DOE/ET/27163-8
Distribution Category UC-66a

BACA GEOTHERMAL DEMONSTRATION PROJECT

EQUATION-OF-STATE FOR WATER-CARBON DIOXIDE MIXTURES:
IMPLICATIONS FOR BACA RESERVOIR

TOPICAL REPORT

Prepared By
J. W. Pritchett
M. H. Rice
T. D. Riney

Systems, Science and Software
P. O. Box 1620
La Jolla, California 92038

Date Published - February 1981

Prepared Under Subcontract to
WESTEC Services, Inc.

Prepared for
UNION GEOTHERMAL COMPANY OF NEW MEXICO
AND

PUBLIC SERVICE COMPANY OF NEW MEXICO
UNDER CONTRACT NO. GEO-CLS-25

Work Sponsored By
THE U. S. DEPARTMENT OF ENERGY
DIVISION OF GEOTHERMAL ENERGY
UNDER COOPERATIVE AGREEMENT NO. DE-FC03-78ET27163

DISCLAIMER

This book 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.

MASTER

DISCLAIMER

"This report was prepared as an account of work performed for Union Geothermal Company of New Mexico, Public Service Company of New Mexico, and the U.S. Department of Energy, an agency of the United States Government. Neither Union Geothermal Company of New Mexico, nor Public Service Company of New Mexico, nor the United States Government nor any agency thereof, nor any of their employees or subcontractors, 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 Union Geothermal Company of New Mexico, or Public Service Company of New Mexico, or the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of Union Geothermal Company of New Mexico, or Public Service Company of New Mexico, or the United States Government or any agency thereof."

Printed in the United States of America

Available from:

WESTEC Services, Inc.
505 Marquette, N.W., Suite 1000
Albuquerque, NM 87102

ABSTRACT

An equation-of-state package for water-carbon dioxide mixtures has been constructed from available thermodynamic data that covers the range of interest to the Baca reservoir system. The package has been used to examine the thermodynamic state of the Baca reservoir fluid for conditions of temperature, pressure and CO₂ content believed to bracket conditions existing at the production depth of the wells in the Redondo Creek area. It is shown that the reservoir fluid may be either all-liquid or two-phase at various well locations and depths, depending on the CO₂ content. It is also shown that the CO₂ content at reservoir conditions cannot be reliably inferred from pressure/temperature measurements made on flowing wells. The equation-of-state package has been incorporated into a general purpose geothermal reservoir simulator and a series of calculations made which show that the CO₂ content of the produced fluid may be less than or greater than that of the reservoir fluid. The characteristics of the produced fluid are sensitive to the CO₂ content in the reservoir.

TABLE OF CONTENTS

	<u>Page</u>
<u>SECTION 1</u> INTRODUCTION	
1.1 Introduction	1
1.2 Scope of the Report	2
1.3 Summary and Conclusions	6
1.4 Recommendations for Future Study	7
<u>SECTION 2</u> EQUATION-OF-STATE PACKAGE	
2.1 Introduction	9
2.2 Summary	9
2.3 Calculational Procedure	11
2.4 Partition of Carbon Dioxide	14
2.5 Specific Volume and Energy of Mixture Components	15
2.6 Viscosity of Mixture Components	23
2.7 Thermal Conductivity of Mixture Components	25
2.8 Energy of Solution	28
<u>SECTION 3</u> EFFECTS OF CO₂ ON BACA RESERVOIR STATES	
3.1 Introduction	29
3.2 Summary	29
3.3 Effects of CO ₂ on Thermodynamic States	30
3.4 Effects of CO ₂ on Baca Reservoir Conditions	34
3.5 Need for Chemical Measurements of Baca Discharge Fluids	38
<u>SECTION 4</u> EFFECTS OF CO₂ ON WELL FLOWING TESTS	
4.1 Introduction	45
4.2 Summary	45
4.3 Simulated Production from Gassy Reservoirs	46
4.4 Inapplicability of Conventional Well-Test Analysis	48
4.5 Character of Discharge Fluids	50
REFERENCES	53

LIST OF FIGURES

	<u>Page</u>
Figure 2.1 Effect of Carbon-Dioxide Mass Fraction on Behavior of H ₂ O/CO ₂ Mixtures.	10
Figure 3.1 Saturation Curve for Pure Water, $P_{sat}(T)$	31
Figure 3.2 Phase Diagram for Water with CO ₂ Mass Fraction (α) Equal to 0.01. Dashed Line is $P_{sat}(T)$ for Pure Water.	33
Figure 3.3 Dependence of $\delta P = [P_{max}(T, \alpha) - P_{sat}(T)]/\alpha$ on Temperature and CO ₂ Mass Fraction (α).	35
Figure 3.4 Critical Temperature for Two-Phase Behavior in Baca Field as a Function of Elevation Above Sea Level for Various Assumed Values of the CO ₂ Mass Fraction in the Field (α). Dashed Lines Represent Measured Temperatures.	36
Figure 3.5 Expansion at Constant Enthalpy from Initial Pressure (120 Bars) to Final Pressure (5 Bars) for Initial Temperature = 290°C, for α (CO ₂ Mass/Total Mass) = 0 and 0.008: $\alpha=0$ Case Boils at $P=74.3$ Bars; $\alpha=0.008$ Case Boils at $P=87.6$ Bars.	40
Figure 3.6 Composition of Liquid and Gas Phases for Isenthalpic Expansion from $P=120$ Bars, $T=300^\circ\text{C}$, for Overall CO ₂ Mass Fraction (α) Equal to 0.008.	42
Figure 3.7 Temperature Difference Between Pure H ₂ O Case and Cases with Finite CO ₂ Mass Fractions During Isenthalpic Expansion from $P=120$ Bars and $T=290^\circ\text{C}$.	43
Figure 4.1 Sandface Pressure Histories from CHARGR Drawdown Test Simulations.	49

SECTION 1: INTRODUCTION

1.1 Introduction

The Public Services Company of New Mexico and the Union Geothermal Company of New Mexico, a subsidiary of Union Oil Company of California, plan to have a 50 MWe geothermal power plant installed in 1982 in the Redondo Creek area on Baca Location No. 1 within the Valles Caldera. The caldera is located in the Jemez Mountains in North Central New Mexico. This development was selected by the Department of Energy (DOE) as the first Geothermal Demonstration Power Plant (GDPP) Project. Under this arrangement DOE will contribute to the initial funding of the project in return for all technical, economic, and institutional data resulting from it. PNM and Union, acting together as the Participant, will make the data available for interested parties through a Data Gathering, Evaluation and Dissemination subcontractor. WESTEC Services, Inc. is the subcontractor selected by the Participant for this phase of the GDPP Project. Systems, Science and Software (S³) is the member of the WESTEC team responsible for the geological, geophysical and reservoir engineering aspects of the subcontract.

S³ is specifically tasked to synthesize the evolving geological and geophysical data base, fluid production and well test information, reservoir performance data, and to develop forecasts for the future performance of the Baca reservoir system. S³ will employ its geothermal reservoir simulator as a framework within which the evolving data sets will be synthesized to develop a quantitative model of the system. For this purpose it is important to identify the thermodynamic state of the Baca system prior to its development as part of the construction of the reservoir performance model.

The geothermal wells in the Redondo Creek area produce from fractures in the Bandalier Tuff, a thick deposit of welded volcanic ash-flow deposits of rhyolite ash and pumice (Hartz [1976]). The

reservoir fluid is a gassy, high temperature, low salinity water. Fluid temperatures over the productive intervals of the wells are 260-315°C. Geological and geochemical evidence furthermore indicates that the reservoir system extends below the Bandalier Tuff to great depth in an older series of volcanic and sedimentary rocks and that temperatures in excess of 315°C are found there.

Samples of produced fluids from five of the early wells were gathered by the Participant [1978] during various production tests. Chemical analyses were performed on the produced water, steam condensate, and noncondensable gases from each of these wells. Table 1.1 lists the average values for the chemical analyses performed on the produced water and steam condensate. The water salinity is approximately 6000-7000 parts-per-million in the production interval of the reservoir. Table 1.2 lists the average values for the chemical analyses performed on the noncondensable gases found in the steam. The noncondensable gases consist primarily of carbon dioxide (about 99+ percent) with small amounts of hydrogen sulphide, nitrogen, hydrogen, methane and ethane. The average noncondensable gas content of the flashed stream is approximately 3 percent by weight. Since CO₂ is preferentially separated into the gas state relative to the liquid state when the fluid is flashed, the noncondensable mass fraction in the reservoir fluid is significantly lower. Table 1.3 presents steam fraction and noncondensable gas content data for the fluid produced from four individual wells in the Redondo Creek area. Since the noncondensable gas is nearly all in the steam, the implied mass fraction for the reservoir fluid lies in the range 0.3 - 1.5 percent. The value of 0.8 percent suggested by Grant [1979] lies within this range.

1.2 Scope of the Report

From the chemical analyses presented in Tables 1.1, 1.2 and 1.3 it appears that the thermodynamic behavior of the Baca reservoir fluid may be adequately represented by a mixture of CO₂ and pure

Table 1.1
 AVERAGE PRODUCED FLUID CHEMISTRY
 (From Participant Proposal to DOE [1978])

	Brine Uncorrected for Flash		Condensate	
	Avg.	(No. of Samples)	Avg.	(No. of Samples)
pH	7.2	(26)	4.5	(20)
Suspended Solids, mg/l	319	(13)	4.9	(16)
Total Dissolved Solids, mg/l	6093	(24)	29	(21)
SiO ₂ , mg/l	599	(40)	29	(21)
CO ₃ ⁼	19	(27)	0	(20)
HCO ₃ ⁻	127	(26)	6.6	(19)
S ⁻	2	(15)	8.6	(1)
SO ₄ ⁼	64	(23)	1.8	(17)
Cl ⁻	3061	(43)	17	(25)
Na	1749	(43)	6	(23)
K	370	(43)	1.4	(23)
Ca	15	(42)	0.4	(19)
Mg	0.3	(21)	0.2	(21)
Ba	0.05	(6)	0.04	(7)
B	23	(26)	0.8	(21)
F	6	(21)	<0.2	(8)

Table 1.2
AVERAGE NONCONDENSIBLE GAS CHEMISTRY
(From Participant Proposal to DOE [1978])

Noncondensible Gases in Steam Phase:
2.51 percent by weight (29 samples)
1.04 percent by volume

	Avg. ppm by wt.	Avg. ppm by vol.	Samples
CO ₂	28,254	11,973	(28)
H ₂ S	204	125	(31)
N ₂	42	28	(26)
H ₂	1.6	14	(31)
CH ₄	1.4	1.6	(21)

Table 1.3
PROPERTIES OF PRODUCED FLUIDS FROM INDIVIDUAL WELLS (Hartz [1976])

Well	Avg. TDS In Brine	Avg. TDS In Condensate	Silica (ppm) In Brine	Noncondensible Gas % by Wt.	H ₂ S Concentration (ppm)		Average	
					Noncondensible	Total Steam	Flash %,	Flowrate lbs/hr Total
Baca 4	5100	28	302 (167-701)	3.16	165 (150-180)	165 (117-213)	26.8	171,000
Baca 6	6018 (5800-6230)	23 (3-65)	453 (160-600)	1.33 (1.27-1.38)	61 (60-61)	99 (69-257)	27.8	163,700
Baca 11	6895 (6056-7593)	59 (7-105)	740 (640-835)	3.76 (2.30-5.94)	365 (222-564)	477 (290-867)	39.7	227,100
Baca 13	6477 (5500-8684)	13 (7-25)	786 (556-963)	2.93 (1.93-3.94)	81 (57-96)	149 (86.3-205)	28.4	284,600

- NOTE:**
1. Some samples from Baca 4 were diluted prior to analysis. The results from these analyses are not included in the above.
 2. Left out values obtained from low rate of two-rate test on Baca 13.

water. Section 2 describes an equation-of-state package for water-carbon dioxide mixtures that has been constructed from available thermodynamic data. The package also includes thermal conductivity and viscosity data for the fluid mixtures. Section 3 presents results obtained by applying the equation-of-state package to examine the thermodynamic state of the Baca reservoir fluid for conditions of temperature, pressure and CO₂ content believed to bracket conditions existing in the Redondo Creek area. Calculations are also presented which examine the possibility of inferring the CO₂ content of the fluid under reservoir conditions from pressure/temperature measurements made on flowing wells. The equation-of-state package has been incorporated into S³'s newest general purpose geothermal reservoir simulator CHARGR (Pritchett [1980]). Section 4 presents results obtained by applying the CHARGR simulator, with the equation-of-state package incorporated as a subroutine, to study the effect that CO₂ content will have on well flow tests. Five well test simulations were performed in which the initial CO₂ mass fraction of the reservoir fluid was varied as follows: 0.4, 0.6, 0.8, 1.0 and 1.2.

1.3 Summary and Conclusions

An equation-of-state package with a pressure and temperature range ($1 \text{ bar} \leq p \leq 600 \text{ bars}$; $50^\circ\text{C} \leq T \leq 350^\circ\text{C}$) that adequately covers the Baca geothermal reservoir fluid states of interest has been developed. Calculations are presented which show that the reservoir fluid in the Redondo Creek area may be either all-liquid or two-phase depending on the CO₂ content. Calculations are also presented which show that the CO₂ content under the reservoir conditions cannot be reliably inferred from pressure/temperature measurements made on flowing wells. Finally, the equation-of-state package was incorporated into a general purpose geothermal reservoir simulator (CHARGR) and a series of calculations made which show that the CO₂ content can have a profound influence on well flow tests. It is found that the CO₂

content of the produced fluid may be less than or greater than that of the reservoir fluid. The flowing enthalpy is also strongly dependent on the CO_2 content. It is also shown that the classical interpretation of the drawdown pressure-time data will infer much smaller formation permeability than exists in the reservoir and that the discrepancy increases with CO_2 content.

1.4 Recommendations for Future Study

The CHARGR simulator with the new equation-of-state package incorporated provides an essential tool for analysis of the Baca reservoir system. The parametric calculations presented in this report demonstrate that more accurate determination of the CO_2 content of the reservoir fluid in the Redondo Creek area is needed for proper characterization of the reservoir system. The simulator will be employed by S^3 to analyze the pressure transient data from the Baca wells which have been provided by the Participant. This capability for treating gassy two-phase reservoirs will also eventually be used in simulation studies of the performance of the Baca reservoir system under alternate production/injection scenarios.

SECTION 2: EQUATION-OF-STATE PACKAGE

2.1 Introduction

An equation-of-state package for water-carbon dioxide mixtures has been constructed for use in the recently developed CHARGR geothermal reservoir simulator. The package is similar to one developed previously for water-methane mixtures (Garg, et al. [1977]), with the exception that the gaseous phase may contain water vapor as well as carbon dioxide. The useful temperature range extends to 350°C and the pressure range to ~ 600 bars.

2.2 Summary

The calling arguments, or independent variables, are the pressure (dyne/cm²), the specific internal energy of the mixture (erg/g), and the mass fraction of CO₂. Values for the following quantities and their derivatives with respect to the calling arguments are calculated: densities of the liquid and vapor phases, internal energies of the liquid and vapor phases, mass-fraction compositions of the liquid and vapor phases, volume fractions of the liquid and vapor phases, viscosities of the liquid and vapor phases, and temperature. In addition, numerical values for the thermal conductivities of the liquid and vapor phases are returned.

Within the package, quantities are calculated from analytic and/or tabular fits to experimental data with pressure and temperature as the independent variables. A Newton-Raphson iteration procedure is used for the conversion to pressure and energy as the independent variables.

An example of the output of the package is given in Figure 2.1, which shows the calculated pressure-volume relationships for 200°C isotherms corresponding to four different carbon-dioxide mass fractions. It is evident that the presence of CO₂ has a significant effect on the flash pressure.

Figure 2.1. Effect of Carbon-Dioxide Mass Fraction on Behavior of H₂O/CO₂ Mixtures.

2.3 Calculational Procedure

Depending upon the input values for the temperature, pressure, and mass fraction of CO_2 , the equation-of-state package output state may be (a) an all liquid solution of CO_2 in water, (b) a mixture of liquid solution and vapor, or (c) an all vapor solution of CO_2 in steam.

2.3.1 All-Liquid

If the input pressure is greater than the saturation pressure of pure water at the input temperature, and if the liquid solubility of CO_2 is greater than the input mass fraction, then the state of the fluid mixture is all liquid.

For the all-liquid state, the specific volume of the solution is taken to be the same as that of pure water,

$$V(P, T, \alpha) = V_w(P, T) \quad (2.1)$$

where α is the overall mass fraction of CO_2 and $V_w(P, T)$ is the specific volume of water as a function of pressure and temperature (Section 2.5). The specific internal energy of the solution is calculated from

$$E(P, T, \alpha) = (1 - \alpha) E_w(P, T) + \alpha(E_c(P, T) + E_{\text{sol}}(P, T)) \quad (2.2)$$

where $E_w(P, T)$ and $E_c(P, T)$ are the specific internal energies of water and gaseous CO_2 respectively as a function of temperature and pressure (Section 2.5), and $E_{\text{sol}}(P, T)$ is the energy of solution (Section 2.8). This completes the description of the all-liquid state except for the straightforward evaluation of the output derivatives.

2.3.2 Liquid-Vapor Mixture

If the input pressure is greater than the saturation pressure of pure water, but the input mass fraction of CO_2 is greater than the liquid solubility, then the state is a liquid-vapor mixture.

The specific volume and energy of the liquid component are calculated from

$$V_l(P, T, \alpha_{cl}) = V_w(P, T) , \quad (2.3)$$

$$E_l(P, T, \alpha_{cl}) = (1 - \alpha_{cl}) E_w(P, T) + \alpha_{cl}(E_c(P, T) + E_{sol}(P, T)) \quad (2.4)$$

where α_{cl} is the mass fraction solubility of CO_2 as a function of temperature and pressure,

$$\alpha_{cl} = (\text{mass } \text{CO}_2 \text{ in liquid})/(\text{mass of liquid}). \quad (2.5)$$

The functional dependence of α_{cl} is discussed in Section 2.4.1.

The density of the vapor component is computed from

$$\rho_v = 1/V_s(P_s, T) + 1/V_c(P_c, T), \quad (2.6)$$

where V_s and V_c are the specific volumes of steam and CO_2 respectively, $P_s = P_s(T)$ is the saturation pressure of pure steam, and P_c is the partial pressure of CO_2 .

$$P_c \equiv P - P_s(T) . \quad (2.7)$$

The internal energy of the vapor is determined from

$$E_v(P, T, \alpha_{cv}) = (1 - \alpha_{cv}) E_s(P_s, T) + \alpha_{cv} E_c(P_c, T) , \quad (2.8)$$

where α_{cv} is the mass fraction of CO_2 in the vapor (Section 2.4.2),

$$\alpha_{cv} \equiv (\text{mass } \text{CO}_2 \text{ in vapor}) / (\text{mass of vapor}) . \quad (2.9)$$

The overall specific volume and energy of the liquid-vapor mixture are calculated from

$$V(P, T, \alpha) = \alpha_l V_l + (1 - \alpha_l) V_v , \quad (2.10)$$

$$E(P, T, \alpha) = \alpha_l E_l + (1 - \alpha_l) E_v , \quad (2.11)$$

where α_l is the mass fraction of liquid,

$$\alpha_l = \frac{\alpha_{cv} - \alpha_c}{\alpha_{cv} - \alpha_c} . \quad (2.12)$$

2.3.3 All-Vapor

The remaining possible state is all-vapor. The density of the vapor is determined from

$$\rho(P, T, \alpha) = 1/V_s(P_s, T) + 1/V_c(P_c, T) , \quad (2.13)$$

where $P_c(P, T, \alpha)$ is the partial pressure of the CO_2 (Section 2.4.2), and

$$P_s = P - P_c . \quad (2.14)$$

The specific internal energy is given by

$$E(P, T, \alpha) = (1 - \alpha) E_s(P_s, T) + \alpha E_c(P_c, T) . \quad (2.15)$$

The viscosity and thermal conductivity of water-carbon dioxide solutions are taken to be the same as those for pure water. For the vapor component, a mass weighted average of the values for steam and carbon dioxide is used,

$$\mu_V = \alpha_{CV} \mu_C + (1 - \alpha_{CV}) \mu_S , \quad (2.16)$$

$$K_V = \alpha_{CV} K_C + (1 - \alpha_{CV}) K_S . \quad (2.17)$$

A discussion of the analytic and/or tabular fits used in the package and the sources of data follows.

2.4 Partition of Carbon Dioxide

2.4.1 Solubility in Water

The following fit to the solubility of carbon dioxide in water as a function of pressure and temperature is based on the data of Takenouchi and Kennedy [1964],

$$\alpha_{cl} = \frac{P_C}{A(T) + B(T)P_C} , \quad (2.18)$$

where α_{cl} is the mass fraction of CO_2 and P_C is the partial pressure of CO_2 in the coexisting vapor phase,

$$P_C(P, T) \equiv P - P_S(T) , \quad (2.19)$$

where $P_S(T)$ is the saturation pressure of pure water.

The functions $A(T)$ and $B(T)$ are calculated from the following fits,

$$A(T) = A_0 + A_1 T_C + A_2 T_C^2 , \quad (2.20)$$

$$B(T) = B_0 + B_1 T_C + B_2 T_C^2 , \quad (2.21)$$

where T_C is the temperature in $^{\circ}C$, and

$$\begin{aligned} A_0 &= 1.03549 \times 10^3 \\ A_1 &= 1.60369 \times 10^1 \\ A_2 &= -4.83594 \times 10^{-2} \end{aligned}$$

$$\begin{aligned} B_0 &= 2.04465 \times 10^1 \\ B_1 &= -1.07449 \times 10^{-1} \\ B_2 &= 1.44701 \times 10^{-4} \end{aligned}$$

2.4.2 Vapor Mass Fraction

For states of geothermal interest, the expression

$$\alpha_{cv} = \frac{P_c}{P} \quad (2.22)$$

for the mass fraction of CO_2 in vapor which is in equilibrium with liquid fits the experimental data of Takemouchi and Kennedy [1964] quite well. The above relation, where P_c is the partial pressure of CO_2

$$P_c(P, T) = P - P_s(T) \quad , \quad (2.23)$$

$P_s(T)$ being the saturation pressure of pure water, has also been used by Sutton [1976].

For states which consist of all vapor, the above relation is used to obtain P_c as a function of P and α ,

$$P_c = \alpha P \quad , \quad (2.24)$$

where α is the overall mass fraction of CO_2 .

2.5 Specific Volume and Energy of Mixture Components

2.5.1 Water

Fits to the specific volume and energy of liquid water are based on the data in the ASME Steam Tables [1977].

For temperatures between 0°C and 250°C the specific volume is calculated from

$$V_w = V_{50}(P) + B(P)(T_c - 50) + C(P)(T_c - 50)^2, \quad (2.25)$$

where V_w is in cm^3/g and T_c is the temperature in °C. For temperatures between 250°C and 300°C, an additional term

$$D(P)(T_c - 250)^2 \quad (2.26)$$

is added to the above expression; and for temperatures between 300°C and 350°C; a second additional term

$$E(P)(T_c - 300)^2 \quad (2.27)$$

is added. The term $V_{50}(P)$ is the specific volume as a function of pressure at 50°C and is computed from the fit

$$V_{50}(P) = 1.01208 - 4.4282 \times 10^{-5} (P - 1) + 5.5115 \times 10^{-9} (P - 1)^2 \quad (2.28)$$

for $1 \text{ bar} < P < 1000 \text{ bar}$. The remaining pressure-dependent coefficients are given by

$$B(P) = 4.339 \times 10^{-4}$$

$$C(P) = C_0(P) = 4.0564 \times 10^{-3} / (P + 1010.35), \quad (2.29)$$

$$P \leq 100 \text{ bar}$$

$$C(P) = C_0(P) + 1.224 \times 10^{-13} (20.25 \times 10^4 - (P - 550)^2), \quad (2.30)$$

$$100 \text{ bar} < P < 1000 \text{ bar}$$

$$D(P) = 4.27 \times 10^{-3} / (P + 100), \quad (2.31)$$

$$E(P) = -8.8 \times 10^{-6} + 4.69532 \times 10^{-3} / (P^* - 90.0573) , \quad (2.32)$$

where

$$P^* = P, \quad P > 165 \text{ bar}$$

$$P^* = 165, \quad P < 165 \text{ bar}$$

The specific internal energy in joule/g is calculated from the fit

$$E_w = E_0 + A(P)T_c + B(P)T_c^2 + C(P)T_c^3 \quad (2.33)$$

where T_c is the temperature in °C, $E_0 = -107.31$ joule/g, and the coefficients $A(P)$, $B(P)$, $C(P)$ are determined from the cubic fits,

$$A(P) = A_0 + A_1P + A_2P^2 + A_3P^3 , \quad (2.34)$$

where P is the pressure in bars, and

$A_0 = 4.34796$	$B_0 = -2.44743 \times 10^{-3}$
$A_1 = -8.44131 \times 10^{-4}$	$B_1 = 7.31469 \times 10^{-6}$
$A_2 = 7.19136 \times 10^{-7}$	$B_2 = -8.30859 \times 10^{-9}$
$A_3 = -2.84443 \times 10^{-10}$	$B_3 = 3.45199 \times 10^{-12}$
$C_0 = 9.97386 \times 10^{-6}$	
$C_1 = -2.48961 \times 10^{-8}$	
$C_2 = 2.66846 \times 10^{-11}$	
$C_3 = -1.08695 \times 10^{-14}$	

2.5.2 Steam

The specific volume of steam as a function of pressure and temperature is calculated from

$$V = Z(P, T) RT/P , \quad (2.35)$$

where $Z(P, T)$ is the compressibility factor and R is the gas constant,

$$R = 4.6151 \times 10^6 \text{ erg/g-}^\circ\text{K} .$$

The following fit to the compressibility factor is based on data as given in the ASME Steam Tables [1977]:

$$Z(P, T) = 1 + A(T)P + B(T)P^2 + C(T)P^3 , \quad (2.36)$$

where P is the pressure in bars. The temperature dependent coefficients $A(T)$, $B(T)$ and $C(T)$ are determined from cubic fits,

$$A(T) = A_0 + A_1T_c + A_2T_c^2 + A_3T_c^3 , \quad (2.37)$$

with similar expressions for $B(T)$ and $C(T)$, where T_c is the temperature in $^\circ\text{C}$. The numerical values of the coefficients are

$$\begin{aligned} A_0 &= -2.37918 \times 10^{-2} & B_0 &= -7.25220 \times 10^{-4} \\ A_1 &= 1.55521 \times 10^{-4} & B_1 &= 6.46307 \times 10^{-6} \\ A_2 &= -3.67839 \times 10^{-7} & B_2 &= -1.96479 \times 10^{-8} \\ A_3 &= 2.88121 \times 10^{-10} & B_3 &= 2.04230 \times 10^{-11} \\ C_0 &= -8.09048 \times 10^{-6} \\ C_1 &= 7.55338 \times 10^{-8} \\ C_2 &= -2.38834 \times 10^{-10} \\ C_3 &= 2.52922 \times 10^{-13} \end{aligned}$$

The specific internal energy (joule/g) is calculated from a fit of the form,

$$E(P, T) = E_{00}(T_p) + F(P)(T - T_p) + G(P)(T - T_p)^2 , \quad (2.38)$$

where $E_{00}(T_p)$ is the specific internal energy at the phase line and T_p is the phase-line temperature as a function of P .

The pressure dependent coefficient $F(P)$ is calculated from

$$F(P) = F_0 + F_1P + F_2P^2 + F_3P^3, \quad (2.39)$$

the appropriate values of the coefficients for P in bars being

$$\begin{aligned} F_0 &= 1.48927 \\ F_1 &= 3.74852 \times 10^{-2} \\ F_2 &= -3.08764 \times 10^{-4} \\ F_3 &= 2.19976 \times 10^{-6} \end{aligned}$$

The coefficient $G(P)$ is determined from

$$G(P) = G_1(P - 1) + G_2(P - 1)^2 + G_3(P - 1)^3 + G_4(P - 1)^4, \quad (2.40)$$

where P is the pressure in bars, and

$$\begin{aligned} G_1 &= -5.40894 \times 10^{-5} \\ G_2 &= -9.71673 \times 10^{-7} \\ G_3 &= 1.34636 \times 10^{-8} \\ G_4 &= -1.20074 \times 10^{-10} \end{aligned}$$

The internal energy on the phase line in joule/gram is fitted by

$$E_{00}(T_p) = E_0 + E_1T_p + E_2T_p^2 + E_3T_p^3 + E_4T_p^4. \quad (2.41)$$

The coefficients for T_p in $^{\circ}\text{C}$ are

$$\begin{aligned} E_0 &= 2.20405 \times 10^3 \\ E_1 &= 5.845654 \\ E_2 &= -4.06761 \times 10^{-2} \\ E_3 &= 1.48212 \times 10^{-4} \\ E_4 &= -2.13708 \times 10^{-7} \end{aligned}$$

Finally, the phase-line temperature in degrees Kelvin, as a function of pressure, is given by the fit

$$T_p = 1/[A + B \ln P + C(\ln P)^2] , \quad (2.42)$$

where P is the pressure in bars, and

$$\begin{aligned} A &= 2.68410 \times 10^{-3} \\ B &= -0.204057 \times 10^{-3} \\ C &= -1.47106 \times 10^{-6}. \end{aligned}$$

2.5.3 Carbon Dioxide

The specific volume of CO_2 as a function of pressure and temperature is calculated from the expression

$$V = Z(P, T) RT/P , \quad (2.43)$$

where $Z(P, T)$ is the compressibility factor. The analytic fits to the compressibility factor given below are based on the data to 600 bars as tabulated by Vargaftik [1975].

For pressures less than 300 bars,

$$\begin{aligned} Z(P, T) &= A(T) + B(T)(P - 300) + C(T)(P - 300)^2 \\ &\quad + D(T)(P - 300)^3 + E(T)(P - 300)^4 , \end{aligned} \quad (2.44)$$

where P is the pressure in bars. The temperature dependent coefficients in the above expression are calculated from the quartic fits,

$$A(T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + A_4 T^4 , \quad (2.45)$$

with similar expressions for $B(T)$, $C(T)$ and $D(T)$, where T is the temperature in degrees Kelvin. The following numerical values give an adequate fit to the experimental data for temperatures between 350°K and 623°K:

$$\begin{aligned} A_0 &= 8.09759 \\ A_1 &= -7.10670 \times 10^{-2} \\ A_2 &= 2.38501 \times 10^{-4} \\ A_3 &= -3.36774 \times 10^{-7} \\ A_4 &= 1.72976 \times 10^{-10} \end{aligned}$$

$$\begin{aligned} B_0 &= -3.62183 \times 10^{-2} \\ B_1 &= 3.73836 \times 10^{-4} \\ B_2 &= -1.32285 \times 10^{-6} \\ B_3 &= 1.97631 \times 10^{-9} \\ B_4 &= -1.06871 \times 10^{-12} \end{aligned}$$

$$\begin{aligned} C_0 &= -3.43992 \times 10^{-3} \\ C_1 &= 2.77555 \times 10^{-5} \\ C_2 &= -8.30370 \times 10^{-8} \\ C_3 &= 1.09429 \times 10^{-10} \\ C_4 &= -5.36712 \times 10^{-14} \end{aligned}$$

$$\begin{aligned} D_0 &= -2.10949 \times 10^{-5} \\ D_1 &= 1.66021 \times 10^{-7} \\ D_2 &= -4.86891 \times 10^{-10} \\ D_3 &= 6.31079 \times 10^{-13} \\ D_4 &= -3.05175 \times 10^{-16} \end{aligned}$$

The remaining coefficient, $E(T)$, is determined from the requirement that the value of the compressibility factor be unity at zero pressure,

$$E(T) = (1 - A(T) + 300 B(T) - 300^2 C(T) + 300^3 D(T)) / 300^4 \quad (2.46)$$

For pressures greater than 300 bars the following representation is used,

$$Z(P, T) = A(T) + B(T)(P - 300) + F(T)(P - 300)^2, \quad (2.47)$$

where

$$F(T) = F_0 + F_1 T + F_2 T^2 + F_3 T^3 + F_4 T^4, \quad (2.48)$$

the coefficients F_i being given by

$$\begin{aligned}
F_0 &= 6.82528 \times 10^{-5} \\
F_1 &= -6.70714 \times 10^{-7} \\
F_2 &= 2.37181 \times 10^{-9} \\
F_3 &= -3.57746 \times 10^{-12} \\
F_4 &= 1.95665 \times 10^{-15}
\end{aligned}$$

The numerical value of the gas constant R in Equation (2.43) is

$$R = 1.88919 \times 10^6 \text{ erg/g-}^\circ\text{K} .$$

The determination of the specific internal energy as a function of temperature and pressure uses the above analytic fits for the compressibility factor and the following fit to the enthalpy as a function of absolute temperature at $P = 200$ bar,

$$H_{00}(T) = H_0 + H_1T + H_2T^2 + H_3T^3 , \quad (2.49)$$

where T is in degrees Kelvin. For $H_{00}(T)$ in erg/g, the values for the coefficients are

$$\begin{aligned}
H_0 &= -1.25623 \times 10^{10} \\
H_1 &= 5.91644 \times 10^7 \\
H_2 &= -7.31648 \times 10^4 \\
H_3 &= 3.74832 \times 10^1 .
\end{aligned}$$

The enthalpy at other pressures is evaluated from the thermodynamic identity

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V = -\frac{RT^2}{P} \frac{\partial Z}{\partial T} , \quad (2.50)$$

i.e.,

$$H(P, T) = H_{00}(T) - RT^2 \int_{200 \text{ bar}}^P \frac{1}{P} \frac{\partial Z}{\partial T} dP . \quad (2.51)$$

2.6 Viscosity of Mixture Components

2.6.1 Water

The viscosity of water is calculated from the fit as given in the ASME Steam Tables [1977],

$$\mu(\text{micropoise}) = 241.4 [1 + (P - P_s) \times 10^{-6}] \times \exp[570.58/(T(^{\circ}\text{K}) - 140)] \quad (2.52)$$

where P is the pressure in bars and P_s is the saturation pressure,

$$P_s(\text{bar}) = \exp[12.7401 - 4736.98/T(^{\circ}\text{K})] \quad (2.53)$$

The function ϕ is defined by

$$\phi = 1.0467[T(^{\circ}\text{K}) - 305] \quad .$$

2.6.2 Steam

The following fits for the viscosity of steam are based on data as given in the ASME Steam Tables [1977]. for pressures less than 150 bars, the viscosity μ in poise is calculated from

$$\mu \times 10^5 = 8.30476 + 4.01714 \times 10^{-2} T_c \quad , \quad (2.54)$$

where T_c is the temperature in $^{\circ}\text{C}$. For pressures greater than 150 bars,

$$\mu \times 10^5 = A(P) + 4.01714 \times 10^{-2} T_c \quad , \quad (2.55)$$

where $A(P)$ is found from a linear interpolation between the following tabulated values,

<u>P(bar)</u>	<u>A</u>
150	8.30476
200	10.275
225	32.625
250	43.225
<u>P(bar)</u>	<u>A</u>
300	49.325
400	55.725
500	60.325
700	66.925
1000	74.225

2.6.3 Carbon-Dioxide

Fits to the viscosity of CO₂ as a function of pressure and temperature are based on the data as tabulated by Vargaftik [1975]. For the viscosity μ in poise,

$$\mu \times 10^7 = A(P) + B(P)T_C + C(P)T_C^2 + D(P)T_C^3 + E(P)T_C^4, \quad (2.56)$$

where T_C is the temperature in °C. The pressure dependent coefficients are found from a linear interpolation between the following tabulated values:

<u>P(bar)</u>	<u>A</u>	<u>B</u>	<u>C</u>
0	1357.8	4.9227	-2.9661×10^{-3}
100	3918.9	-35.984	2.5825×10^{-1}
150	9660.7	-135.479	9.0087×10^{-1}
200	13156.6	-179.352	1.12474
300	14796.8	-160.731	8.50257×10^{-1}
400	15758.3	-144.887	6.73731×10^{-1}
500	16171.6	-125.341	5.00750×10^{-1}
600	16839.4	-115.700	4.08927×10^{-1}

<u>P(bar)</u>	<u>D</u>	<u>E</u>
0	2.8529×10^{-6}	-2.1829×10^{-9}
100	-7.1178×10^{-4}	6.9578×10^{-7}
150	-2.4727×10^{-3}	2.4156×10^{-6}
200	-2.98864×10^{-3}	2.85911×10^{-6}
300	-1.99076×10^{-3}	1.73423×10^{-6}
400	-1.4199×10^{-3}	1.13548×10^{-6}
500	-9.04721×10^{-4}	6.19087×10^{-7}
600	-6.35032×10^{-4}	3.53981×10^{-7}

2.7 Thermal Conductivity of Mixture Components

2.7.1 Water

The thermal conductivity of water is calculated from the fit as given in the ASME Steam Tables [1977],

$$\begin{aligned}
 K(\text{milliwatt/m}^{\circ}\text{K}) = & A_0 + A_1 T_R + A_2 T_R^2 + A_3 T_R^3 + A_4 T_R^4 \\
 & + (P - P_s)[B_0 + B_1 T_R + B_2 T_R^2 + B_3 T_R^3] \\
 & + (P - P_s)^2[C_0 + C_1 T_R + C_2 T_R^2 + C_3 T_R^3] ,
 \end{aligned} \tag{2.57}$$

where

$$\begin{array}{lll}
 A_0 = -9227.47 & B_0 = -0.9473 & C_0 = 1.6563 \times 10^{-3} \\
 A_1 = 2839.5 & B_1 = 2.5186 & C_1 = -3.8929 \times 10^{-3} \\
 A_2 = -1800.7 & B_2 = -2.0012 & C_2 = 2.9323 \times 10^{-3} \\
 A_3 = 525.77 & B_3 = 0.51536 & C_3 = -7.1693 \times 10^{-4} \\
 A_4 = -73.44 & &
 \end{array}$$

In Equation (2.57) the quantity T_R is given by

$$T_R \equiv T(^{\circ}\text{K})/273.15 \quad ,$$

P is the pressure in bars, and P_s is the saturation pressure,

$$P_s(\text{bar}) = \exp[12.7401 - 4736.98/T(^{\circ}\text{K})] \quad . \quad (2.58)$$

2.7.2 Steam

The following fit for the thermal conductivity of steam are based on data tabulated in the ASME Steam Tables [1977]. For the conductivity K in cm-sec- $^{\circ}\text{K}$,

$$K \times 10^{-2} = A(P) + B(P)T_C + C(P)T_C^2 \quad , \quad (2.59)$$

where T_C is the temperature in $^{\circ}\text{C}$. The pressure dependent coefficients are determined from a linear interpolation between the following tabulated values:

<u>P(bar)</u>	<u>A</u>	<u>B</u>	<u>C</u>
1	17.6643	6.29286×10^{-2}	7.57143×10^{-5}
10	22.5429	4.18857×10^{-2}	1.02857×10^{-4}
25	38.85	-3.39984×10^{-2}	2.0×10^{-4}
50	75.0	-1.89024×10^{-1}	3.8×10^{-4}
100	142.0	-0.39861	5.4×10^{-4}
150	177.0		
200	199.0		
300	492.0		
400	541.0		
500	574.0		

For pressures greater than 100 bar, B(P) and C(P) are held constant at the values -0.39861 and 5.4×10^{-4} respectively.

2.7.3 Carbon Dioxide

The following fits to the thermal conductivity of CO_2 are based upon data tabulated by Vargaftik [1975]. For the conductivity K in $\text{erg/cm-sec-}^\circ\text{K}$,

$$K \times 10^{-2} = A(P) + B(P)T + C(P)T^2 + D(P)T^3 + E(P)T^4, \quad (2.60)$$

where T is the temperature in degrees Kelvin. The pressure dependent coefficients are determined from a linear interpolation between the following tabulated values:

<u>P(bar)</u>	<u>A</u>	<u>B</u>	<u>C</u>
0	-6.87194	0.103039	-1.69133×10^{-4}
100	292.49	-1.94999	5.26027×10^{-3}
150	1105.95	-7.97267	2.20549×10^{-2}
200	1830.72	-13.3437	3.71189×10^{-2}
300	1798.61	-12.5286	3.37142×10^{-2}
400	1352.93	-8.79097	2.26115×10^{-2}
500	701.153	-3.50397	7.0788×10^{-3}
600	718.238	-3.62828	7.56822×10^{-3}

<u>P(bar)</u>	<u>D</u>	<u>E</u>
0	3.65509×10^{-7}	-2.4941×10^{-10}
100	-6.0497×10^{-6}	2.59136×10^{-9}
150	-2.68145×10^{-5}	1.21732×10^{-8}
200	-4.55986×10^{-5}	2.09314×10^{-8}
300	-4.02797×10^{-5}	1.80499×10^{-8}
400	-2.60224×10^{-5}	1.13105×10^{-8}
500	-6.10837×10^{-6}	1.86513×10^{-9}
600	-6.85987×10^{-6}	2.24086×10^{-9}

2.8 Energy of Solution

The following fit to the energy of solution is based on the values for the heat of solution, ΔH_s° , as given by Ellis and Golding [1963]. For ΔE_{s01} in erg/g and T_c in $^\circ\text{C}$,

$$\Delta E_s = A + BT_c + CT_c^2 + DT_c^3, \quad (2.61)$$

where

$$A = -6.426 \times 10^9$$

$$B = 8.410 \times 10^7$$

$$C = -3.869 \times 10^5$$

$$D = 8.178 \times 10^2$$

SECTION 3: EFFECTS OF CO₂ ON BACA RESERVOIR STATES

3.1 Introduction

In this section the equation-of-state package for water-carbon dioxide mixtures is first used to illustrate the quantitative effect of CO₂ content on the thermodynamic states assumed by the reservoir fluids in representative geothermal systems. The package is then applied specifically to the Baca reservoir in the Redondo Creek area to show the importance of CO₂ content to the in situ state of this reservoir. The package is also applied to investigate the changing state of individual parcels of Baca reservoir fluid as each flows from the reservoir to the sandface of a producing well, enters the well, and then flows up to the surface. Parcels are considered that correspond to the production intervals of various wells located in the Redondo Creek area.

3.2 Summary

With CO₂ present, the two-phase region for the water-carbon dioxide mixture is a band bounded by $P_{\max}$ (the "boiling pressure") and $P_{\min}$ (the "condensation pressure"). The width of the band will decrease with decreasing CO₂ mass fraction (α), becoming a single curve (saturation line) for pure water. The depth and the lateral distribution of a two-phase region in the Baca reservoir is found to be very sensitive as to the assumed value of α . Therefore, a reasonably accurate determination of the CO₂ mass fraction is essential to proper characterization of the reservoir system. Consideration of the changing thermodynamic states of a parcel of reservoir fluid as it moves from the reservoir to the surface shows that once it begins to boil, CO₂ is preferentially transferred to the gaseous phase. The CO₂ content of the liquid phase is reduced correspondingly. It is shown that a consequence of this partitioning of the CO₂ content is that pressure/temperature measurements correlations in flowing wells are unlikely to prove

useful for determination of the reservoir CO_2 content in the Baca system. Thus, CO_2 content must be determined directly by chemical analyses of the discharge fluids.

3.3 Effects of CO_2 on Thermodynamic States

For pure water, in pressure-temperature space, the loci of points which may exhibit two-phase behavior consist of a line called the "saturation curve"; a few points on this curve are shown in Table 3.1. If the fluid pressures are such that the actual pressure is less than the "saturation pressure" for that temperature, the system consists of superheated steam only. If the fluid pressure exceeds the saturation pressure, the fluid consists of compressed liquid water. All two-phase states (mixtures of liquid water and steam) are constrained to lie on the saturation curve, with $P = P_{\text{sat}}(T)$, as depicted in Figure 3.1.

Table 3.1
PRESSURE/TEMPERATURE POINTS ON THE SATURATION CURVE FOR PURE WATER

<u>Temperature ($^{\circ}\text{C}$)</u>	<u>Saturation Pressure (bars)</u>
100	1.01
120	1.99
140	3.61
160	6.18
180	10.0
200	15.6
220	23.2
240	33.5
260	46.9
280	64.2
300	85.9
320	113

Figure 3.1. Saturation Curve for Pure Water, $P_{\text{sat}}(T)$.

If CO_2 is present in the system, two related effects occur which alter the above situation. First, the "boiling pressure" for a fixed temperature increases. In other words, if a system consisting of pure H_2O in the compressed-liquid region undergoes a pressure decrease, it will remain single-phase until the pressure reaches the saturation curve ($P_{\text{sat}}(T)$). As CO_2 is added, the pressure at which two-phase behavior begins becomes higher and higher. On the other hand, if an element of $\text{H}_2\text{O}/\text{CO}_2$ mixture which is initially in the gaseous state ($P < P_{\text{sat}}$) is compressed, liquid water will form at a particular pressure: in the absence of CO_2 , this occurs at $P_{\text{sat}}(T)$. Even if CO_2 is present, the "condensation pressure" is only slightly greater than for pure water. Thus, with CO_2 present, the "boiling pressure" (at which liquid water becomes two-phase) will exceed the "condensation pressure" (at which a gaseous mixture condenses), and both will exceed $P_{\text{sat}}(T)$ which is the saturation curve for pure water. Figure 3.2 shows the situation for a mixture containing 1 percent CO_2 by mass ($\alpha = 0.01$). For comparison, the saturation curve for pure water is shown as a dashed line. As Figure 3.2 illustrates, the two-phase region is a band, bounded by P_{max} (the "boiling pressure") and P_{min} (the "condensation pressure"). If the CO_2 mass fraction (α) is varied, the width of the band will increase with increasing α .

Quantitatively, the condensation pressure (P_{min}) is quite close to P_{sat} for pure H_2O ; it is given by:

$$P_{\text{min}}(T, \alpha) = P_{\text{sat}}(T)/(1-\alpha) \quad (3.1)$$

The value of the "boiling pressure" may be expressed as follows:

$$P_{\text{max}}(T, \alpha) = P_{\text{sat}}(T) + \alpha \delta P(T, \alpha) \quad (3.2)$$

Figure 3.2. Phase Diagram for Water with CO₂ Mass Fraction (α) Equal to 0.01. Dashed Line is $P_{sat}(T)$ for Pure Water.

where $\delta P(T, \alpha)$ is depicted in Figure 3.3 for $0 \leq \alpha \leq 0.012$ and for $100^\circ\text{C} \leq T \leq 320^\circ\text{C}$. It is noteworthy that although δP depends on α (the CO_2 mass fraction), this dependence is fairly weak, particularly at high temperatures.

3.4 Effects of CO_2 on Baca Reservoir Conditions

Measured equilibrium reservoir pressures at depth in the Baca geothermal field are reasonably uniform horizontally. At a level of 3000 feet above sea level, the reservoir pressure is about 1710 psia, and the vertical pressure gradient is about 0.35 psi/ft. The ground surface in the area is from 8000 to 9600 feet above sea level. This suggests that for $Z \leq 2000$ meters or so (Z is the altitude above sea level), states reservoir pressure at Baca are given approximately by:

$$P \text{ (bars)} = 190.3 - 0.0792 Z \text{ (meters)} \quad (3.3)$$

Assuming the above pressure distribution, the hypothetical temperature-altitude profiles shown in Figure 3.4 may be constructed. These profiles represent the temperature, for a particular altitude, at which two-phase behavior will begin; profiles are presented for various values of α (0, 0.004, 0.008 and 0.012). The physical significance of the profiles is as follows. If α (the CO_2 mass fraction in the reservoir fluid) is known, and if the reservoir temperature at a particular depth is also known, then if the measured temperature lies to the left of the appropriate profile, the reservoir fluid is single-phase liquid at that location. If the measured temperature lies to the right of the profile, the system is two-phase at that level.

Measurements of equilibrium reservoir temperatures are, of course, difficult to obtain. Figure 3.4 also shows (as dashed lines) reservoir temperatures in various regions estimated from measurements in shut-in wells at points where significant fluid entries are believed to be present. These temperatures could be in

Figure 3.3. Dependence of $\delta P = [P_{\max}(T, \alpha) - P_{\text{sat}}(T)]/\alpha$ on Temperature and CO_2 Mass Fraction (α).

Figure 3.4. Critical Temperature for Two-Phase Behavior in Baca Field as a Function of Elevation Above Sea Level for Various Assumed Values of the CO₂ Mass Fraction in the Field (α). Dashed Lines Represent Measured Temperatures.

significant error, but the values shown will suffice for discussion purposes. Three groups of data are represented: from Well B-4, from wells B-11 and B-13, and from wells B-10 and B-18.

These results show the importance of CO_2 content to reservoir behavior. For example, if the Baca reservoir fluid contained no CO_2 , the results for Well B-4 suggest that the system would be single-phase liquid below $Z = 1310$ meters in the vicinity of B-4. On the other hand, if the CO_2 content were as high as 1.2 percent ($\alpha = 0.012$) by mass, two-phase conditions would prevail above $Z = 950$ meters. Similarly, for Wells B-11 and B-13, $\alpha = 0$ implies a boiling level of $Z = 1820$ meters, whereas $\alpha = 0.004$ implies $Z = 1630$ m; $\alpha = 0.008$ implies $Z = 1430$ meters; and $\alpha = 0.012$ implies; $Z = 1220$ meters. Wells B-10 and B-18, which lie in a cooler part of the system, probably penetrate a single-phase region (it is unlikely that the proper α for Baca exceeds 0.012 as will be seen below). As discussed earlier, the measured temperature data presented in Figure 3.4 could be in significant error, but the essential point is that variation of the CO_2 content (α) from zero to 0.012 could imply variability in the depth of the two-phase region of up to 600 meters (~ 2000 feet). Therefore, a reasonably accurate determination of the CO_2 mass fraction in the reservoir fluid is essential to proper characterization of the system.

Chemical analyses of the discharge fluids from Baca Wells B-4, B-6, B-11 and B-13 have been presented by Hartz [1976] and are summarized in Table 1.3. Although considerable scatter is present in these data (some of which is probably due to the substantial separation of the wells considered), the average value for α in the discharge fluid is about 0.008 ± 0.0004 , with the lowest values based on two samples) coming from Well B-6. Well B-4 yielded a value of $\alpha = 0.0085$ based on a single sample, and Well B-13 (with 12 samples) provided α values ranging from 0.005 to 0.012, with mean value 0.0083. In connection with these figures, it should be kept in mind that the reported CO_2 contents are those of the fluid

discharging from wells in transient flow tests, which could differ appreciably from the appropriate average static CO_2 mass fraction in the reservoir itself (Section 4).

3.5 Need for Chemical Measurements of Baca Discharge Fluids

Atkinson [1980] believes that the CO_2 content of the Baca system is much lower, based upon temperature and pressure measurements made within flowing wells during long-term well tests. He notes that the loci of (P,T) points in such measurements are in close agreement with the saturation curve for pure water. The tests in question involve ambient reservoir conditions of pressure and temperature ($P = P_0 \sim 120$ bars and $T = T_0 \sim 290^\circ\text{C}$). During the test, pressure near the well quickly declines, so that sandface pressures are typically about 60 bars at bottomhole, and decline with height up the well. Thus, two-phase conditions are present within the well during the test (saturation pressure for $T = 290^\circ\text{C}$ is about 74 bars). Atkinson notes that the partial pressure of CO_2 associated with $T = 290^\circ\text{C}$ and $\alpha = 0.008$ is in the range 13 to 18 bars, and that the measured (P,T) relations within flowing wells do not depart from the saturation curve for pure water by nearly so great an amount. He, therefore, concludes that the CO_2 mass fraction at Baca must be much lower than 0.008. In fact, the partial pressure data reported herein indicate that the CO_2 partial pressure for $\alpha = 0.008$ is about 13 bars (not 15.5 ± 2.5), but this discrepancy is not important. The essential difficulty with the Atkinson analysis is the assumption that the partial pressure of CO_2 remains the same throughout the fluid's path through the reservoir and up the well.

The physical situation may be idealized as follows. Once the flow test has been carried on for a substantial time, a quasi-steady condition will be reached in which pressures within the reservoir will become nearly steady and heat conduction in shallower layers (which at early times cools the upper part of the well by heat

transfer to the surrounding rock) will become unimportant. Furthermore, the flow within the reservoir will be essentially horizontal (directed radially toward the well). Under these circumstances, a parcel of fluid will flow towards the sandface, enter the well, and then flow upwards without significant changes in its overall composition (CO_2 mass fraction) or energy content (enthalpy). Thus, the state of the fluid, both in the well and radially outward within the reservoir, will correspond to the successive states of an element of fluid which starting at initial reservoir conditions ($P = P_0 \sim 120$ bars, $T = T_0 \sim 290^\circ\text{C}$), is expanded holding enthalpy and composition constant.

To investigate the fluid production process, calculations were carried out which involve the isenthalpic expansion of a fluid parcel starting at $P = 120$ bars, $T = 290^\circ\text{C}$ for various initial CO_2 mass fractions ($\alpha = 0, 0.002, 0.004, 0.006, 0.008, 0.010$ and 0.012). In all cases, the expansion was continued until the pressure reached 5 bars. Figure 3.5 shows the results for $\alpha = 0$ and $\alpha = 0.008$. Until the pressure drops to 87.6 bars (from the initial value of 120 bars), results are virtually identical for both cases, since both are single-phase, and the temperature declines only by a fraction of a degree. At 87.6 bars, the gassy fluid parcel ($\alpha = 0.008$ case) enters the two-phase region; as pressure is further lowered, the gas saturation rises above zero and the temperature begins to decline. The pure-water fluid parcel ($\alpha = 0$ case), on the other hand, remains single-phase until the pressure reaches 74.3 bars. Then, the temperature in the fluid parcel declines also and the gas (steam) saturation increases. Note, however, that as pressure further declines, the temperatures for the two fluid parcels approach each other more and more closely.

The temperatures of the fluid parcels for the two cases approach each other upon further expansion because of the non-uniform transfer of CO_2 from the liquid phase to the gas phase. That is, once the gassy fluid parcel begins to boil, CO_2

Figure 3.5. Expansion at Constant Enthalpy from Initial Pressure (120 Bars) to Final Pressure (5 Bars) for Initial Temperature = 290°C, for α (CO₂ Mass/Total Mass) = 0 and 0.008: $\alpha=0$ Case Boils at $P=74.3$ Bars; $\alpha=0.008$ Case Boils at $P=87.6$ Bars.

is preferentially transferred to the gaseous phase; although the initial composition of the parcel in the liquid phase was 0.8 percent CO_2 by mass, at incipient boiling the gas phase composition is about 15 percent CO_2 by mass. Therefore, the CO_2 content of the liquid phase considered alone declines during the expansion. It reaches 0.4 percent (half the initial value) at $P = 70$ bars, 0.2 percent at $P = 54$ bars, 0.1 percent at $P = 39$ bars and 0.05 percent at $P = 27$ bars (see Figure 3.6). Of course, the overall CO_2 mass fraction (liquid plus gas) remains at 0.8 percent throughout, but it is the composition of the liquid phase alone which determines partial pressure effects. The result is that the temperatures at substantial expansion are nearly indistinguishable between $\alpha = 0$ and $\alpha = 0.008$.

Figure 3.7 shows the temperature difference as a function of pressure which would be observed between the pure-water case and $\alpha = 0.002, 0.004, 0.006, 0.008, 0.0010$ and 0.012 upon isenthalpic expansion from $P = 120$ bars, $T = 290^\circ\text{C}$. Since the maximum pressure within the well at bottomhole is typically about 60 bars, measurements within a well producing from a reservoir with $\alpha = 0.008$ would produce a plot of pressure versus temperature which would differ from the pure-water saturation curve by a maximum of 5°C at bottomhole, and by much smaller amounts at higher levels. Considering the inherent difficulty of obtaining accurate simultaneous pressure and temperature measurements inside discharging wells, such a weak effect may well be undetectable. For example, at a point within the well where the measured temperature is 200°C (assuming that this temperature is measured exactly), a pure-water system would have a pressure of 15.55 bars (225 psia) whereas a well discharging from a reservoir with $\alpha = 0.008$ would be expected to have a pressure of 16.07 bars (233 psia) at the same temperature. This small pressure difference (8 psia) is probably undetectable, and is vastly less than the pressure difference (190 psi to 260 psi) expected by Atkinson [1980] to be associated with a CO_2 content of $\alpha = 0.008$. We conclude that pressure/temperature measurement correlations in flowing wells are unlikely to prove

Figure 3.6. Composition of Liquid and Gas Phases for Isenthalpic Expansion from $P=120$ Bars, $T=300^{\circ}\text{C}$, for Overall CO_2 Mass Fraction (α) Equal to 0.008.

Figure 3.7. Temperature Difference Between Pure H_2O Case and Cases with Finite CO_2 Mass Fractions During Isenthalpic Expansion from $P=120$ Bars and $T=290^{\circ}C$.

useful for determination of reservoir CO_2 content unless the CO_2 content is much greater than that believed to prevail at Baca; chemical analyses of discharge fluids should prove much more reliable indicators.

SECTION 4: EFFECTS OF CO₂ ON WELL FLOWING TESTS

4.1 Introduction

The equation-of-state for H₂O/CO₂ mixtures described in Section 2 of this report has been configured to match the CHARGR geothermal reservoir simulator, so that detailed calculations may now be carried out concerning reservoir behavior when substantial quantities of CO₂ are present. Preliminary computations have been performed to illustrate the impact of CO₂ content upon transient well-test response; the results of these calculations are described in this section of the report. The simulated reservoir pressure and temperature conditions are representative of conditions in the Baca reservoir at the production depths of the wells in the Redondo Creek area.

4.2 Summary

Five cases were considered in which the initial CO₂ mass fraction was varied as follows: $\alpha_0 = 0.004, 0.006, 0.008, 0.010,$ and 0.012 . In all cases the sandface pressure drops linearly with the logarithm of time, but the slope is much greater for the high CO₂ content cases. Underestimating the CO₂ content of the reservoir can lead to drastic underestimates of the true permeability of the reservoir. The higher the CO₂ content, the higher the discharge enthalpy. For cases with low CO₂ content the CO₂ content of the discharge fluid is less than the initial reservoir value ($\alpha < \alpha_0$). For cases with high CO₂ content, the discharge fluid CO₂ content is greater than the initial reservoir value ($\alpha > \alpha_0$). For the Baca reservoir, the CO₂ mass fraction measured in the discharge fluids should be regarded as a lower bound on the CO₂ mass fraction of the produced section of the reservoir system.

4.3 Simulated Production from Gassy Reservoirs

Five cases were considered, which differed only in the initial value of CO_2 mass fraction present in the reservoir. The flow toward the well was treated as one-dimensional (radial) and unsteady, with conditions at zero time being uniform within the system. The reservoir properties and aquifer thickness are also uniform. The well radius is 0.11 meter (4-1/3 inches); sixty computational zones were employed, with $\Delta r_{i+1} = 1.2 \Delta r_i$; this yields an outer grid radius of 31 kilometers which is far beyond the radius of influence of the pressure signals induced by the well-tests simulated by the calculations, so that the results are the same as if the grid had been infinite in extent. The production rate for the simulated well-test was in all cases taken as 0.14 kilograms of fluid per second per meter of thickness starting at zero time; the calculations were carried out to $t = 64$ hours.

The properties of the reservoir rock were taken as: grain density, 2.65 grams/cm³; porosity, 0.1; heat capacity, 1 joule/gram-°C; permeability, 5×10^{-14} m² (~ 50 millidarcies). Corey relative permeabilities were employed, with residual liquid saturation = 0.3 and residual gas saturation = 0.05. Thus, the relative permeabilities are given by:

$$\begin{array}{l} \underline{0 \leq S \leq 0.05} \\ R_L = 1, \quad R_G = 0 \end{array} \quad (4.1)$$

$$\begin{array}{l} \underline{0.05 \leq S \leq 0.7} \\ R_L = Q^4, \quad R_G = (1-Q^2)(1-Q)^2 \end{array} \quad (4.2)$$

$$\text{where } Q = (0.7-S)/0.65$$

$$\begin{array}{l} \underline{0.7 \leq S \leq 1} \\ R_L = 0, \quad R_G = 1 \end{array} \quad (4.3)$$

where S is the gas saturation (gas volume/fluid volume) and where R_L , R_G are the relative permeabilities to the liquid and gas phases, respectively.

For all five cases, the initial reservoir pressure and temperature were the same; 97.86 bars (1419 psia) and 300°C (572°F) respectively. The initial mass fractions of CO_2 in the fluid mixture varied from case to case. Some of the cases involved two-phase initial conditions; the initial reservoir state was as shown in Table 4.1. The initial pressure ($P_0 = 97.86$ bars) was chosen so that Case 3 would have initial gas saturation $S_0 = 0.05$, which is also the residual gas saturation for the relative permeability curves chosen.

Table 4.1
INITIAL RESERVOIR STATE OF FIVE CASES SIMULATED

	P_0 (bars)	T_0 (°C)	α_0	S_0
Case 1	97.86	300	0.004	0
Case 2	97.86	300	0.006	0
Case 3	97.86	300	0.008	0.050
Case 4	97.86	300	0.010	0.224
Case 5	97.86	300	0.012	0.348

In Case 1 ($\alpha_0 = 0.004$), the flow remains single-phase liquid throughout the duration of the test (64 hours). In Case 2, although the system is initially single-phase, after less than one minute of production the fluid starts to boil at the sandface and subsequently two-phase behavior propagates outward into the reservoir: after 64 hours, the boiling region extends 11 meters into the formation. The remaining cases (3, 4, and 5) are, of course, two-phase throughout their history.

Figure 4.1 summarizes the histories of sandface pressure for all five cases expressed in terms of pressure drop relative to initial reservoir pressure. As the extent of two-phase behavior increases due to increasing CO_2 content for the later cases, the pressure drop becomes more pronounced. In all cases, at late times the sandface pressure drop varies linearly with the logarithm of time, but, as Figure 4.1 shows, the slope is much greater for the cases with higher α_0 . At 64 hours, the sandface pressure and pressure decline rate (i.e., bars/decade) were as shown in Table 4.2 (recall that the initial reservoir pressure was 97.86 bars in all cases).

Table 4.2
SIMULATED SANDFACE CONDITIONS AT $t = 64$ HRS.

	$P_{\text{sand}}(64 \text{ hrs})$	$dP_{\text{sand}}/d(\log_{10} t)$
Case 1 ($\alpha_0=0.004$)	92.69 bars	0.67 bars
Case 2 ($\alpha_0=0.006$)	90.63 bars	1.56 bars
Case 3 ($\alpha_0=0.008$)	90.15 bars	1.92 bars
Case 4 ($\alpha_0=0.010$)	77.06 bars	4.53 bars
Case 5 ($\alpha_0=0.012$)	67.46 bars	7.14 bars

4.4 Inapplicability of Conventional Well-Test Analysis

In conventional well-test analysis, if the flow is single-phase liquid, the absolute permeability of the formation may be deduced from the late-time behavior of the sandface pressure during a discharge test. It may be shown that the permeability will be given by:

$$k = 0.18323 \frac{v_m}{(dP/d \log_{10} t)} \quad (4.4)$$

Figure 4.1. Sandface Pressure Histories from CHARGR Drawdown Test Simulations.

where k is permeability, ν is the kinematic viscosity of the reservoir fluid, $\dot{m}$ is the production rate per unit reservoir thickness, and $(dP/d \log_{10} t)$ is the late-time pressure decline rate per decade when the pressure history is plotted on semi-logarithmic paper. (The numerical constant 0.18323 is equal to $\ln_e(10)/4\pi$). For the present case, if these results were observed from actual well tests and interpreted as if the flow were single-phase (which it would be, were little or no CO_2 present) erroneous permeability values would be determined. In these problems, the true permeability was $5 \times 10^{-14} \text{ m}^2$ (50 millidarcies); the kinematic viscosity of water at $P = 92.69$ bars, $T = 300^\circ\text{C}$ is about $1.3 \times 10^{-7} \text{ m}^2/\text{sec}$. Use of the above formula would yield the values shown in Table 4.3 for permeability based on the values of $(dP/d \log_{10} t)$ listed in Table 4.2.

Table 4.3
IMPLIED PERMEABILITY (MILLIDARCIES)

Case 1 ($\alpha=0.004$)	50 (correct)
Case 2 ($\alpha=0.006$)	21
Case 3 ($\alpha=0.008$)	17
Case 4 ($\alpha=0.010$)	7.4
Case 5 ($\alpha=0.012$)	4.7

Table 4.3 clearly shows that underestimating the CO_2 content of the system, and therefore erroneously concluding that the flow is single phase, can lead to drastic underestimates of the true permeability of the reservoir.

4.5 Character of Discharge Fluids

A substantial variation among the five cases was also found in the character of the discharge fluid. For example, the enthalpy and bulk CO_2 mass fraction of the fluid entering the well at $t = 64$ hours were as shown in Table 4.4. The discharge enthalpy for Cases 1-3 is essentially that of liquid water, since the gas phase

(if present at all) is initially immobile. Cases 4 and 5, which involve substantial initial reservoir gas saturation, are characterized by higher enthalpies, reflecting the presence of substantial quantities of steam in the flow stream. The initial enthalpy of the gas phase alone in Cases 3-5 was 2438 joules/gram. In connection with these results, the enthalpy scale is chosen such that a CO₂-free state at a pressure of one bar at 0°C has zero enthalpy.

Table 4.4
CHARACTER OF DISCHARGE FLUIDS AT $t = 64$ HRS.

	<u>Discharge Enthalpy</u>	<u>CO₂ Mass Fraction in Discharge</u>
Case 1 ($\alpha_0=0.004$)	1340 joules/gram	0.0040
Case 2 ($\alpha_0=0.006$)	1339 joules/gram	0.0058
Case 3 ($\alpha_0=0.008$)	1344 joules/gram	0.0072
Case 4 ($\alpha_0=0.010$)	1532 joules/gram	0.0184
Case 5 ($\alpha_0=0.012$)	2170 joules/gram	0.0532

The composition of the discharge fluid also varies significantly from case to case. For Case 1, since the flow is single-phase throughout, the flowing CO₂ mass fraction is always equal to the initial reservoir value ($\alpha_0 = 0.004$). Cases 2 and 3 involve two-phase flow, but gas saturations are low enough that little gas enters the well (as indicated by the flowing enthalpies). In these cases, the CO₂ mass fraction in the discharge fluid is somewhat less than the initial reservoir value; for Case 2, $\alpha_{\text{flowing}} = 0.0058$ whereas $\alpha_0 = 0.006$; for Case 3, $\alpha_{\text{flowing}} = 0.0072$ whereas $\alpha_0 = 0.008$. As noted earlier, the CO₂ component does not partition itself evenly between the liquid and gas phases; for $P = 97.86$ bars and $T = 300^\circ\text{C}$, the equilibrium two-phase composition of the two phases is:

Dissolved CO_2 mass/liquid mass = 0.00754

Gaseous CO_2 mass/gas mass = 0.1163

Since, for Cases 2 and 3, little gas enters the well, the flowing fluid is derived mainly from the liquid phases which is characterized by a lower CO_2 content than the bulk value for α for the liquid/gas mixture as a whole. Case 4 and 5, on the other hand, involve substantial quantities of mobile gas; thus, the gas entering the well, characterized by a much higher CO_2 concentration, causes the net CO_2 flowing fraction to exceed the initial reservoir value.

Thus, as can be seen, the mass fraction of CO_2 in the fluid flowing from a well during a transient test may be either higher or lower than that prevailing in the reservoir as a whole. If a gas phase is present but at a low gas saturation such that the gas phase is nearly immobile, the CO_2 fraction in the discharge will generally be somewhat less than that of the reservoir. If a substantial gas saturation is present initially, the discharge fluid will be enriched in CO_2 relative to the reservoir as a whole. Of course, the latter case is unlikely to be encountered in practice when investigating an unexploited system. If the gas saturation is high enough that gas may flow readily, gravity segregation will in time cause a separation of the two phases into an upper gas cap and a lower liquid layer. Accordingly, when considering relatively undisturbed systems such as Baca, CO_2 mass fractions measured in the discharge fluids should be regarded as a lower bound on the appropriate CO_2 mass fraction characterizing the system as a whole.

REFERENCES

ASME STEAM TABLES, Third Edition, The American Society of Mechanical Engineers (1977).

ATKINSON, P. G. "Geothermal Reservoir Initial State, Baca Location No. 1 - New Mexico, Redondo Creek Field," Geothermal Resources Council, Transactions Vol. 4, September 1980.

ELLIS, A. J. and R. M. Golding, "The Solubility of Carbon Dioxide Above 100°C in Water and in Sodium Chloride Solutions," Am. J. Sci., Vol. 261, p. 47 (1963).

GARG, S. K., J. W. Pritchett, M. H. Rice and T. D. Riney, "U. S. Gulf Coast Geopressured Geothermal Reservoir Simulation," Systems, Science and Software Report SSS-R-77-3147, February. 1977.

HARTZ, J. D., "Geothermal Reservoir Evaluation of the Redondo Creek Area, Sandoval County, New Mexico," Union Oil Company of California, September 1976.

PARTICIPANT, "Geothermal Demonstration Power Plant, Proposal to Department of Energy, Volume II, January 1978.

PRITCHETT, J. W., "Geothermal Reservoir Engineering Computer Code Comparison and Validation Calculations Using MUSHRM and CHARGR Geothermal Reservoir Simulators, Systems, Science and Software Report SSS-R-81-4749, November 1980.

SUTTON, F. M., "Pressure-Temperature Curves for a Two-Phase Mixture of Water and Carbon Dioxide," N. Z. Journal of Science, Vol. 19, p. 297 (1976).

TAKENOUCHI, S. and G. C. Kennedy, "The Binary System H₂O- CO₂ at High Temperatures and Pressures," Am. J. Sci., Vol. 262, p. 1055 (1964).

VARGAFTIK, N. B., Tables on the Thermophysical Properties of Liquids and Gases, Second Edition, John Wiley and Sons, Inc., New York.