ReactVessel: An ActiveX Component in Visual Basic for Numerical Simulation of H_2O-CO_2 Interaction in a Geothermal Reservoir

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ABSTRACT

An ActiveX component, ReactVessel, is written in Visual Basic 6.0 in order to study the H_2O-CO_2 interaction in a geothermal reservoir. The reservoir is considered as a reaction vessel of constant volume, which contains a varying amount of H_2O, CO_2 and alkalinity, caused by the addition of acid HCl and base NaOH. There may be three phases in the Reaction Vessel: liquid, vapor and solid. The minerals $NaHCO_3$, Na_2CO_3 and NaOH may precipitate only in the extreme case while all the water is converting into the vapor phase or when there is an initial high concentration of the minerals in the liquid phase. However, the solid phase is not considered here since the thermodynamic data of the solid species are not available at high temperature (T) and pressure (P).

Although there is only one independent variable from T and P, both T and P increase along the saturation curve. Therefore, the equilibrium constants are fitted in a quadratic polynomial of P and inverse of T. Using ReactVessel a demonstration program is developed in order to simulate the reservoir characteristics during the heating and exploitation stage. The pressure in the reaction vessel is, in general, first controlled by CO_2, then by water vapor and in the last stage again by CO_2, while all the water is converting to the liquid phase.

On extracting vapor from the reaction vessel, the total amount of CO_2 decreases, while it remains constant on extracting liquid phase. In other words, CO_2 remains mostly in the vapor phase except for highly alkaline fluid. The variation of gaseous species concentration with time may provide useful information on the geothermal reservoir fluid characteristics.

1. INTRODUCTION

Geothermal systems are formed as a result of hot rock and meteoric water (or seawater in some cases) interaction in the upper crust. The meteoric water infiltrates deeply through faults and factures and recovers heat from the hot country rocks through mainly convective process. During the process it dissolves some minerals. Similarly, there may be input of some magmatic components like CO_2, H_2S, SO_2, HCl, etc. into the geothermal fluid. Thus, the composition of geothermal fluid is a consequence of complex processes in its reservoir.

Verma (2002) presented a simplified algorithm combining the approaches, used by geochemists and reservoir engineers, for the CO_2-H_2O interaction modeling in a geothermal reservoir. From the reservoir engineering point of view, the influence of non-condensable gases and salts on the power production by geothermal systems is discussed by Michaelides (1982) and Michaelides and Shafaie (1986). They discuss the phase equilibrium in the reservoir. It consists of:

a.) heat transfer between any two phases

b.) displacement of a phase boundary

c.) mass transfer of any component in the system across a phase boundary.

They do not consider the chemical reactions among species in the geothermal reservoir. However, the CO_2 in the solution presents itself in the form of carbonic species and its distribution between vapor and liquid phases also depends on pH. Verma (2002) considered the temperature dependence of the pertinent equilibrium constants along the saturation curves, which has been used in most of the commercial computer programs.

In nature, a chemical system is not always along the saturation curve. For example, the conditions of P and T in many geothermal systems are in the superheated steam regions such as at Geysers, USA, in the compressed liquid regions such as at Los Azufres, Mexico, and in the supercritical fluid regions such as at Los Humeros, Mexico. It is well known that petroleum reservoirs have higher pressures than the saturated pressures corresponding to their temperatures. Similarly, there is high P at the bottom of seas and oceans, whereas their T is, in general, 0ºC. Verma (2002) simulated numerically the CO_2-H_2O heating in a geothermal reservoir and found that the system was not always along the saturation curve. Thus, the T and P dependence of all the pertinent equilibrium constants in a geothermal system is needed.

Most of the geochemical modeling programs work along the liquid-vapor saturation curve. Initially, we also fitted the equilibrium constants as a function of T (Verma, 2002), so there were some inconsistencies in the results for the conditions of P and T faraway from the saturation curve. Therefore, the equilibrium constants are refitted as a function of T and P. Thus this is an extension of previous works where T and P are considered as independent variables instead of T (or P).

In this work an ActiveX component, ReactVessel in Visual Basic 6.0 is developed in order to study the H_2O-CO_2 interaction in a geothermal reservoir. The geothermal reservoir is simplified as a constant volume reaction vessel containing water, carbon dioxide and alkalinity (strong base NaOH and/or strong acid HCl). A systematic study is presented on heating reaction vessel with a varying amount of water, carbon dioxide and alkalinity. Similarly, the variation of physical-chemical characteristics of the fluid on extracting a constant amount (mass) from vapor and liquid phases in the container is studied.

2. FUNDAMENTALS

2.1 CO$_2$ Chemistry

To develop an algorithm for H$_2$O-CO$_2$ heating in a constant volume reaction vessel, the PVT characteristics of water and the carbonic system chemistry are required. The basic chemistry of carbonic system is well documented in textbooks on aquatic chemistry (e.g. Stumm and Morgan, 1981). Table 1 summarizes the equations involved in the CO$_2$ chemistry for closed and open systems.

Table 1: The equations for a carbonic system (after Verma 2002)

Closed System

Known parameters:	C_T, alkalinity (alk)
Species:	H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-

Equations:

1. $K_1 = \dfrac{[H^+][HCO_3^-]}{[H_2CO_3]}$

2. $K_2 = \dfrac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$

3. $K_W = [H^+][OH^-]$

4. $C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

5. $alk = [OH^-] - [H^+] + [HCO_3^-] + 2[CO_3^{2-}]$

Equation solution:

On solving the equation 5 for H^+ (pH), we get the following solution:

$[H_2CO_3] = C_T \cdot \alpha_0$ $[H^+] = 10^{-pH}$

$[HCO_3^-] = C_T \cdot \alpha_1$ $[OH^-] = 10^{-(pK_W - pH)}$

$[CO_3^{2-}] = C_T \cdot \alpha_2$

Where

$\alpha_0 = \dfrac{1}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}$ $\alpha_1 = \dfrac{\frac{K_1}{[H^+]}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}$ $\alpha_2 = \dfrac{\frac{K_1 K_2}{[H^+]^2}}{1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}}$

Open system

Known Parameters	Partial pressure of atmospheric CO$_2$ (p_{CO_2}) and alkalinity (alk)
Species:	$CO_{2(g)}$, H_2CO_3, HCO_3^-, CO_3^{2-}, H^+, OH^-
Equations:	Equations 1 to 5 are same as for the closed system

6. $K_H = \dfrac{[H_2CO_3]}{p_{CO_2}}$

Equation solution:

$[H_2CO_3] = K_H \cdot p_{CO_2}$ $C_T = K_H \cdot p_{CO_2} / \alpha_0$

$[HCO_3^-] = \dfrac{K_1}{[H^+]} K_H \cdot p_{CO_2}$ $[H^+] = 10^{-pH}$

$[CO_3^{2-}] = \dfrac{K_1 K_2}{[H^+]^2} K_H \cdot p_{CO_2}$ $[OH^-] = 10^{-(pK_W - pH)}$

In the case of heating in a constant volume reaction vessel, the distribution of CO$_2$ is governed by the partial pressure of CO$_2$ in the vapor and liquid phases. The equation is the following:

$$p_{CO_2} = \frac{[H_2CO_3]}{K_H} = \frac{n_{CO_2(Vapor)} RT}{V_{vapor}} \qquad (1)$$

where $n_{CO2\ (vapor)}$ is the number of mole of CO$_2$ in the vapor phase, R is gas constant and T is absolute temperature.

2.2 Thermodynamic constants

In order to deal with the chemical modeling of a natural system or in a laboratory, it is first required to find the temperature and pressure dependence of the equilibrium constants of all the pertinent chemical reactions. In our system of CO$_2$-H$_2$O with varying amounts of alkalinity, caused by the addition of HCl and/or NaOH, there may exist three phases: liquid, vapor and solid. In the liquid phase there may be H$_2$O, H$^+$, OH$^-$, H$_2$CO$_3$(CO$_2$), HCO$_3^-$, CO$_3^{2-}$, Na$^+$, Cl$^-$ and some complexes of the species. The difference between the concentration of Na$^+$ and Cl$^-$ as a consequence of the addition of HCl and NaOH is considered as initial alkalinity. The formation of complexes is not considered here. Thus we need the values of the dissociation constants of water (K$_W$) and carbonic acid (K$_1$ and K$_2$) and Henry's constant of CO$_2$ (K$_H$) at given T and P.

Figure 1 shows the values of dissociation constants for water (K$_W$) and carbonic acid (K$_1$ and K$_2$) and Henry's constant (K$_H$) for CO$_2$ along the water saturation curve. The values of K$_W$, K$_1$ and K$_2$ up to 300ºC are taken from Henley et al. (1984). Sander (1999) compiled the values of Henry's constant for many gases and posted them in an Internet web page. The values of K$_H$ are taken from his work.
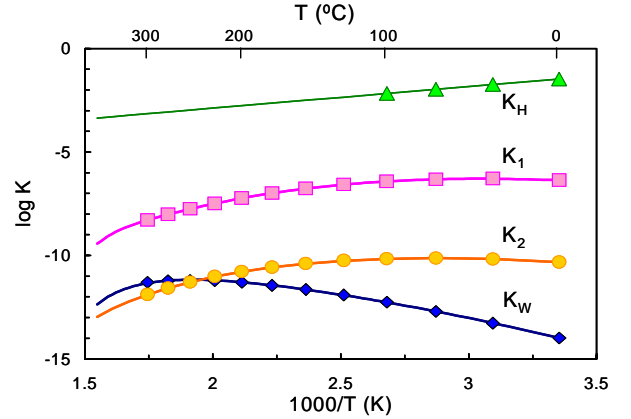

Figure 1: Values of dissociation constants for carbonic acid (K$_1$ and K$_2$) and water (K$_W$) and Henry's constant K$_H$ for CO$_2$. The data were fitted in a quadratic polynomial of P and inverse of T (Verma 2004).

There is only one independent variable (say from T and P) along the liquid-vapor saturation curve. However both of them are varying. In general, the chemical equilibrium constants are fitted as function of T along the saturation. Verma (2003a) showed that the quartz solubility data fitted well in a quadratic function of P and inverse of T. Similarly, Verma (2004) showed that the values of K$_W$ along the saturation curve were reliable. He used the fitted quadratic polynomial function to derive the thermodynamic consistent values of K$_W$ in the compressed liquid region. Here the values of all the equilibrium constants were fitted in the following quadratic polynomial of T (K) and P (MPa):

$$\log K = a + b\frac{1}{T} + cP + d\frac{1}{T^2} + e\frac{P}{T} + fP^2 \qquad (2)$$

where a, b, c, d, e, and f are coefficients. The values of the coefficients are given in Table 2.

Table 2: Values of the coefficients of the quadratic polynomial equation (2) for the dissociation constants of carbonic acid (K_1 and K_2) and water (K_W) and the Henry's constant for CO_2.

Coef.	K_1	K_2	K_W	K_H
a	-13.787	-16.476	-10.3946	-4.9644
b	4932.700	4490.311	797.992	1.0423E3
c	0.47664	0.25677	-0.11343	
d	-8.1040E5	-7.9232E5	-5.5744E5	
e	-2.9921E2	-1.9846E2	2.5048E1	
f	-3.4304E-3	-9.2798E-4	-4.9319E-4	

The values of K_H are available below 100ºC; therefore those were fitted only in a straight line. We are working to compile all the CO_2 solubility data and calculate the values of K_H at high temperature. The fitted polynomials are also shown in Figure 1 and extrapolated up to the critical point of water along the saturation curve.

In the vapor phase, the amount of CO_2 is controlled by Henry's law. The amount of water is calculated through the PVT characteristics of water (Wagner and Pruβ 2002, Verma 2003b). The presence of HCl vapor in the vapor phase is possible when whole water is converted into vapor and when originally there was an excess of HCl. The second possibility is very low pH (<-2) of the liquid phase. Both these extreme cases will not be discussed here.

The values of solubility products for NaOH, $NaHCO_3$ and Na_2CO_3 are taken from Perry et al. (1998) and are fitted in quadratic polynomials and extrapolated up to 374ºC (Figure 2).
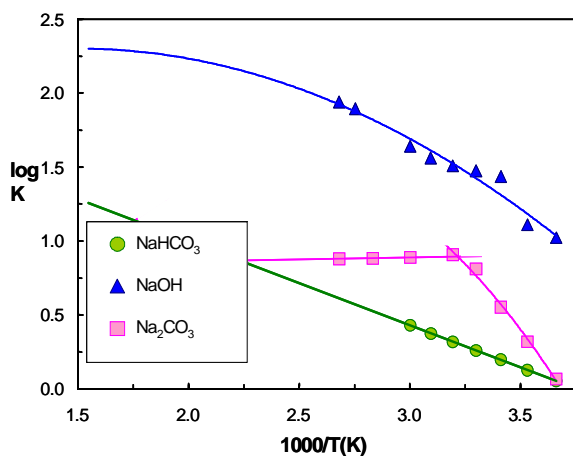

Figure 2: Values of solubility product for $NaHCO_3$, Na2CO3 and NaOH (taken from Perry et al. 1998).

The polynomials for NaOH and $NaHCO_3$ are in accordance with the corresponding polynomials obtained by the Geochemist's Workbench computer program (Bethke, 1998). The Geochemist's Workbench does not deal with the Na_2CO_3 mineral. Similarly, the solubility product values from Perry et al. (1998) also are not very reliable. However, the values of solubility product for Na_2CO_3 are higher than the corresponding values for $NaHCO_3$. Thus, the precipitation of the minerals is only possible in the extreme case when all of the water is converted into vapor phase. We will also not discuss this here.

3. DESCRIPTION OF COMPUTER PROGRAM

The computer program, ReactVessel is written in Visual Basic 6.0 as an ActiveX component in the library "MyPrograms". An ActiveX component is a server application that exposes its functionality through an interface consisting of properties, methods and events. Programmers may access the module within their projects in any language that supports OLE (Object Link Embedding) in the Windows environment. This approach also avoids name conflicting among various variables as the object variables are identified together with an object name. Verma (2003b) explained the use of an ActiveX component, SteamTables95 in a MS-Excel Worksheet. The ReactVessel can be implemented in MS-Excel using the same procedure described by Verma (2003b).

The ReactVessel has properties: Temperature, Pressure, Volume, H_2O, CO_2, alk, Vapor, Liquid, ExtractVapor, and ExtractLiquid, and methods: Update and ExtractUpdate. The object, Vapor, has properties: volume, H_2O, pH_2O (partial pressure of water), CO_2 and pCO_2 (partial pressure of CO_2). Similarly, the properties of the object Liquid are Volume, H_2O, alk, pH, CO_{2T}, H_2CO_3, HCO_3^-, and CO_3^{2-}.

The algorithm of the program is quite simple. It starts with considering all the water as liquid only. Then the total amount of CO_2 is distributed between the liquid and vapor phase till the equation is fulfilled. If the partial pressure of CO_2 in vapor phase is less then the saturation pressure corresponding to the temperature, some water is transferred to the vapor phase and the process of CO_2 distribution is repeated. In this way we get the distribution of water and CO_2 in both of the phases. The chemical calculation procedure in the liquid phase is well documented in the textbooks (e.g. Stumm and Morgan 1981, Morel 1983). The distribution of CO_2 according to the equation (1) is useful in order to study the CO_2 chemistry in both vapor and liquid phases simultaneously.

4. RESULTS AND DISCUSSION

The geothermal reservoir is considered as a container of 10 m³ and it has different amounts of H_2O, CO_2 and alkalinity (NaOH and/or HCl). The reservoir fluid characteristics are dealt with during the heating and extracting of a small amount of fluid from the liquid and vapor phases.

First, we consider the alkaline solution (0.01 eq/kg) in the container with no CO_2 in order to verify the functionality of the ReactVessel comparing the PVT characteristics through the steam tables. Figure 3 shows the variation of P with T in the container, filled with 1000, 3105.6, and 5000 kg of the solution.
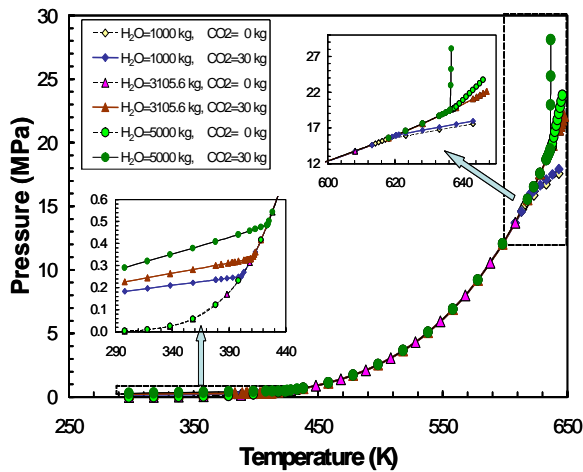
Figure 3: PT diagram for a solution (alk=0.01 eq/kg) with varying amounts of H$_2$O and CO$_2$ in the reaction vessel of 10 m3.

The PVT characteristics are similar to those of pure water obtained by the SteamTables95 (Verma 2003b). The pressure is along the saturation curve up to the point where whole water converts to vapor or liquid only. In the case of 1000 kg of water, vapor is above 343ºC. Whereas in the case of 5000 kg, there is liquid of water only above 364ºC. In the case of 3105.6 kg of water, the PT characteristics are along the saturation curve up to the critical point. Above the critical point, it should be along the critical isochor if the total specific volume is precisely equal to the critical specific volume. In practice, such precisions are difficult to obtain in the values of input parameters, reaction vessel volume, amount of water, etc.

The temperature dependence of pressure in the case of 30 kg of CO$_2$ with different amounts of alkaline water (alkalinity=0.01 eq/kg) is also shown in Figure 3. The pressure is, in general, first controlled by CO$_2$, then by water vapor and in the last stage, again, by CO$_2$ when the total specific volume is greater than the critical volume of water.

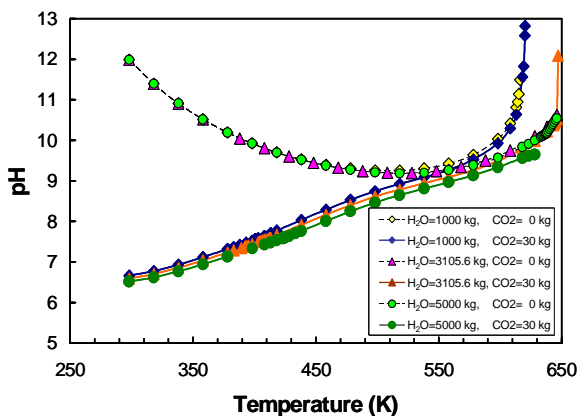Figure 4 shows the variation of pH with T for different cases.

Figure 4: pH variation of a solution (alk=0.01 eq/kg) with varying amounts of H$_2$O and CO$_2$ in the reaction vessel of 10 m^3.

When there is no CO$_2$ in the container the pH decreases first on heating, but there is increase in pH at higher

temperature for the cases of 1000 and 3105.6 kg of water. This is related to the concentrate of alkalinity, which is due to the conversion of liquid into vapor.

In the presence of CO$_2$ the pH increases with T (Figure 4). This is due to the fact that there is partition of CO$_2$ in the vapor phase. In the case of 1000 kg of water, there is a sudden increase in pH due to the concentrate of alkalinity during the conversion of liquid to vapor phase.

Figure 5 shows the variation of partial P of CO$_2$ in the vapor, which is equal to the partial P of CO$_2$ in the liquid phase in the container. The partial P is higher in the case of 5000 kg of water and it increases exponentially when the whole water is converted into liquid.
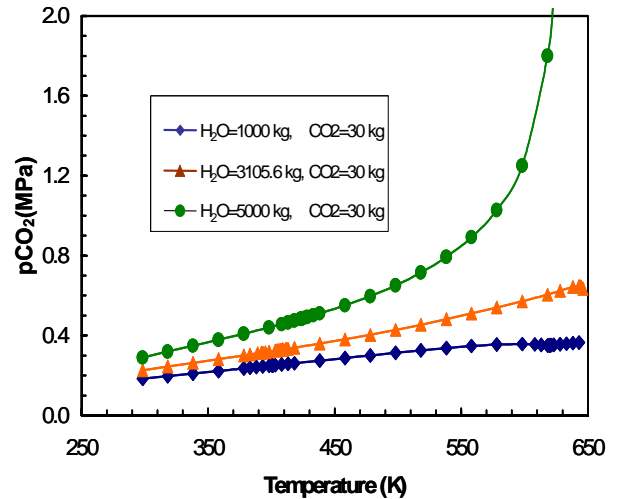

Figure 5: pCO$_2$ variation of a solution (alk=0.01 eq/kg) with varying amounts of H$_2$O in the reaction vessel of 10 m^3.

Figure 6 shows the effect of alkalinity on the amount of CO$_2$ remaining in the vapor and liquid phases on extracting 10 kg of vapor in steps from a solution containing 5000 kg of water (alkalinity= 0.01, 0.00 or -0.01 eq/kg) and 30 kg of CO$_2$ in the reaction vessel at 250ºC.
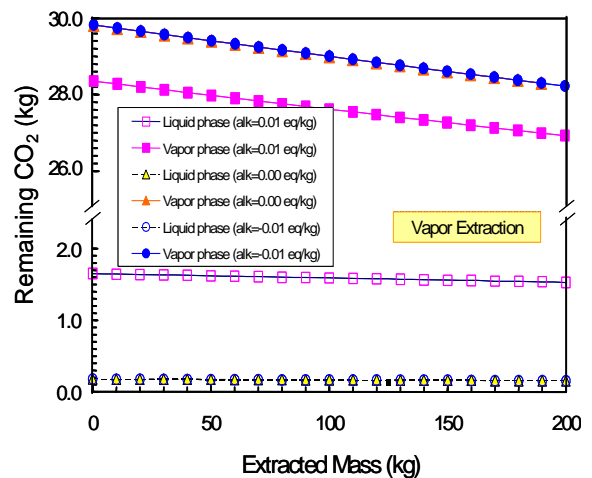

Figure 6: Effect of alkalinity on the amount of CO$_2$ in the vapor and liquid phases on extracting 10 kg of vapor in steps from a solution containing 5000 kg of water and 30 kg of CO$_2$ in a reaction vessel of 10 m^3 at 250ºC.

The amount of CO_2 decreases in the vapor phase, whereas it remains approximately constant in the liquid phase, but the total amount of CO_2 decreases (i.e. degassing occurs first).

Similarly, Figure 7 shows the effect of alkalinity on the remaining CO_2 on extracting liquid from the container. It can be observed that the total amount of CO_2 remains approximately constant. However, the amount of CO_2 increases in the vapor phase.
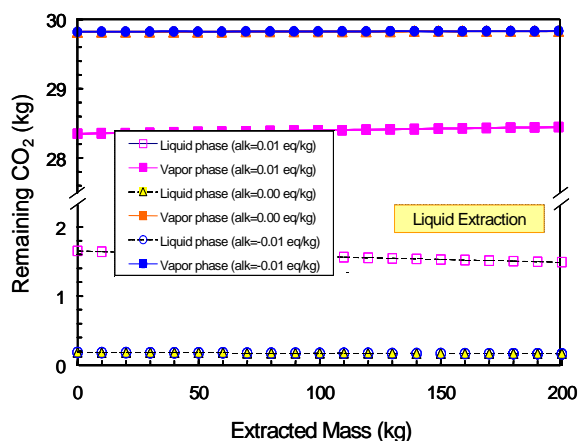

Figure 7: Effect of alkalinity on the amount of CO_2 in the vapor and liquid phases on extracting 10 kg of liquid in steps from a solution containing 5000 kg of water and 30 kg of CO_2 in a reaction vessel of 10 m^3 at 250ºC.

A study of the temporal and special variation of CO_2 in the production wells of a geothermal field may be useful to characterize the reservoir fluid characteristics. On extracting fluid from liquid phase, the amount of CO_2 in vapor phase decreases linearly in case of alkaline fluid whereas increases in case of acidic fluid. Similarly there is an increase of CO_2 in liquid phase in case of alkaline solution, whereas it decreases in case of acidic fluid. Thus the variation of gaseous species in the produced geothermal fluid may provide useful parameter for understanding the characteristics of geothermal reservoir fluid. The fundamental limitation still is the quality and availability of values of the equilibrium constants of all the pertinent chemical reactions in the reservoir at high T and P.

5. CONCLUSIONS

A numerical simulation of geothermal reservoir shows that the production and reservoir fluid characteristics depend on various factors like amount of water, CO_2 and alkalinity as well as temperature and pressure. Similarly, the production fluid characteristics are useful in predicting the characteristics of geothermal reservoir fluid.

The geothermal reservoir T and P conditions are not always along the liquid-vapor saturation curve of water. Therefore, knowledge of T and P dependence of the equilibrium constants is necessary. Here a very simplified model for the geothermal reservoir is considered. The fundamental advantage of the present algorithm is that T and P are independent variables. However, this work is still in need of further improvements in order to include the effects of other

gases and salts, and permeability and porosity of the reservoir.

It can be concluded that there is increase in the CO_2 concentration in the production fluid from a liquid dominating alkaline geothermal reservoir and vice versa. Thus the time and space variation of CO_2 could be an important tool for geothermal reservoir characterization.

REFERENCES

Bethke, C.: The Geochemist's Workbench: a user's guide to Rxn, Act2, Tact, React and Gtplot, Release 3.0, University of Illinois (1998).

Henley, R.W, Truesdell, A.H., Barton, P.B., and Whitney, J.A.: Fluid-mineral equilibria in hydrothermal systems, Society Economic Geology, El Paso, TX (1984).

Michaelides, E.E.: The influence of non-condensable gases on the net work produced by the geothermal steam power plants, *Gothermics*, **11**, (1982), 163-145.

Michaelides, E.E., and Shafaie, F.F.: A numerical study of geothermal well flow with salts and non-condensables present, *J. Energy Research and Technology*, **108**, (1986), 140-145.

Morel, F.M.M.: Principles of aquatic chemistry, John Wiley & Sons, USA (1983).

Perry, R.H., Green, D.W., and Maloney, J.O.: Perry's chemical engineers' handbook, Sixth Edition, McGraw-Hill Book Company, NY (1998).

Sander, R.: Compilation of Henry's law constants for inorganic and organic species of potential importance in environmental chemistry, Internet Web Page, http://WWW.mpchmainz.mpg.de/˜sander/res/henry.html, (1999).

Stumm, W., and Morgan, J.J.: Aquatic chemistry: an introduction emphasizing chemical equilibria in natural waters, Wiley, NY (1981).

Verma, M.P.: A numerical simulation of H_2O-CO_2 heating in a geothermal reservoir, *Proceedings,* 27th Workshop on Geothermal Reservoir Engineering, Stanford University, Stanford, CA (2002).

Verma, M.P.: QrtzGeotherm: a computer program for the quartz solubility geothermometer in moderately saline brines up to 370ºC, *Proceedings* Geothermal Research Council, (2003a).

Verma, M.P.: Steam tables for pure water as an ActiveX component in Visual Basic 6.0, *Computers & Geosciences,* **29**, (2003b), 1155-1163.

Verma, M.P.: Temperature and pressure dependence of the dissociation constant of water: a review, Revista Mexicana de Física, (2004), submitted.

Wagner, W., and Pruβ, A.: The IAPWS for the thermodynamic properties of ordinary water substance for general and scientific use. Journal of Physical and Chemical Reference Data, 31, (2002), 387-535.