited exactly as it was originally positioned. Second, some silica was lost from the system through the spring outlet.

Also of interest in the theoretical evolution of a low-temperature geothermal system, is the behavior of the oxygen-18. As with the silica transport, the oxygen-18 transport is governed primarily by the kinetic reactions, throughout both the heating and cooling periods of the system. Although the kinetic rates of the oxygen-18 are not as rapid as those of the silica within the the system, the oxygen-18 contents still follows closely to the temperatures developing in the system. During the heating of the system, the oxygen-18 within the warm region slowly begins to increase due to kinetic transport (Figure 56). When the system cools, the oxygen-18 content slowly returns to the original lower values.

The most interesting result seen during the heating of the system is the very high content of oxygen-18 evolving in the heated region of the system. By the end of 3,200 years of heating, the average value of the oxygen-18 content in the warmed area is -4.0 per mil. After 100,000 years of heating, the value of the oxygen-18 has increased to -1.0 per mil (see Figure 56). In most real low-temperature geothermal systems, the oxygen-18 content within the system is much lower than either of these values, usually falling in a range of -7.0 to -11.0 per mil. But, all of the oxygen-18 data reviewed by the author prior to the present study was taken several years after the initiation of production. Either the oxygen-18 content in many systems is not in isotopic equilibrium due to a very transient flow regime or the oxygen-18 is decreasing during production due to recharge from cooler waters lower in oxygen-18. Both explanations are plausible, and a choice between the two is not necessary to try to explain the behavior of every system. However, the latter explanation does lend support to the oxygen-18 content estimated previously for the Ellidaar geothermal field prior to production (see section

Figure 56.

Oxygen-18 contours for the evolving system after 100,000 of heating. Contour units are in per mil.

3.3).

A thorough review of the results from the theoretical studies of the plausible evolution of low-temperature systems can help to answer many questions. The areal extent of a low-temperature system appears to be directly governed by the size of the heat source, covering only the portion directly above the incoming heat flux. Conduction appears to play a major role in heating even a permeable system, with convection being confined to the outer regions of the plume. This causes the cool water, as it nears the heat plume region at depth, to be warmed quickly and rises buoyantly, before it can travel far enough horizontally to mix with the waters directly above the plume. Without the mixing of cool and warm waters above the plume, the dissolution of silica becomes significant in this region.

Also, a review of the results can reveal important topics for further investigation. One interesting idea arising from the study that should be pursued, is just what could be the lasting effects of silica precipitation and dissolution on the porosity and permeability of the system. It was theorized that the pattern of precipitation and dissolution would be the same after the heating cycle, whether or not permeability changes were taken into account. But, at the end of the cooling cycle, it would seem doubtful that the permeabilities within the system would remain unchanged from the original values. Another idea to pursue could be to study how much of the importance of the conductivity seen in the above study is actual, and how much is due to the design of the grid. By studying the unanswered questions such as these, important areas for further study can be sketched.

5.0 CONCLUSION

The main objective of the present study was to develop a method to reliably estimate the cooling rate of a low-temperature geothermal field. To achieve this goal, the various methods of modeling geothermal fields including hydrological methods, geochemical methods and numerical methods were carefully reviewed. Through the review, it became clear that work on modeling geothermal systems by integrating all the available data including pressure, temperature and chemical, was lacking. The present work was based on the idea that utilizing all available data on a geothermal system would enable the most reliable determinations of field parameters as well as the most detailed understanding of the system. A clear understanding of the system, its flow patterns and areas of recharge, would enable the determination of the rate of cooling of the system. Once this has been established, it can be decided whether a geothermal project will be economical or not, subsequently decreasing the risk involved in developing low-temperature geothermal systems.

To successfully integrate chemical transport into heat and mass transport modeling, a thorough background on the behavior of the chemical components common to low-temperature systems was essential. First, the chemical components found in natural waters were reviewed. Components which could not be modeled conservatively were listed and recommended to be excluded from a modeling scheme. It was found that silica and the stable isotope oxygen-18 could not be modeled conservatively, but information existed on their kinetic reactions within natural systems. Their behavior was examined in greater detail so they could be incorporated into a modeling scheme which included kinetic reactions.

The next step in achieving the objective of this study involved a careful review of the equations governing mass, heat and chemical transport. The equations were then transferred into numerical form. The existing codes, PT, capable of modeling mass and heat transport and PTC, the version of PT modified previously to include silica transport, were examined. Additions made in the present study to incorporate multi-component chemical transport were described and the performance of the new code

tested.

Before applying the code to a field example, the sensitivity of the convective transport of components as well as the kinetic transport of silica and oxygen-18 to various field parameters (e.g. porosity, field volume, temperature, surface area per volume, average grain radius) was examined. Next, the governing equation for chemical transport was simplified and non-dimensionalized, defining several dimensionless groups. Although an analytical solution to the equation was still not possible, the dimensionless groups aided in reducing the number of parameters affecting the chemical transport. Further sensitivity studies were performed and their assistance in modeling geothermal systems was demonstrated by matching field data from the Ellidaar geothermal field, in Iceland.

The background attained through the literature review and chemical reviews and the sensitivity studies was then applied to two field examples. The first involved the modeling of the Ellidaar geothermal field using a simple two-layer mesh. The field had been modeled previously, so the results of the present work could be compared to the results of the previous study to test the applicability of the new code. The comparison was very good, and helped to indicate the strengths of integrated multi-component, heat and mass transport modeling. The second field example involved the Seltjarnarnes geothermal area in Iceland. Several points were demonstrated by modeling this field. As a first step, a simple, two-layer model was chosen. By matching the temperature and chemistry data, estimates for the field volume, porosity and the amount of recharge from the cooler, more saline top relative to the side were determined. As a second step, pressure and temperature data were matched numerically, using a much finer mesh, to estimate the permeability porosity and field volume. After confirming the results of the simpler mesh by comparison with those of the more complex model, chemical transport was added to the complex model. With the aid of chemical data the boundary between the meteoric water and seawater near the well field region was established. From the example, it was seen that chemical transport data could aid in determining field parameters, amounts and zones of recharge as well as the amount of influx into the field of waters with potentially damaging chemical constituents.

As a final application of the code, the evolution of a hypothetical geothermal system influenced by a heat source at depth and surface infiltration of cool rainwater was examined. The theoretical example provided helpful insight into low-temperature systems. The system was allowed to evolve under the influence of the heat source to an approximate steady condition. The effects of the heat migrating into the system combined with the percolating cool surface waters on the silica and oxygen-18 contents of the fluid were documented. Zones of silica precipitation and dissolution were determined and reviewed along with the possible effects this might have on the permeability and flow pattern of a system. It was seen that the incoming heat rapidly increased the amount of oxygen-18 in the fluid to a level greater than normally seen in most systems, suggesting that many geothermal systems are not in isotopic equilibrium and are much more transient than the hypothetical system modeled.

Although the main objective of the present work to develop a method of reliably predicting the cooling rate in low-temperature geothermal systems was achieved, there are some drawbacks that must be understood. A major drawback involves the kinetic reactions of silica and oxygen-18. The kinetic reactions are governed significantly by the value of the surface area per volume (A/V), or in the case of oxygen-18, the average grain radius (ω). It is very difficult to measure either of these values in the field. From the results documented on the field examples in section 4.3, ω appears to be an effective average grain radius, characterized by the size of the blocks within the system surrounded by fluid flow and not the size of the actual grains. The method of using the kinetic information gained on one component to determine the kinetic data on the other by using Eq. 50 alleviates this problem, if data on both oxygen-18 and silica are available. However, the field data available to test the theory relating the (A/V) and (ω) values was not sufficient to demonstrate that the theory was firmly established.

A second drawback also concerns kinetic reactions. In both of the field examples investigated, the role of the kinetic transport of oxygen-18 was insignificant when compared to the convective transport. This suggests that oxygen-18 could be considered a conservative species. In general, modeling more than two conservative species will be redundant. The more components that are available with quantitative information on

their kinetic behavior, the more information that can be gained on a system being studied. If oxygen-18 behaves essentially as a conservative species within low-temperature geothermal systems, it will not be as significant an aid in modeling. The conservative species are modeled on the basis of a mass balance determined by the fluid in minus the fluid out of a particular node. Thus, the rate of change for all conservative species will be the same, and no new information will be gained. However, as a side note, it is good practice to model two conservative species, as it is unknown how significantly a species will enter into ionic-exchange or other reactions. By modeling two species, effects of reactivity on either species can be averaged out.

There are exceptions to the statement that modeling more than two conservative species will give redundant results. If the field data on the chemistry of a system indicates that several species show different or opposing patterns of change with time, it is most likely due to separate zones of recharge containing fluids of differing concentrations. In this case, to achieve the most accurate simulation, all components exhibiting differing behavior should be included in the modeling scheme. An example of this is the change with time in the oxygen-18 content of Seltjarnarnes as compared to the change with time in the chloride content. The kinetic transport of oxygen-18 in the Seltjarnarnes field is insignificant relative to the convective transport, thus could be considered in this case a conservative species. Although the chloride in the system increased rapidly due to the influx of seawater into the system, the oxygen-18 content showed a slight decrease with time even though the seawater had a much higher oxygen-18 content than that of the meteoric water. This is a clear indication that there must be another source of water recharging the field, containing a lower oxygen-18 content than the water originally in the system.

The problem then encountered is how to model this new source of recharge. In order to best utilize chemical modeling, there must be information available on, not only the field area, but also on the fluids in the surrounding regions. This information is rarely available, thus the quality of the chemical modeling is lowered significantly. Where these data are available, the information gained by chemical modeling will be substantial as well as reliable.

Understanding the shortcomings of chemical modeling is a necessary first step towards solving them. Future work should include a more extensive study of the kinetic behavior of silica and oxygen-18 to determine the connection, if any, between the values for A/V and ω . As the benefits of utilizing chemical data become more evident, the methods of gathering information on the chemistry of geothermal systems should be improved and extended.

APPENDIX A: EQUATION OF STATE FOR LIQUID WATER (SOURCE: BODVARSSON, 1982)

The viscosity of liquid water is calculated based on the following expression:

$$\mu = d_1 10^{\left[\frac{d_2}{T+d_3} \right]}$$

where $d_1 = 2.414 \times 10^{-5}$, $d_2 = 247.8$, and $d_3 = 133.15$. The fluid density is calculated as a function of pressure and temperature as follows (Buscheck, 1980):

$$\rho(P,T) = A(T) + C(T) \cdot B(P)$$

where

$$\begin{aligned} A(T) = & a_1 + a_2(T - T_{\text{ref}}) + a_3(T - T_{\text{ref}})^2 \\ & + a_4(T - T_{\text{ref}})^3 + a_5(T - T_{\text{ref}})^4 \end{aligned}$$

$$\begin{aligned} B(P) = & b_1 + b_2(P - P_{\text{ref}}) + b_3(P - P_{\text{ref}})^2 \\ & + b_4(P - P_{\text{ref}})^3 \end{aligned}$$

$$\begin{aligned} C(T) = & c_1 + c_2(T - T_{\text{ref}}) + c_3(T - T_{\text{ref}})^2 \\ & + c_4(T - T_{\text{ref}})^3 + c_5(T - T_{\text{ref}})^4 \\ & + c_6(T - T_{\text{ref}})^5 + c_7(T - T_{\text{ref}})^6 \end{aligned}$$

The coefficients are:

$$0 < T < 199^{\circ}\text{C}, \quad T_{\text{ref}} = 100^{\circ}\text{C}$$

$$a_1 = .96628$$

$$a_2 = -.70650 \times 10^{-3}$$

$$a_3 = -.28521 \times 10^{-5}$$

$$a_4 = .59365 \times 10^{-8}$$

$$a_5 = .32285 \times 10^{-10}$$

$$199 < T < 350^{\circ}\text{C}, \quad T_{\text{ref}} = 260^{\circ}\text{C}$$

$$a_1 = .79829$$

$$a_2 = -.14906 \times 10^{-2}$$

$$a_3 = -.57448 \times 10^{-5}$$

$$a_4 = .40265 \times 10^{-7}$$

$$a_5 = .17661 \times 10^{-9}$$

$$0 < P < 4 \times 10^7 \text{ pa}$$

$$b_1 = -.12953 \times 10^{-2}$$

$$b_2 = .51594 \times 10^{-4}$$

$$b_3 = -.99714 \times 10^{-8}$$

$$b_4 = .10275 \times 10^{-9}$$

$$0 < T < 149^{\circ}\text{C}, \quad C(T) = 1.0$$

$$140 < T < 220^{\circ}\text{C}, \quad T_{\text{ref}} = 180^{\circ}\text{C}$$

$$c_1 = 1.2092$$

$$c_2 = .70811 \times 10^{-2}$$

$$c_3 = .71415 \times 10^{-4}$$

$$c_4 = -.79423 \times 10^{-6}$$

$$c_5 = -.53925 \times 10^{-8}$$

$$c_6 = .5148 \times 10^{-9}$$

$$c_7 = -.54612 \times 10^{-11}$$

$$220 < T < 350^{\circ}\text{C}, \quad T_{\text{ref}} = 260^{\circ}\text{C}$$

$$c_1 = .2.2437$$

$$c_2 = .23865 \times 10^{-1}$$

$$c_3 = .215671 \times 10^{-4}$$

$$c_4 = .81759 \times 10^{-7}$$

$$c_5 = .54541 \times 10^{-8}$$

$$c_6 = .36389 \times 10^{-8}$$

$$c_7 = .48355 \times 10^{-11}$$

This density function is accurate to within 1% for $0 < T < 300^{\circ}\text{C}$, and 5% for $300 < T < 350^{\circ}\text{C}$. The fluid compressibility and thermal expansivity are calculated from the density function on the basis of their definitions:

$$\beta_w = \left[\frac{1}{\rho} \frac{d\rho}{dP} \right]_T$$

$$\alpha_w = \left[\frac{1}{\rho} \frac{d\rho}{dT} \right]_P$$

APPENDIX B: SUBROUTINE INCORPORATED INTO THE CODE PTCC TO CALCULATE THE KINETIC REACTIONS OF OXYGEN-18.

```

C
C
C      Subroutine isokin calculates the kinetic transport
C      equations for oxygen-18 in fluid.
C
C
C      by amanda l. spencer; march 1986
C
C      description of parameters:
C
C      AOXF - moles oxygen in fluid
C      AOXS - moles oxygen in solid
C      D - density of fluid
C      DENS - density of rock
C      DELT - change in time per timestep
C      DDOX - change in oxygen-18 per timestep
C      FRACTEQ - equilibrium fractionation factor
C      GRAD - average grain radius
C      INKIN - variable to specify rock/water system
C      OX - oxygen-18 content of the fluid
C      OXEQ - equilibrium constant for oxygen-18
C      OXRATE - kinetic rate constant
C      OXROK - oxygen-18 content in the rock
C      POR - porosity
C      SAREA - surface area open to reaction
C      T - temperature
C      VOL - volume
C
C
C      SUBROUTINE ISOKIN(N,INKIN,T,OX,OXEQ,OXROK,DDOX,VOL,D,POR,GRAD,
C      1DELT,OXIN,DENS,KCYC,I,NUM)
C      DIMENSION T(800),OX(800),VOL(800),D(800),POR(800),
C      1DENS(800),OXROK(800),DDOX(800),OXEQ(800)
C      DIMENSION SUMDD(800)
C      REAL GRAD,FRACTEQ
C      INTEGER INKIN(800),N
C      IF (GRAD .EQ. 0.) GO TO 1500
C      TT=T(N) + 273.0
C      TSQR=T(N)*T(N)
C      ALPHA=0.0
C      IF (INKIN(N) .EQ. 1) GO TO 1101
C      IF (INKIN(N) .EQ. 2) GO TO 1201
C      IF (INKIN(N) .EQ. 3) GO TO 1301
C      IF (INKIN(N) .EQ. 4) GO TO 1401
C      IF (INKIN(N) .EQ. 5) GO TO 1501
C
C      **** BASALT - SEAWATER ****
C
C      IF (KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.0) OXROK(N)=5.6
C      OXRATE=10.0*((-2520./TT)-4.00)
C      XFRAC=28.5
C      IF (INKIN(N) .EQ. 6) GO TO 1701
C      FRACTEQ=-0.052*T(N) + 15.2
C      GO TO 2101
C
C      ***** BASALT/WATER *****
C
C      1601 FRACTEQ = -(0.01463*T(N)) + 7.85
C      GO TO 2101

```

```

C
C ***** QUARTZ SANDSTONE - WATER *****
C
1101 OXRATE=10.**((-1250./TT)-6.55)
   IF(KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.0) OXROK(N)=7.5
   XFRACT= 33.333
   FRACTEQ = -(0.050*T(N)) + 22.0
   GO TO 2101

C
C ***** GRANITE - WATER *****
C
1201 OXRATE=10.**((-1375./TT)-5.725)
   IF(KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.) OXROK(N)=2.5
   XFRACT=31.4
   FRACTEQ = -(0.075*T(N)) + 23.5
   GO TO 2101

C
C ***** GRANITE - SALT SOLUTION *****
C
1301 OXRATE=10.**((-2000./TT)-4.15)
   IF(KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.) OXROK(N)=2.5
   XFRACT=31.4
   FRACTEQ = -(0.075*T(N)) +23.5
   GO TO 2101

C
C ***** CALCITE - WATER *****
C
1401 OXRATE=10.**((-2250./TT)-3.35)
   IF(KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.) OXROK(N)=6.5
   XFRACT=30.0
   FRACTEQ = -0.038*T(N) + 18.1
   GO TO 2201

C
C ***** DOLOMITE - WATER *****
C
1501 OXRATE=10.**((-2500./TT)-2.75)
   IF(KCYC .LE. 0 .AND. OXROK(N) .EQ. 0.) OXROK(N)=6.5
   XFRACT=32.0
   FRACTEQ = -0.046*T(N) + 21.4
   GO TO 2201
2101 SAREA=(3.0*VOL(N)*(1.0-POR(N)))/(GRAD)
   GO TO 2501
2201 SAREA=(VOL(N)*(1.0-POR(N)))/(2.0*(GRAD))
2501 AOXS=XFRACT*(1.0-POR(N))*VOL(N)*DENS(I)
   AOXF=55.6556*VOL(N)*O(N)*POR(N)
   YY=(AOXF+AOXS)/(AOXF+AOXS)
   OXRKOLD=OXROK(N)
   WOVER=AOXF/AOXS
   OXROK(N)=OXROK(N) - DDOX(N)*WOVER
   OXEQ(N)=(OXROK(N)-FRACTEQ + WOVER*OX(N))/(1.+WOVER)
   OXEQ(N)=(OXROK(N)-FRACTEQ + WOVER*OXIN)/(1.+WOVER)
   DDOX(N)=YY*SAREA*OXRATE*(OXEQ(N) - OX(N))*DELT
   IF(KCYC .LE. 0 .AND. N .EQ. NUM) PRINT 2115,N,AOXS,AOXF,
1 FRACTEQ,OXEQ(N),SAREA,OXRATE
2115 FORMAT(/, ' N      AOXS      AOXF      FRACTEQ      OXEQ      SAREA
1 OXRATE      ',/,I5,2X,6(E10.4,2X))
   OX(N)=OX(N) + DDOX(N)
1500 RETURN
END

```

REFERENCES

- ADAMS M.C. - Geochemistry of the Wendel-Amedee Geothermal Systems, California; Geothermal Resources Council, TRANSACTIONS, Vol. 8, August 1979
- AIREY, P.L., G.E. CALF, P.E. HARTLEY - Use of Environmental Isotopes and Artificial Tracers to Study Recharge to Groundwater in the Burdekin Delta, Queensland; Isotope Hydrology, proceedings symposium, IAEA, 1974
- ARP, J.J. - Analysis of Decline Curves; Transactions, AIME, 228, 1945
- ARP, J.J. - Estimation of Primary Oil Reserves; Transactions, AIME, 207, 1956
- BENSON, S.M. - Well Test Data Analysis from a Naturally Fractured, Liquid-Dominated System; Geothermal Resources Council, TRANSACTIONS, Vol.6, October 1982
- BODVARSSON, G.S. - Mathematical Modeling of the Behavior of Geothermal Systems under Exploitation; PhD. Thesis, U.C. Berkeley, 1982
- BOHLMANN, E.B., R.E. MESMER, P.BERLINSKI - Kinetics of Silica Deposition from Simulated Geothermal Brines; Oak Ridge National Laboratory; Dept. of Energy, 1980
- BUSCHECK, E.B. - Equation of State for Liquid water; LBL-Internal Memo, Lawrence Berkeley Laboratory, Berkeley, California, 1980
- CAPUANO, R.M. - Water Chemistry as an Aid in Reconnaissance Exploration for a Low-Temperature Geothermal System, Artesian City Area, Idaho; Geothermal Resources Council, TRANSACTIONS, Vol. 5, October 1981
- CATHLES, L.M. - An Analysis of the Cooling of Intrusives by Ground Water Convection which Includes Boiling; Economic Geology, Vol. 72, p.804-826, 1977
- CHENG, P., K.C. YEUNG, K.H. LAU - Numerical Solutions for Steady Free Convection in Island Geothermal Reservoirs; from "Future Energy Production Systems", p.429-448, Hemisphere Publishing Corp., Washington D.C., 1976
- CHENG, P. - Heat Transfer in Geothermal Systems; from "Advances in Heat Transfer", Vol. 14, copyright 1978, Academic Press
- CLAYTON, R.N., J.R. O'NEIL, T.K. MAYEDA - Oxygen isotope exchange between quartz and water; J. Geophysical Research, Vol. 77, p.3057- 3067, 1972
- COATS, K.H. - Geothermal Reservoir Modeling; paper presented at the SPE 52nd Annual Fall Technical Conference and Exhibition, Denver, Colo., SPE-6892, 1977
- COLE, D.R., H. OHMOTO, A.D. LASAGA - Isotopic Exchange in Mineral-Fluid

- Systems. 1. Theoretical evaluation of Oxygen Isotopic Exchange Accompanying Surface Reactions and Diffusion.; *Geochimica et Cosmochimica Acta*, Vol. 47, No. 10, October 1983
- COLE, D.R., M.T. MOTTTL, H. OHMOTO - Isotopic Exchange in Mineral-Fluid Systems. 2. Oxygen and Hydrogen Isotopic Investigation of the Experimental Basalt/Seawater System.; submitted to *Geochimica et Cosmochimica Acta*, 1986
- COLE, D.R. - Time Estimates for Oxygen Isotopic During Mineral-Fluid Interaction in Hydrothermal Systems; Geothermal Resources Council, TRANSACTIONS, Vol. 7, October 1983
- COLELLA, P. - Multidimensional Upwind Methods for Hyperbolic Conservation Laws; LBL-17023, Lawrence Berkeley Laboratory, Berkeley, California, 1984
- CRAIG, H. - The Isotopic Geochemistry of Water and Carbon in Geothermal Areas; in "Nuclear Geology in Geothermal Areas: Pisa, Italy.", Consiglio Nazionale delle Laboratorio de Geologia Nuclear, p. 17-53, 1963
- DOMINGUEZ, B. A., M.J. LIPPMANN - Some Comments on the La Primavera Geothermal Field, Mexico; Proceedings Ninth Workshop Geothermal Reservoir Engineering Stanford University, Stanford, California, December 1983
- DUFF, I.S. - MA-28: A Set of Fortran Subroutines for Sparse Unsymmetric Linear Equations; AERE Harwell Report R 8730, July 1977
- EDWARDS, A.L. - TRUMP: A Computer Program for Transient and Steady State Temperature Distribution in Multidimensional Systems; Lawrence Livermore Laboratory, Livermore, California, UCRL-14754, Rev. 3, 1972
- ELDER, J.W. - Steady-Free Convection in a Porous Medium Heated from Below; *J. Fluid Mechanics*, 1967, Vol. 27, p.29-48
- FAUST, C.R., J.W. MERCER - Geothermal Reservoir Simulation: Mathematical Models for Liquid- and Vapor-dominated Hydrothermal Systems; Water Resources Research, February 1979
- FOUILLAC, C., G. MICHARD - Sodium/Lithium Ratio in Water Applied to the Geothermometry of Geothermal Waters; *Geothermics*, Vol. 10, p. 55-70, 1980
- FOURNIER, R.O. - Chemical Geothermometers and Mixing Models for Geothermal Systems.; *Geothermics*, Vol. 5, p. 41-50, 1977
- FOURNIER, R.O., R.W. POTTER- An Equation Correlating the Solubility of Quartz in Water from 25 °C to 900 °C at Pressures up to 10,000 bars; *Geochimica et Cosmochimica Acta*, Vol. 46, p. 1969-77, June 1982
- FOURNIER, R.O., R.J. ROSENBAUER, J.L. BISCHOFF - The Solubility of Quartz in

- Aqueous Sodium Chloride Solution at 350 °C and 180 to 500 bars.; *Geochimica et Cosmochimica Acta*, Vol. 46, p. 1975-1978, 1982
- FOURNIER, R.O., A.H. TRUESDELL - An Emperical Na-K-Ca Geothermometer for Natural Waters; *Geochimica et Cosmochimica Acta*, Vol. 37, p. 1255 -1275, 1973
- FRIEDMAN, I., J.R. O'NEIL - Compilation of Stable Isotope Fractionation Factors of Geochemical Interest; Geological Survey Professional Paper, 440-KK, 1977
- GARG, S.K., J.W. PRITCHETT, D.H. BROWNELL - Transport and Energy in Porous Media; Proceedings, Second U.N. Symposium on the Development and Use of Geothermal Resources, San Franscisco, 3, p. 1651, 1975
- GERTSCH, W.D., R.W. JUNCAL - Low to Moderate Temperature Direct Use Geothermal Projects in N. Eastern, California; Geothermal Resources Council, TRANSACTION, Vol. 8, Aug. 1984
- GIGENBACH, W.F., R. GONFIANTINI, B.L. JANGI, A.G. TRUESDELL - Isotopic and Chemical Composition of Parbati Valley Geothermal Discharges, North-West Himalaya, India; *Geothermics*, Vol. 12, p. 199-222, 1983
- GILLETI, B.J., T.F. ANDERSON - Studies in Diffusion-II. Oxygen in phlogopite Mica; *Earth Planet Science Letters*, Vol. 28, p. 225-233, 1975
- GILLETI, B.J., M.P. SEMET, R.A. YUND - Studies in Diffusion-III. Oxygen in Feldspars: an Ion Microprobe Determination; *Geochimica et Cosmochimica Acta*, Vol. 42, p. 45-47, 1978
- GUDMUNDSON, J.S., G. PALMASON - World Survey of Low Temperature Geothermal Energy Utilization; IAE Report, p. 148, 1981
- GUDMUNDSON, J.S., G. PALMASON - World Uses of Low Temperature (<150 °C) Geothermal Resources in 1980; Geothermal Resources Council, TRANSACTIONS, Vol. 6, October 1982
- HALFMAN, S.E., M.J. LIPPMAN, R. ZELWER, J.H. HOWARD - Identification of Fluid Flow Paths in the Cerro Prieto Geothermal Field; Geothermal Resources Council, TRANSACTIONS, Vol. 6, October 1982
- HEM, J.D. - Study and Interpretation of the Chemical Characteristics of Natural Water; Geological Survey Water Supply Paper 1473, 1970
- HETTLING, H.K. - The Chemical and Isotopic Changes in the Low-Temperture Areas of Laugarnes, Ellidaar and Reykir.; UNU Geothermal Training Programme, Iceland, Report 1984-3, 1984
- HENLEY, R.W., A.H. TRUESDELL, P.B. BARTON - "Fluid-Mineral Equilibria In Hydrothermal Systems.", reviews in *Economic Geology*, The Economic Geology

Publishing Company, copyright 1984

HILFIKER, K., C. HANLEY, D. HODGE, P. MORGAN, J. MAXWELL, C. SWANBERG - Correlation of Silica Heat Flow and Temperature Gradients, Central and Western New York; Geothermal Resources Council, TRANSACTIONS, Vol. 4, September 1980

HOWARD, K. - Principal Conclusions of the Committee on the Challenges of Modern Society Non-electrical Applications Project; Proceedings, Second U.N. Symposium on the Development and Use of Geothermal Resources, San Francisco, p 2127-2139, 1975

HULEN, J.H., D.L. NIELSON - Stratigraphic Permeability in the Baca Geothermal System, Redondo Creek Area, Valles Caldera, New Mexico;

ITOI, R., H. MAEKAWA, K. TATSUTA, M. FUKADA, K. JINNO, K. HATANAKA, T. YOKOYAMA - Experimental Study on the Silica Deposition in a Porous Medium; Geothermal Resources Council, TRANSACTIONS, Vol. 8, August 1984

ITOI, R., H. MAEKAWA, K. TATSUTA, M. FUKADA, K. JINNO, K. HATANAKA, S. NASAKI, T. YOKOYAMA - A Mathematical Model of Silica Deposition in a Porous Medium; Geothermal Resources Council, TRANSACTIONS, Vol. 9, August 1985

KANDARPA, V., O.J. VETTER - Prediction of Salt Precipitations Due To Injecting Foreign Waters into Geothermal Reservoirs; Geothermal Resources Council, TRANSACTIONS, Vol. 5, October 1981

KANG, J.M., J.AHERN - Finite Element Analysis of a Thermal Flow Motion in Geothermal Chambers; Geothermal Resources Council, TRANSACTIONS, Vol. 8, August 1984

KEITH, L.A., P.T. DELANEY, D.E. MOORE - Permeability Reduction Due to Precipitation of Quartz Under Non-isothermal Conditions; Proceedings Ninth Workshop Geothermal Reservoir Engineering, Stanford University, Stanford, California, Dec. 1983

KONIKOW, L.F. - Modeling Chloride Movement in the Alluvial Aquifer at the Rocky Mountain Arsenal, Colorado; USGS Water Supply Paper # 2049, 1977

KRISTMANNSDOTTIR, H. - Exploitation Induced Infiltration of Seawater into the Seltjarnarnes Geothermal Field, Geothermal Resources Council TRANSACTIONS, Vol. 9, August 1985

KRISTMANNSDOTTIR, H. - Geochemistry of the Seltjarnarnes Geothermal Field,

- Iceland National Energy Authority, Report OS-83106/JHD-19, 1983
- LAI, C.H., G.S. BODVARSSON, P.A. WITHERSPOON - Numerical Studies of Silica Precipitation/Dissolution; Economic Geology, 1984
- LAI, C.H. - Mathematical Models of Thermal and Chemical Transport in Geologic Media; Ph.D. Thesis, U.C. Berkeley, Berkeley, California, December 1985
- LASSETER, T.J., P.A. WITHERSPOON, M.J. LIPPMAN - Multiphase, Multidimensional Simulation of Geothermal Systems; Proceedings, Second U.N. Symposium on the Development and Use of Geothermal Resources; San Francisco, California, 3, p1715-1723, 1975
- LI, T.M.C. - Axisymmetric Numerical Simulation of Hydrothermal Systems Including Changes in Porosity and Permeability Due to Silica-Water Reactions; Ph.D. thesis, Penn. State University, 240 p., 1980
- LIPPMANN, M.J., G.S. BODVARSSON - The Heber Geothermal Field, California: Natural State and Exploitation Modeling Studies; J. Geophysical Research, Vol. 90, No. 131, p. 745-58, Jan. 1985
- MERCER JR., J.W., G.F. PINDER, I.G. DONALDSON - A Galerkin Finite Element Analysis to the Hydrothermal System at Wairakei, New Zealand; J. of Geophysical Research, Vol. 80, 17, p. 2608-2621
- MICHELS, D.E. - A Simple Formula for Saturation Temperature/Pressure of NaCl Solutions; Proceedings Ninth Workshop Geothermal Reservoir Engineering Stanford University, Stanford, California, December 1983
- MOENCH, A.F. - Steam Transport in Porous Media; Proceedings Second Workshop Geothermal Reservoir Engineering, Stanford University, Stanford, California, 1976
- MOORE, D.E., C.A. MORROW, J.D. BYERLEE, - SiO₂ Precipitation Accompanying Fluid Flow Through Granite Held in a Temperature Gradient; Proceedings, Seventh Workshop Geothermal Reservoir Engineering, Stanford University, Stanford, California, 1981
- NARASIMHAN, T.N., P.A. WITHERSPOON - An Integrated Finite-Difference Method for Analyzing Fluid Flow in Porous Media; Water Resources Research, 12, 1, p. 57-64, 1976
- NORTHROP, D.A., R.N. CLAYTON - Oxygen Isotope Fractionation in Systems Containing Dolomite; J. Geology, Vol. 74, p.174-196, 1966
- NORTON, D., H.P. TAYLOR - Quantitative Simulation of the Hydrothermal Systems of Crystallizing Magmas on the Basis of Transport Theory and Oxygen Isotope

- Data: An Analysis of the Skaergaard Intrusion; J. Petrology, Vol. 20, part 3, p. 421-486, 1979
- NORTON, D., J. KNIGHT - Transport Phenomena in Hydrothermal Systems: Cooling Plutons; Am. J. of Science, Vol 277, p.937-981, October 1977
- O'NEIL, J.R., Y.K. KHARAKA - Hydrogen and Oxygen Isotope Exchange Reactions between Clay Minerals and Water; Geochimica et Cosmochimica Acta, Vol. 40, p.241-246, 1976
- O'NEIL, J.R., H.P. TAYLOR JR. - Oxygen Isotope Equilibrium between Muscovite and Water; J. Geophysical Research, Vol. 74, p. 6012-6022, 1969
- O'NEIL, J.R., R.N. CLAYTON, T.K. MAYEDA - Oxygen Isotope Fractionation in Divalent Metal Carbonates; J. Chem. Phys., Vol. 51, p. 5547-5558, 1969
- O'NEIL, J.R., H.P. TAYLOR JR. - The Oxygen Isotope and Cation Exchange Chemistry of Feldspar; Amer. Mineral., Vol. 52, p.1414-1437, 1967
- O'NEIL, J.R. - Oxygen Isotope Fractionation Studies in Mineral Systems; PhD. Thesis, University of Chicago, 1963; (unpublished)
- PAYNE, B.R., Y.YURTSEVER - Environmental Isotopes as a Hydrogeological Tool in Nicaragua; Isotope Hydrology, proceedings symposium at Vienna, IAEA, 1974
- PARMENTIER, E.M. - Numerical Experiments on O-18 Depletion in Igneous Intrusion Cooling by Groundwater Convections; J. Geophysical Research, Vol. 86, No. 88, p. 7131-7144, August 1981
- PANICHI, C., R. CELATI, P. NOTO, P. SQUARCI, L. TAVVI, E. TONGIORGI - Oxygen and Hydrogen Isotope Studies of the Larderello (Italy) Geothermal System; Isotope Hydrology, proceedings symposium at Vienna, IAEA, 1973
- PRUESS, K., J.M. ZERZAN, R.C. SCHROADER - Description of the Three-Dimensional Simulator SHAFT78 for Use in Geothermal Reservoir Studies; paper presented at the SPE Fifth Symposium on Reservoir Simulation, Denver, Colorado; SPE 7699, 1979
- RANA, R., R.N. HORNE, P.CHENG - Natural Convection in a Multilayered Geothermal Reservoir; J. of Heat Transfer, Vol. 101, August 1979
- RIMSTIDT, J.D., H.L.BARNES - The Kinetics of Silica-Water Reactions; Geochimica et Cosmochimica Acta, Vol. 44, p. 1683-99 1979
- ROBINSON B.A., - Quartz Dissolution and Silica Deposition in Hot Dry Rock Geothermal Systems, LA-9404-T, Los Alamos Laboratory, July 1982
- SOREY, M.L. - Numerical Modeling of Liquid Geothermal Systems; Ph.D. thesis, U.C. Berkeley, Berkeley, California, 1975

- TAYLOR JR., H.P. - Oxygen and Hydrogen Isotope Relationships in Hydrothermal Mineral Deposits; in "Geochemistry of Hydrothermal Ore Deposits", Second Edition, p. 356-377, 1979
- THOMPSON, J.M., A.L. GRUNDER, W. HILDRETH - Selected Chemical Analysis and Geothermometry of Hot Spring Waters from the Calabozos Caldera, Central Chile; Geothermal Resources Council, TRANSACTIONS, Vol. 7, October 1983
- TILLOTSON, P.M., D.R. NIELSEN- Scale Factors in Soil Science; Soil Science Society of America Journal, Vol. 48, no. 5, Sept.-Oct. 1984
- TOMASSON, J., G.K. HALLDORSSON - The Cooling of the Selfoss Geothermal Area, South Iceland; Geothermal Resources Council, TRANSACTIONS, Vol. 5, October 1981
- TOMASSON, J. - The Selfoss Geothermal Area; Icelandic NEA Report, 1966
- TONANI, F.B., M.A. TEILMAN - Geochemistry at Momotombo, Nicaragua: One Aspect in a Geothermal Field Case History; Geothermal Resources Council, TRANSACTIONS, Vol. 4, September 1980
- TORONYI, R.M., FAROUQ ALI - Two-phase, Two-Dimensional Simulation of a Geothermal Reservoir and the Wellbore System; paper presented at the SPE \$ 50 sup th \$ Annual Fall Meeting, Dallas, Texas, SPE-5521, September 1975
- TRUEDELL, A.H., F D'AMORE, D.NIEVA - The Effects of Localized Aquifer Boiling on Fluid Production at Cerro Prieto; Geothermal Resources Council, TRANSACTIONS, Vol. 8, August 1984
- TULINIUS, H., G.S. BODVARRSON, A.L. SPENCER, H. KRISTMANNSDOTTIR, T. THORSTEINSSON - Reservoir Studies of the Seltjarnarnes, Iceland Geothermal Field.; Proceedings Twelfth Workshop Geothermal Reservoir Engineering, Stanford University, Stanford, California, January 1987
- VAN LEER, B. - Towards the Ultimate Conservative Difference Scheme IV: A New Approach to Numerical Convection; J. Comp. Physics, Vol. 23, p. 276-99, 1977
- YUND, R.A., T.F. ANDERSON - The Effect of Fluid Pressure on Oxygen Isotope Exchange between Feldspar and Water; Geochimica et Cosmochimica Acta, Vol. 42, p. 235-239, 1978
- YUND, R.A., T.F. ANDERSON - Oxygen Isotope Exchange between Potassium Feldspar and KCl Solutions; in "Geochemical Transport and Kinetics", Carnegie Institute, Washington Publishing (eds A.W. HOFMANN et al.), Vol. 634, p. 99-105, 1974

**ZAIS, E.J., G. BODVARSSON - Production Decline Analysis; Geothermal Resources
Council, TRANSACTIONS, Vol. 4, September 1980**