

THE PREDICTION OF THE PVT/PHASE BEHAVIOR OF THE GEOTHERMAL FLUID MIXTURES

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ABSTRACT

The realistic estimation of the PVT/Phase behavior of geothermal fluid systems plays a very important role in reservoir performance and energy production studies. In this study, two methods to predict the PVT/phase behavior of geothermal systems were evaluated. As a first attempt, the use of a cubic equation of state (EOS) was applied. Experimental data were matched with the Peng-Robinson EOS and a strong dependence of binary interaction coefficients to temperature was observed. The use of experimental correlations giving the solubility of CO₂ and related properties was observed more convenient for this purpose at the pressure-temperature-concentration ranges that are typical for geothermal reservoirs. Therefore, a PVT package which calculates the PVT/phase properties of H₂O-CO₂ systems using empirical correlations was developed. As a second step, the effects of salt content on the thermodynamic properties of geothermal fluids were added into the PVT package developed in the present study. Then, the use of the PVT package for different purposes was evaluated incorporating it into softwares prepared to model reservoir performance and wellbore flow including calcite deposition modeling.

INTRODUCTION

The realistic estimation of the PVT/phase behavior of the fluids is often the most important part of the production and reservoir engineering studies of geothermal fields. The simplest way of determining the PVT and phase behavior properties is to use the Steam Tables (1977) assuming that the reservoir contains pure water only. However, it is the fact that geothermal fluids are not pure water and indeed, they become a brine solution as a result of their natural voyage through the crust of the earth.

Geothermal brines are mainly sodium chloride solutions. Sodium chloride (NaCl) is typically 70-80 % of the total dissolved solids (TDS). In addition to this, potassium is found in substantial quantities, being about 1/10 that of sodium on an atomic basis. Calcium is the other major cationic constituent of geothermal brines. Chloride ion is the only major anionic constituent and second most important anionic ingredient is bicarbonate. Maximum amount of total dissolved solids reaches up to 200,000 ppm (USA, Salton Sea) and the average value of the world's geothermal fluids is around 10,000 ppm. Beside the dissolved solids, geothermal fluids may contain considerable amount of gases. CO₂ is the major gaseous component of most of the geothermal brines and generally it comprises more than 90 % of the total gas content by volume. H₂S and NH₃ are also found in some cases but the amounts of these gases are usually negligible.

In the two fields in Turkey (Kizildere and Germencik), that are considered as the cases in this study, TDS values are approximately 4,000 and 5,000 ppm, respectively (except CO₂, HCO₃⁻ and CO₃²⁻). The CO₂ content of Kizildere Geothermal Field was initially 10,000-15,000 ppm. Currently, this amount has been decreasing

and higher CO₂ concentration was detected in Germencik Field (up to 16,000ppm).

The initial performance prediction studies of the Kizildere Field were made with the assumption that dissolved CO₂ and salts have negligible effect on the PVT/phase behavior of the reservoir fluid (United Nations Report, 1974, Alkan and Satman, 1988). This was a realistic approach for salt content but the field data showed a two-phase flow in the reservoir as well as in the wellbore earlier than the predicted time. This was naturally due to high CO₂ content of the reservoir and it was necessary to insert the CO₂ effect into the modeling studies.

In this paper, a detailed study of PVT/phase behavior calculations of geothermal brines was conducted. Initially, the effects of dissolved gases on the thermodynamics was studied using cubic EOS's. The experimental data were matched to determine the unknown binary interaction coefficients (BIC) of Peng-Robinson EOS. The effects of the polar atomic structure of the H₂O-CO₂ system was modeled using an alternative mixing rules for determining the BIC's.

Although the temperature dependence of the BIC's was taken into account, the results showed that this approach has some deficiencies on predicting the PVT/phase properties of geothermal fluids. Therefore, a thermodynamic package from empirical correlations was prepared and this package was determined to be more convenient to estimate the PVT/phase behavior of H₂O-CO₂ systems. The effect of salt content on the thermodynamics of the geothermal brines was added to the package to minimize the errors arising from empirical analysis.

After testing the performance of the PVT package, it was introduced into reservoir and production studies. Some of the results obtained using the resulting models are presented.

CUBIC EQUATION OF STATE APPROACH

The three parameter Peng-Robinson equation of state (EOS) (Peng and Robinson, 1975) was used to solve the above described problem. The reasons for selecting the Peng-Robinson EOS were the molar volume correction proposed by Peneloux et al (1982) and its reported validity on modeling the PVT/phase properties of various fluid systems. The modifications proposed by Peng-Robinson (1980) were taken into account. This was mainly the temperature dependence of the EOS constant, $\alpha(T_r)$, for water. On the other hand, the effect of salt content was taken into account as proposed by Soreide (1989). The "vapor pressure" lowering the effect of salt concentration was introduced into the EOS constant, $a(T_r)$, using the suggested correlation.

In using the Peng-Robinson cubic EOS, its semi-empirical nature necessitates a matching procedure to regress the uncertain parameters such as volume shift, acentric factor and binary interaction coefficients (BIC) and even critical parameters (p_c and T_c) for complex hydrocarbon mixtures. All critical parameters and acentric factors for the components of a geothermal brine (H₂O and CO₂ in our present case) are well known from experimental studies. Thus, BIC between H₂O and CO₂ was the only possible regression

parameter. Note that the matching of the phase equilibria was our first objective, therefore, volume shifts were not incorporated into the regression operation. The temperature dependence of the volume shifts ($V(T)$) for H_2O were assured introducing the thermal expansion coefficient, c , with the following formula

$$V(T) = V_i(T_0)[1 + c(T - T_0)] \quad (1)$$

where T_0 is the reference temperature

Because of the highly polar nature of water and the asymmetric structure of H_2O - CO_2 system, an unconventional mixing rule proposed by Panagiotopoulos and Reid (1986) was used,

$$a_{i,j} = \sqrt{a_i a_j} [1 - k_{i,j} + (k_{i,j} - k_{j,i}) n_i] \quad (2)$$

As can be seen in this equation, the $k_{i,j}$ were treated as linear functions of the composition, i.e. of the mole fraction of the component (i), n_i . The $k_{i,j}$'s suggested by Panagiotopoulos and Reid (1986) were used and experimental data from literature (Todheide and Frank, 1963, Takenouchi and Kennedy, 1964, Gillespie and Wilson, 1982, Malinin, 1959) on the phase equilibria of H_2O - CO_2 systems were tried to be matched. In the first attempts, no significant variations of the $k_{i,j}$ depending on the CO_2 mole ratios for the typical range of geothermal brines were observed and conventional interaction coefficient concept and mixing rule were introduced into the program. On the contrary, a critical effect of temperature on BIC between H_2O and CO_2 was noticed as reported also by Soreide and Whitson (1992). Experimental data for the given temperatures were matched separately and BIC was adjusted for each case. Finally, BIC's as a function of temperature were tabulated and the relationship between temperature and BIC's was plotted as shown in Fig. 1

Note that at least five experimental vapor-liquid equilibria values were used for each case (i.e. for each temperature) and the "root-mean square" error between calculated and observed values are not higher than 0.09 which indicates a good approximation. Fig. 2 shows the results for two temperature values which are typical for geothermal reservoirs

The performance of the new EOS data on predicting the PVT/phase behavior of the H_2O - CO_2 system was retested by comparing the calculated critical parameters (critical pressure and temperature) with observed ones. The resulting graph is shown in Fig. 3. A reasonable match with the experimental data was obtained in the region of the critical parameters of water. This means that when the CO_2 ratio is decreasing in the mixture, the performance of the Peng-Robinson EOS on predicting the real behavior is increasing. This is a positive aspect of using cubic EOS because the CO_2 mass ratio is often not higher than 1% for most of the geothermal systems

The results described above give an optimistic overview of EOS to describe the PVT/phase behavior of the geothermal systems. Nevertheless, the use of Peng-Robinson equation was inconvenient for practical usage. First of all, the experimental data are not good both quantitatively and qualitatively; especially at the low pressure-temperature ranges ($p < 10$ MPa and $T < 200$ °C) that can represent a typical geothermal system. Some discrepancies occur among various references giving the equilibrium values. This fact, along with the insufficient number of data, can create important errors in spite of resulting rapid and easy regression process. On the other hand, the strong dependence of EOS on BIC's may remove the practical use of cubic EOS for the aimed objective. Although a correlation from Fig. 1 can be used for each temperature step, this may be disadvantageous especially for higher CO_2 content if the polar and asymmetric structure of H_2O - CO_2 system is considered. For these reasons, as well as the reason of simplicity, the empirical correlations were used in the continuation of the study.

EMPIRICAL CORRELATION APPROACH

The thermodynamic properties of pure water were obtained from empirical correlations prepared based on AIME Steam Tables (1977). In addition to saturation pressure and temperature, specific volume, densities, enthalpies, internal energy and entropies were calculated using these polynomial type correlations. The effect of salt and CO_2 content on the PVT/phase behavior of geothermal fluids were introduced by following rules explained below

Compressed Liquid Phase

In compressed liquid phase state, the density of water is calculated using the following formula obtained from the data reported by Chierici et al. (1981)

$$\rho_{cw} = \rho_w [1 + a \rho_w (p - p_{sat})] \quad (3)$$

where

$$a = 10^{b-13} \quad (4)$$

and

$$b = -5.308 + 4.033017 \cdot 10^{-2} T - 9.38612 \cdot 10^{-5} T^2 + 7.734 \cdot 10^{-8} T^3 \quad (5)$$

p is the actual pressure and p_{sat} is the saturation pressure in Pa and densities, ρ_w and ρ_{cw} in kg/m^3

The enthalpy, h_{cw} , and the viscosity of compressed water, μ_{cw} are calculated using the formulas given by Chierici et al. (1981) and Toronyi and Farouq-Ali (1975)

SALT EFFECT

The density behavior of salt solutions is well studied. A linear relationship between brine density and salt concentrations expressed as weight percent of NaCl, KCl and $CaCl_2$ is obvious and no significant differences were concluded among NaCl, KCl and $CaCl_2$ solutions in terms of the density behavior. Since geothermal brines are generally 70 % or more NaCl solutions and the next major component KCl has a density fairly close to the density of NaCl, the following correlation given by Wahl (1977) for an "average" brine (nearly equal to NaCl solution) is used to calculate the density of geothermal brines

$$\rho_s = \rho_w + 0.73[1 + 1.6 \cdot 10^{-6} (T - 273)^2] \omega_s \quad (6)$$

where,

ρ_s density of brine solutions, g/cm^3

ρ_w density of pure water, g/cm^3

ω_s the salt concentration, weight ratio

We can deduce from Eq. 6 that the density of a brine solution, 0.5 % by weight which reflects a maximum value for Kizildere and Germencik geothermal reservoirs, differs from the density of pure water only by 0.3-0.4 %. This is a negligible correction compared to the errors by use of empirical correlations. But, note that for strongly salty waters (>100,000 ppm), pure water assumption can cause errors as high as 10 % and even more

Enthalpy

The enthalpy of brine can be calculated from the following thermodynamical definition.

$$h = \int_{T_0}^T c dT \quad (7)$$

where,

T : current temperature,
 T_0 : reference temperature,
 c : the heat capacity.

The heat capacity of geothermal solutions in the temperature range of 100 to 200 °C and for the salt content below 10 % by weight can be defined as:

$$c = c_w(1 - \omega_s) - 0.8371\omega_s \quad (8)$$

where c_w is the heat capacity of pure water. One can obtain the following expression for the geothermal salt water enthalpy

$$h_s = h_w(1 - \omega_s) - 0.8371\omega_s(T - T_0) \quad (9)$$

where the enthalpies are given in kJ/kg and reference temperature (T_0) is zero when T is in °C. According to this equation, the enthalpy of a geothermal fluid including 10 % salt by weight differs from the enthalpy of pure water by 2-3%. Obviously, this ratio will be much lower for the salinity range corresponding to the geothermal reservoirs in Turkey. Eq. 9 is based on the data obtained for NaCl solutions (Wahl, 1977). However, w can be taken as the ratio of TDS because the heat capacities of NaCl and KCl and even CaCl_2 solutions are nearly the same.

Viscosity:

The viscosity of pure water which is not a PVT/phase property was calculated using a formula given in Steam Tables (1977). The effect of the salts on the pure water viscosity is computed according to the following formula which is arranged using mass ratio weighting mixing rule for an average geothermal brine

$$\mu_s = \mu_w(1 + 1.7\omega_s + 9.95\omega_s^2) \quad (10)$$

CO₂ EFFECT:

Since the amount of CO₂ in the liquid phase is small, the following assumptions for liquid density and viscosity were made

$$\rho_m = \rho_{sc} \text{ and } \mu_m = \mu_{sc} \quad (11)$$

where ρ_m and μ_m are the properties of geothermal fluids including CO₂ and ρ_{sc} and μ_{sc} are those of compressed brine solutions

Finally, the enthalpy of the compressed geothermal brine solution with CO₂ content is determined by Sutton (1976)

$$h_m = h_s(1 - \omega_c) + (h_g + h_{sol})\omega_c \quad (12)$$

where the enthalpy of gaseous CO₂, h_g , and the solution enthalpy, h_{sol} , are calculated using the following expression which is a curve fit to the data given by Sutton (1976):

$$h_g = -2.18 \cdot 10^5 + 732(T + 273) + 0.252(T + 273)^2 - 2.63 \cdot 10^{-5}(T + 273)^3 \quad (13)$$

and

$$h_{sol} = (-1.351 + 0.01692T - 7.5524 \cdot 10^{-5}T^2 + 1.318 \cdot 10^{-7}T^3)10^{-6} \quad (14)$$

Subscript (s) denotes "salty waters" in above equations

Saturated Phase:

Saturation is valid in the case where $p_{sys} \leq p_{sat}$. p_{sat} for pure water can be easily calculated from steam tables for corresponding temperature or vice versa. But, in the case of brine-CO₂ system,

saturation pressure will be affected by the presence of dissolved CO₂ and salts

The saturation pressure of m molal NaCl water at temperature T is lowered by the amount of the following (Michaëlidts, 1987)

$$\Delta p = \frac{18R(T + 273.15)}{v_v - v_l} \frac{m}{55.56} \quad (15)$$

where, Δp is in kPa, T in °C, v_v and v_l are the specific volumes of steam and liquid water in m³/kg, and R is the universal gas constant, 8.314 kJ/kg °K for corresponding units

The effect of CO₂ on the saturation pressure of the geothermal water is taken into the consideration with the partial pressure concept

$$p_{sat} = p_{sat,w} + \alpha_c(T)x_{cli} \quad (16)$$

where $\alpha_c(T)$ is Henry Law constant for CO₂ and x_{cli} is the initial mole ratio of dissolved CO₂. $p_{sat,w}$ is the saturation pressure of pure water or of the brine of salt effects. In order to estimate α_c for brine solutions, data given by Ellis and Golding (1963) were curve fitted and the following correlation was obtained

$$\alpha_c(T) = 10135 \cdot 10^8 (0.401 + 4.64608 \cdot 10^{-2}T + 7.595 \cdot 10^{-5}T^2 - 7.37 \cdot 10^{-7}T^3 + 0.790613m + 0.33259 \cdot 10^{-2}T \cdot m) \quad (17)$$

for $T < 172$ and

$$\alpha_c(T) = 10135 \cdot 10^8 (7.927 + 5.55352 \cdot 10^{-3}T - 7.24915 \cdot 10^{-5}T^2 + 3.16579 \cdot 10^{-5}T^3 + 0.94523m + 3.38482T \cdot m) \quad (18)$$

for $T \geq 172$

where m is NaCl molality. The correlation gives a good match with observed data as shown in Fig. 4

All the salts present in the geothermal fluids are non-volatile and hence, the gas phase in saturated state case is free of salts. Therefore, the effect of salt content on the PVT/phase properties of the liquid phase can be calculated using Eq's. 6 through 10. However, the gas phase of saturated geothermal fluid contains often the non-condensable gases, especially CO₂.

When the system pressure reaches the saturation pressure, a two-phase (liquid-gas) state begins in the system. After the steam quality of salt water (brine), q , is calculated from enthalpies for steam and liquid water, the mole number of H₂O for each phase can be found by the following equations

$$x_{wl} = (W_i - 44x_{cli})(1 - q) / 18 \quad (19)$$

$$x_{wg} = (W_i - 44x_{cli})q / 18 \quad (20)$$

where W_i is the total amount of fluid in kg and x_{cli} is the initial CO₂ mole number in liquid phase

The mole number of CO₂ in the liquid phase is calculated using the CO₂ distribution coefficient given by Gggenbach (1980)

$$B = 10^{(4.7593 - 0.01092T)} \quad (21)$$

and thus

$$x_{cl} = x_{cli}x_{wl} / (x_{wg}B + x_{wl}) \quad (22)$$

The specific volume of CO₂ can be obtained using the formula given by Sutton (1976):

$$v_c = 8.31 \cdot 10^3 (T + 273) / (44 p_c) \quad (23)$$

where the specific volume of CO₂, v_c , is in m³/kg, T is in °C, and p is in Pa. The density of the gas phase will be the sum of the steam and CO₂ gas densities (i.e. $\rho_g = \rho_s + \rho_c$)

The other properties of the gas phase can be calculated according to the mass ratio weighting mixing rule i.e.,

$$\mu_g = \mu_s(1 - \omega_{cg}) + \mu_c \omega_{cg} \quad (24)$$

$$h_g = h_s(1 - \omega_{cg}) + h_c \omega_{cg} \quad (25)$$

$$E_g = E_s(1 - \omega_{cg}) + E_c \omega_{cg} \quad (26)$$

Finally, the dew point pressure of a geothermal system, i.e. the minimum pressure where the two-phase exists, can be computed by the following formula

$$p_{dew} = \frac{p_{sat,s}}{(1 - x_{cg})} \quad (27)$$

APPLICATIONS

The PVT package described above in detail was used in modeling studies to predict production performance and the wellbore flow characteristics of geothermal reservoirs. Initially, it was incorporated into a lumped parameter model to estimate the production performance. The model is based on the general material-energy balance equation given by Whiting and Ramey (1969) for geothermal reservoirs and the PVT package was inserted into this equation to simulate the PVT behavior more realistically. A version of the model that includes the CO₂ effect only was well described by Alkan and Satman (1990). The model was improved with the PVT package including the salt effect. Testing runs for three geothermal reservoirs, namely Cerro Prieto (Italy), Ohaaki (New Zealand), and Bagnore (Italy), were performed. The reservoir and production data were the same as given by Alkan and Satman (1990) whereas the salinity of each reservoir fluid was taken from Wahl (1977) and Atkinson (1980). No significant difference from the previous results was observed for Ohaaki and Bagnore Fields for which a low salt content (in the range of 5,000 ppm) is reported. For Cerro Prieto field, however, reported salinity is up to 25,000 ppm and a slight difference with the previous study, particularly in the pressure level where the reservoir reaches the saturation pressure, i.e. two-phase flow begins to occur, was observed. The resulting match with the observed data is given in Fig. 6

The reservoir performances of Kizildere and Germencik which are the largest geothermal fields in Turkey in terms of energy production capacity were also determined by Alkan and Satman (1992). The effect of salt content for both reservoirs, which is in the range of 4,000–5,000 ppm, was found to be negligible for both cases as expected. Fig. 7 shows the CO₂ fraction in gas phase and gas quality history in the reservoir according to time in the case of 10 MW energy production. For this run, the initial CO₂ content of the reservoir was taken to be 15,000 ppm which reflects the maximum value for the field. All data for Kizildere Field were taken from Alkan and Satman (1992). The data for Germencik Field provided by the same Ref. were updated with respect to the recent reservoir and production studies and the new runs were conducted. The results of performance studies are shown in Fig. 8. One may conclude from the graph that the reservoir has a higher energy production performance than the Kizildere Field and an energy production of 60 MW can be expected with the reported rock and fluid properties.

A second application of the PVT package was performed using it in modeling the wellbore flow of geothermal fluids. A detailed description of the model in which a calcite deposition estimation option was incorporated was given by Satman and Alkan (1988). The pressure drop during the compressed liquid phase flow in the wellbore is calculated isothermally using the well-known flow equations. When the pressure in the wellbore reaches to the saturation pressure which is determined by PVT package depending on the temperature, CO₂ and salt content, a procedure presented by Orkiszewski (1967) with some modification was employed to determine two-phase pressure drop. For a specified temperature drop, the steam quality was calculated initially and all other phase properties including the ratio of liquid water and steam, the ratio of CO₂ in liquid and gaseous phases as well as the densities and related flow properties were estimated using the package. Then, the length of the interval in which the specified temperature drop occurs was calculated with the equation for proper flow regimes. The procedure was repeated until the wellhead is reached. A package to model the probable carbonate precipitation at any point of the wellbore is also incorporated into the program.

Although the verification of the calcium carbonate deposition part of the model is highly difficult because of several practical reasons (data acquisition particularly), the comparison of the calculated pressure-temperature vs. depth values with measured ones is possible if the related wellbore data is available. The percentage deviations for various field cases give an average of 6.6 as reported by Satman and Alkan (1988). An example of the comparison study is given in Fig. 9 representing a good match to observed pressures. A mass fraction of CO₂ of 0.02 is used and all other data are taken from Barelli et al. (1982). The model was applied to estimate the wellhead and bottomhole pressure-temperature of some wells from Kizildere Field also. The bottomhole pressure vs. flow rate relationship for a selected well is given in Fig. 10. In this graph, the static bottomhole pressure was estimated to be 63.9 bar that matches with the actual data using an initial CO₂ mass fraction of 0.009 in the liquid phase which reflects a minimum value for Kizildere.

CONCLUSION

The prediction of the PVT/phase behavior of geothermal fluids by using the equations of state (EOS) and empirical correlations were evaluated in this paper. The effects of salt and CO₂ content on the phase behavior of geothermal fluids are considered simultaneously for both methods. The results were compared with experimental data provided in literature.

Peng-Robinson was selected as the equation of state and the binary interaction coefficient (BIC) between water and CO₂ was attempted to adjust using available experimental data. Taking into account the temperature dependence of the BIC, the EOS approach can be a useful tool especially in modeling wellbore and reservoir conditions that are outside the range considered in available correlations. But, to model the systems with relatively high CO₂ content, the prediction capability of Peng-Robinson was found to be insufficient mainly because of the polar and asymmetric molecular structure of H₂O-CO₂ system.

An alternative package, that is based upon thermodynamical laws and correlated experimental data, was developed and the results on predicting the PVT/phase properties of geothermal fluid mixtures were presented. The pressure-temperature-concentration range that is typical for geothermal reservoirs was covered principally and the correlations for brine-CO₂ systems fitted to experimental data reasonably well. The modeling studies of reservoir and wellbore flow performances showed that the use of this package as a PVT simulation tool will improve the accuracy of the predictions.

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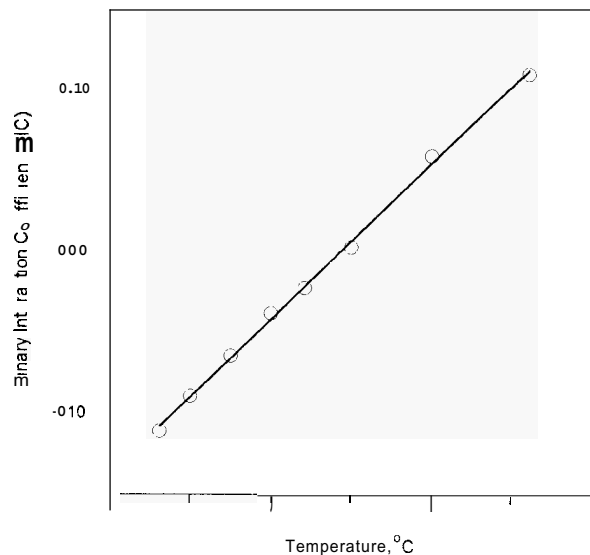


Figure 1 Temperature-BIC relationship for Peng-Robinson H_2O-CO_2 system

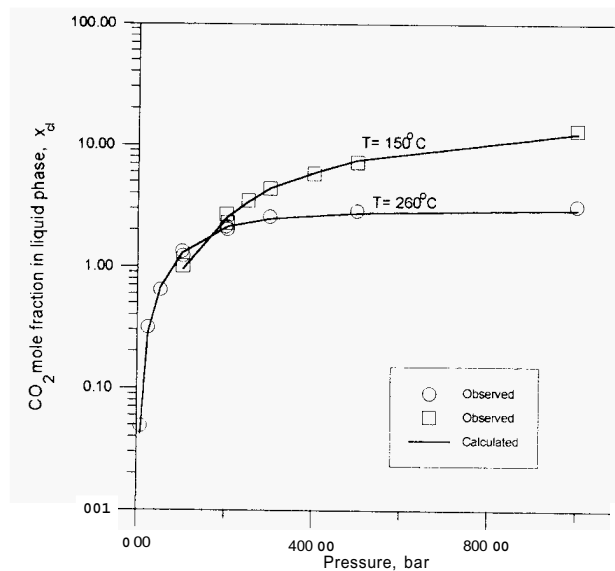


Figure 2 Peng-Robinson phase behavior prediction for H_2O-CO_2 system

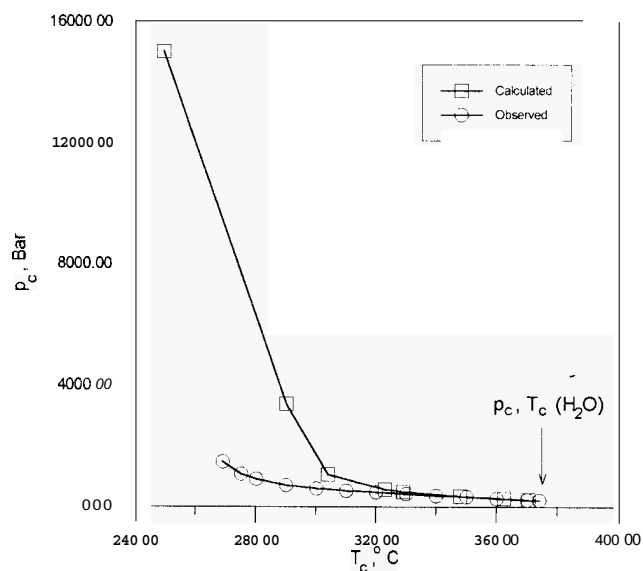


Figure 3 Peng-Robinson critical point prediction for H_2O-CO_2 system

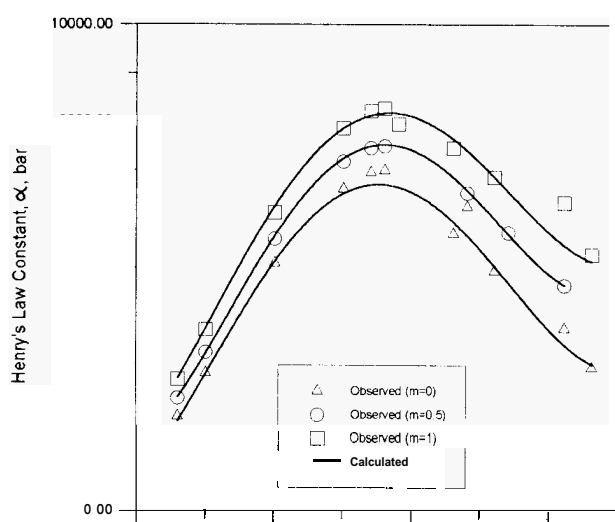


Figure 4 Henry's Law constant estimations for salt solutions

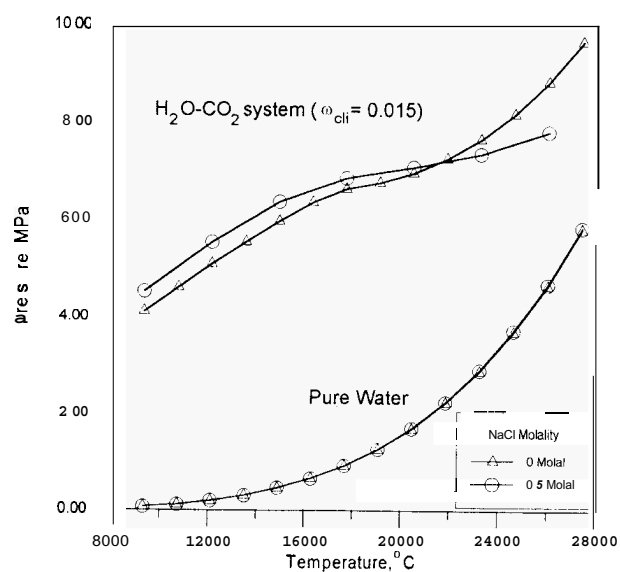


Figure 5 Phase diagram of a typical geothermal fluid system

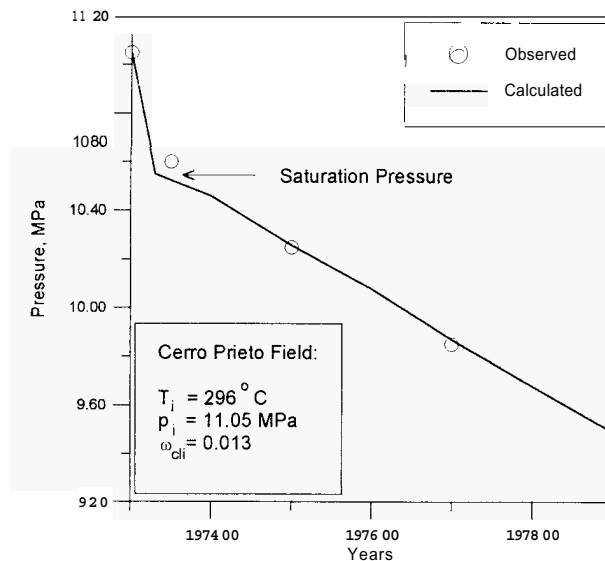


Figure 6: History matching for Cerro Prieto Field

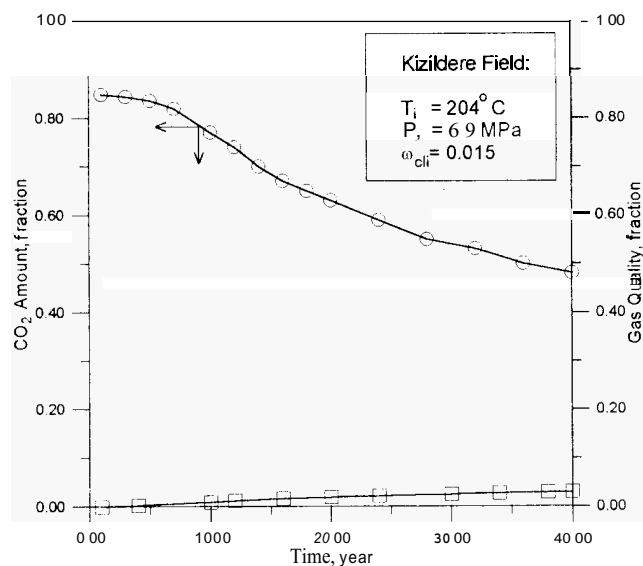


Figure 7 Estimation of CO₂ amount/gas quality history for the Kizildere Field

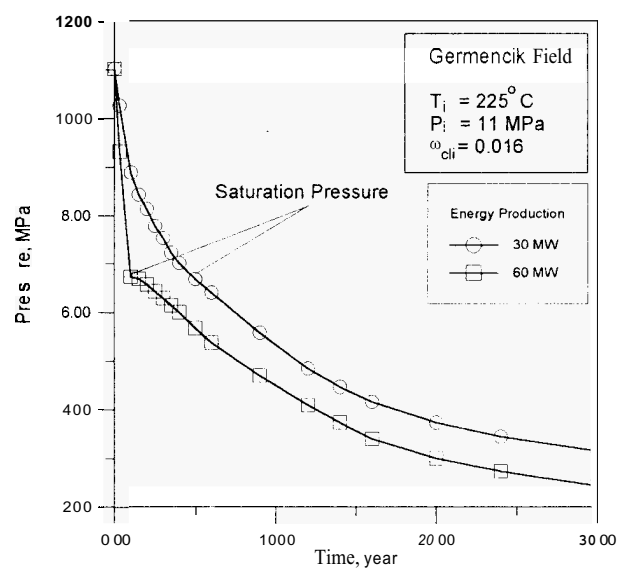


Figure 8 Reservoir performance study for Germencik Field

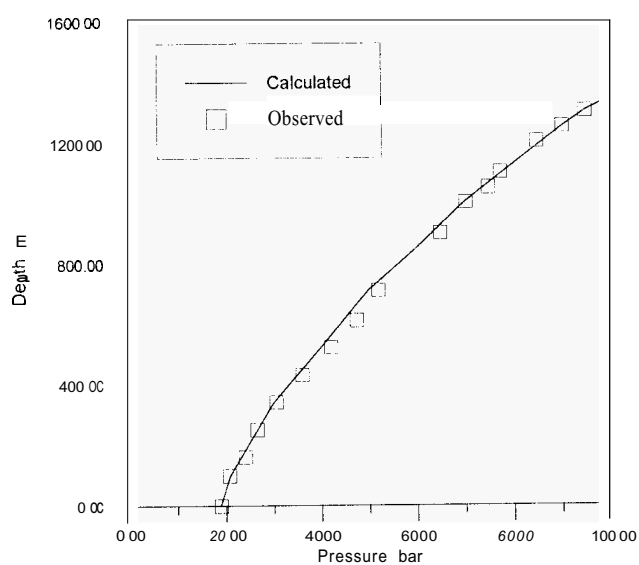


Figure 9 Depth-pressure profile match for Well W2-2 (Barelli et al 1982)

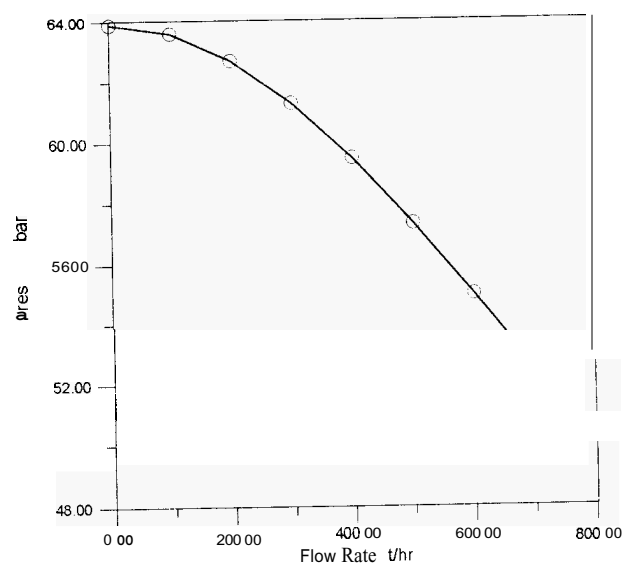


Figure 10 Estimated pressure-flow rate relationship for Kizildere Field at bottomhole