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A NUMERICAL SIMULATION OF H_2O-CO_2 HEATING IN A GEOTHERMAL RESERVOIR

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ABSTRACT

A computer program in Visual Basic 6.0 is written to calculate steam tables for pure water up to 800ºC and 1400 bar. The steam tables are created as a DLL (Dynamic Link Library) object with properties: *temperature, pressure, specific volume, enthalpy and entropy for liquid and vapor phases, and liquid-vapor state.* The steam tables can be incorporated in any computer program on the Windows platform. Using the steam tables a program is written to simulate the heating of water and carbon dioxide in a geothermal reservoir with varying amount of water, carbon dioxide and alkalinity.

The minerals $NaHCO_3$, Na_2CO_3 and NaOH may precipitate only in the extreme case while all the water is converting into vapor phase. It is not discussed here.

The pressure in the reaction vessel is, in general, first controlled by CO_2, then by water vapor and in the last again by CO_2, while all the water is converting to the liquid phase.

On extracting vapor from the reaction vessel, all the CO_2 transfer to vapor phase except for highly alkaline fluid (i.e. degassing occurs first). On the other hand in case of extracting liquid, the amount of CO_2 in the extracted fluid decreases in case of acidic fluid, whereas increases in case of alkaline fluid. Thus the variation of gaseous species concentration with time may provide useful information on the geothermal reservoir fluid characteristics.

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 the geothermal reservoir.

The geochemical modeling computer programs like SOLMNEQ (Kharaka and Barnes, 1973), MINEQ (Westall et al., 1976), WATEQX (van Gaans, 1989), EQ3NR (Wolery, 1983), deal chemical speciation using input parameters as dissolved species concentration, temperature and pH; while others WATEQ (Truesdell and Jones, 1974), WATCH (Arnorsson, 1982), CHILLER (Reed, 1982), EQQYAC (Barragan and Nieva, 1989) may recalculate the pH using charge balance or H^+ mass-balance. NETPATH (Plummer, 1991) and "The Geochemsit's Workbench" (Bethke, 1998) can also take into account mixing, dilution and evaporation processes. Norstrom et al. (1979) reviewed over 30 computerized chemical modeling programs. Every modeling program had been developed for specific purposes; therefore it had its own capacities and limitations. Fundamental limitations were the form of alkalinity input and non-carbonic alkalinity correction, and pH calculation. These limitations are still not resolved completely in the improved versions of these commercial computer programs (Verma, 2000a).

From the reservoir engineering points of view the influence of non-condensable gases and salts on the power production by geothermal systems is discussed by Michaliedes (1982) and Michaelides and Shafaie (1986). They used the distribution of CO_2 between vapor and liquid phases. However, the CO_2 in solution presents in the form of carbonic species and its distribution between vapor and liquid phases also depends on pH.

In this work the geothermal reservoir is simplified as a constant volume reaction vessel containing water, carbon dioxide and alkalinity (strong base NaOH or strong acid HCl). A systematic study is presented on heating reaction vessel with 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.

Table 1: The equations for a carbonic system (Stumm and Morgan, 1981)

Closed System	
Known parameters:	C_T, alkalinity (alk)
Species:	$H_2CO_3,\ HCO_3^-,\ CO_3^{2-},\ H^+,\ OH^-$
Equations:	1. $K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$ 2. $K_2 = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}$ 3. $K_W = [H^+][OH^-]$ 4. $C_T = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$ 5. $\text{alk} = [OH^-] - [H^+] + [HCO_3^-] + 2\,[CO_3^{2-}]$
Equation solution:	On solving the equation 5 for H^+ (pH), we get the following solution: $[H_2CO_3] = C_T \cdot \alpha_0 \qquad [H^+] = 10^{-pH}$ $[HCO_3^-] = C_T \cdot \alpha_1 \qquad [OH^-] = 10^{-(pK_W - pH)}$ $[CO_3^{2-}] = C_T \quad \alpha_2$ Where $\alpha_i = \prod_{j=1}^{i} \left(\frac{K_j}{H^+}\right) \Big/ \sum_{i=1}^{2} \prod_{j=1}^{i} \left(\frac{K_j}{H^+}\right)$
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 closed system 6. $K_H = \frac{[H_2CO_3]}{p_{CO_2}}$
Equation solution:	$H_2CO_3] = K_H \cdot p_{CO_2} \qquad C_T = {K_H \cdot p_{CO_2}} \big/ {\alpha_0}$ $[HCO_3^-] = \frac{K_1}{[H^+]} K_H \cdot p_{CO_2} \qquad [H^+] = 10^{-pH}$ $[CO_3^{2-}] = \frac{K_1 K_2}{[H^+]^2} K_H \cdot p_{CO_2} \quad [OH^-] = 10^{-(pK_W - pH)}$

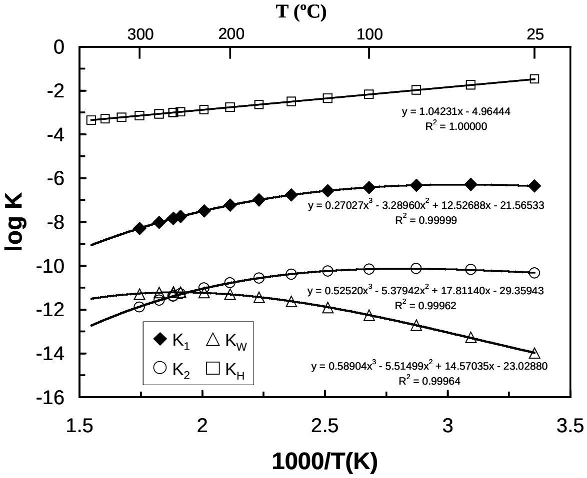

Figure 1: Values of dissociation constants for carbonic acid (K_1 and K_2) and water (K_W), and Henry's constant (K_H) for CO_2.

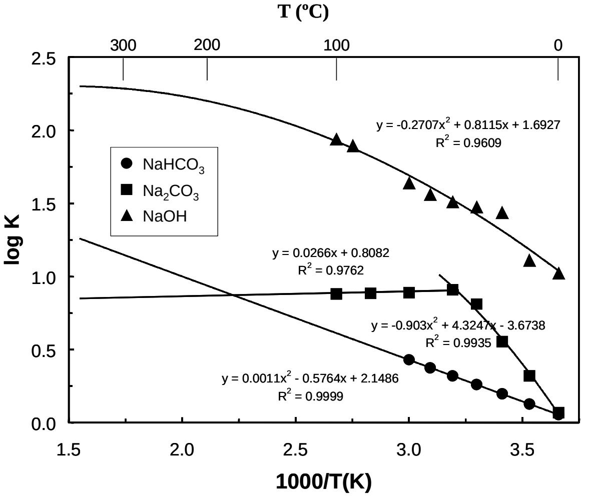

Figure 2: Values of solubility product for $NaHCO_3$, Na_2CO_3 and NaOH (taken from Perry et al, 1998).

FUNDAMENTALS

To develop an algorithm for H_2O-CO_2 heating in a constant volume reaction vessel it requires the PVT characteristics of water and the chemistry of carbonic system. In case of pure water heating, Verma (2000b) presented if the total specific volume of water was greater than the critical specific volume of water ($V_C = 3.106$ cm^3/g), there would be only vapor in the vessel at a certain high temperature below the critical temperature for water ($T<T_C$). To the contrary, when the total specific volume is less than the critical specific volume of water, there will be only liquid at a certain high temperature ($T<T_C$). In case of the total specific volume is equal to the critical specific volume of water, there will be liquid and vapor along the liquid-vapor saturation curve up to the critical point of water. For example, if there is 100 g of water in a vessel of 1000 ml. The total specific volume of water is 10 cm^3/g (i.e. greater than the critical specific volume of water). So, there will be only vapor in the vessel above 343ºC.

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. In 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 following

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

Where $n_{CO2(vapor)}$ is the number of mole of CO_2 in vapor phase, R is gas constant and T is absolute temperature.

Thermodynamic Constants

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) and are compatible with the values used in the Geochemist's Workbench (Bethke, 1998). The corresponding values are fitted in quadratic polynomials in order to extrapolate up to 374ºC along the saturation curve.

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, which fit in a straight line (Figure 1).

There is a possibility of precipitation of minerals like NaOH, $NaHCO_3$, and Na_2CO_3. The values of solubility product for the minerals are taken from Perry et al. (1998). The values are fitted in quadratic polynomials and extrapolated up to 374ºC. The polynomials for NaOH and $NaHCO_3$ are in accordance with the corresponding polynomials obtained by the Geochemist's Workbench computer program. The Geochemist's Workbench does not deal the Na_2CO_3 mineral. Similarly, the solubility product values for it 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 the water is converting in vapor phase. We will not discuss the case, here.

DESCRIPTION OF COMPUTER PROGRAM

An algorithm based on the work of Irvine and Liley (1984) and Haar et al. (1984) for steam tables for pure water up to 800ºC and 1400 bar was developed and programmed as a DDL (Dynamic Link Library) object (*SteamTables*) in Visual Basic 6.0. The *SteamTables* contains read and write properties temperature and pressure. It means that the properties can be modified outside of the object (i.e. one can input the values of temperature and pressure). Similarly, it has read only properties like volume enthalpy and entropy for vapor and liquid and the state of vapor-liquid (*StateOfWaterVapor*) and a private method *UpDate*.

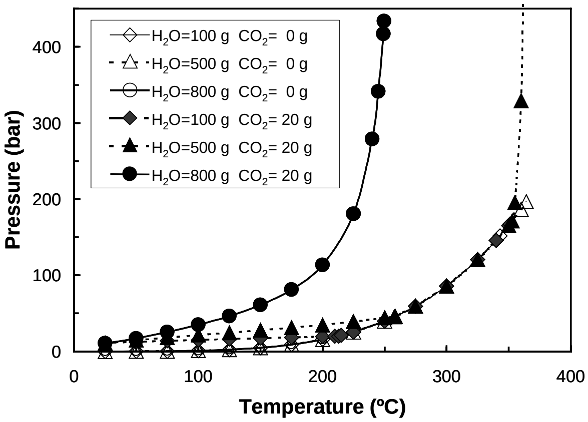

Figure 3: Pressure variation in a reaction (1000 ml) with different amount of water (having alkalinity =0.1 eq/kg) and CO_2.

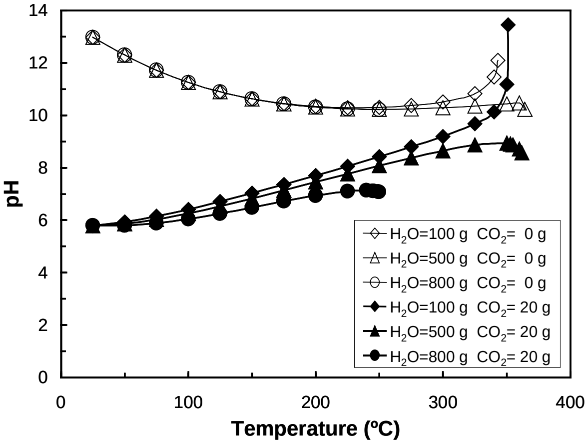

Figure 4: Temperature dependence of pH of the solution with different amount of water (with alkalinity =0.1 eq/kg) and CO_2 in a reaction vessel of 1000 ml.

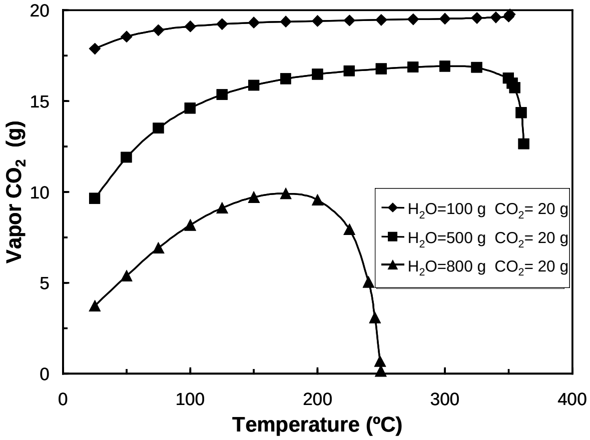

Figure 5: Amount of CO_2 in vapor phase with varying amount of water (alkalinity =0.1 eq/kg) in a reaction vessel of 1000 ml.

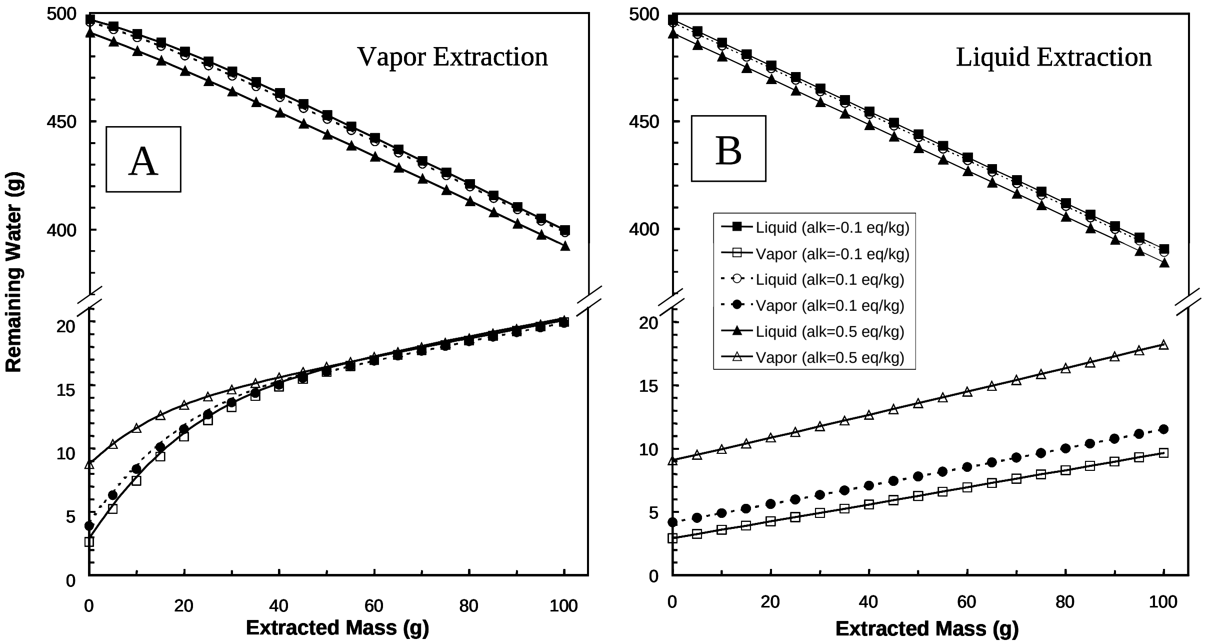

Figure 6: Effect of alkalinity on the amount of water in vapor and liquid phases on extracting 5 g of vapor or liquid in step from a solution containing 500 g of water and 20 g of CO_2 in a reaction vessel of 1000 ml at 300ºC.

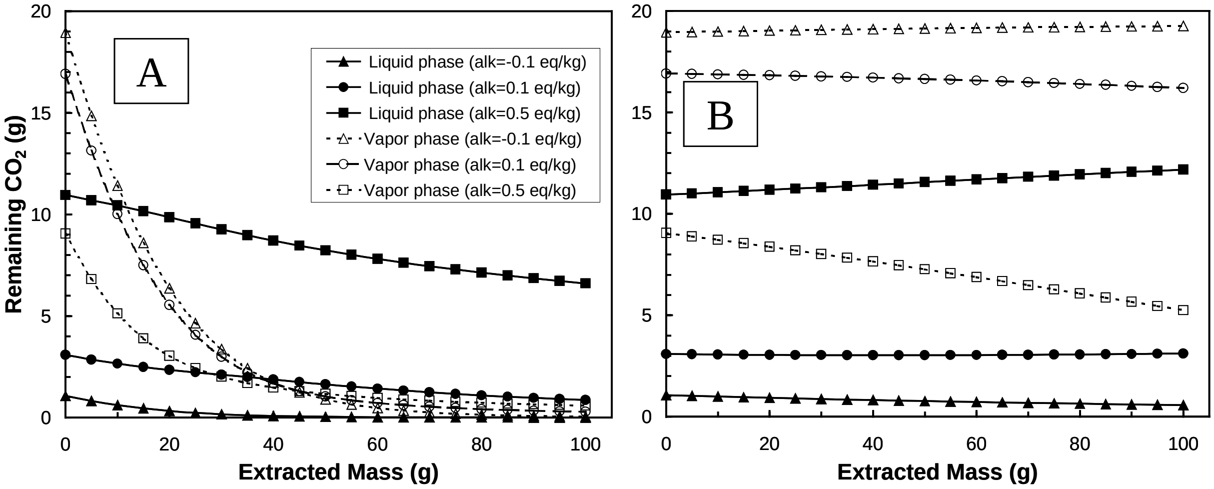

Figure 7: Effect of alkalinity on the amount of CO_2 in vapor and liquid phases on extracting 5 g of vapor (A) or liquid (B) in step from a solution containing 500 g of water and 20 g of CO_2 in a reaction vessel of 1000 ml at 300ºC.

The method *UpDate* updates the values of other properties as soon as the value of temperature or pressure is changed. The values for temperature could be between 0 to 800ºC and for pressure between 0 to 1400 bar. If the value of temperature or pressure is zero, it calculates the values of the properties along the saturation or the extended curve in the fluid region (Verma, 2000b). The property *StateOfWaterVapor* defines the region of the state of liquid and vapor.

The present calculations for the behavior of fluid in a constant volume reaction vessel are performed only along the liquid-vapor saturation of pure water. There could be compressed liquid or superheated steam in the container. To deal such cases it is also necessary to know the values of equilibrium constants under such conditions.

RESULTS AND DISCUSSION

The geothermal reservoir is considered as a container of 1000 ml and it has different amount of water, CO_2 and alkalinity (NaOH or HCl). The reservoir fluid characteristics are dealt during the heating and extracting a small amount of fluid from liquid and vapor phases.

Let us first consider the cases when the container is filled with 100, 500 or 800 ml of alkaline water (0.1 eq/kg) without CO_2 at 25ºC. Figure 3 shows the variation of pressure with temperature in the container. The pressure is along the saturation curve up to the point where whole water converts to vapor or liquid only. In case of 100 ml of water, there is only vapor above 343ºC. In case of 500 and 800 ml of water, there will be only liquid above 364 and 250ºC, respectively.

The temperature dependence of pressure in case of 20 g of CO_2 with different amount of alkaline water is also shown in Figure 3. The pressure is in general first controlled by CO_2, then by water vapor and in the last again by CO_2. In case of 800 g of water, the pressure is always controlled by CO_2. The pressure is much higher than the saturation pressure. It means that there is also need of considering the pressure dependence of equilibrium constants.

Figure 4 shows the variation of pH with temperature for the cases. 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 case of 100 ml water. This is related to concentrating of alkalinity due to conversion of liquid into vapor.

In presence of CO_2 the pH increases with temperature (Figure 4). This is due to the fact that there is partition of CO_2 in vapor phase as shown in Figure 5. In case of 100 ml of water there is sudden increase in pH due to concentrating of alkalinity during the conversion of liquid to vapor phase. In case of 500 and 800 ml of water, the amount of CO_2 increases first and then decreases. It is due to the dissolution of CO_2 in the liquid phase with increase in pressure.

Figure 6 shows the effect of alkalinity on the amount of water remaining in vapor and liquid phase on extracting 5g of vapor or liquid in step from a solution containing 500 g of water and 20 g of CO_2 in the reaction vessel at 300ºC. Similarly, Figure 7 shows the effect of alkalinity on the remaining CO_2. On extracting vapor from the container, the amount of water vapor increases whereas the CO_2 decreases exponentially in the vapor phase.

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 increase of CO_2 in liquid phase in case of alkaline solution, whereas decrease in case of acidic fluid. Thus the variation of gaseous species in the produced geothermal fluid may provide useful information about the characteristics of geothermal reservoir fluid.

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 temperature and pressure conditions are not always along the liquid-vapor saturation curve of water. Therefore, knowledge of pressure and temperature dependence of the equilibrium constants is necessary. Here a very simplified model for the geothermal reservoir is considered. Thus this work is needed to extend with including effects of other gases and salts, and permeability and porosity of the reservoir. However, it can be concluded that there is increase in the concentration of CO_2 in the geothermal production fluid from a liquid dominating alkaline geothermal reservoir and vice versa.

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