Computation of reservoir geochemical conditions from excess-enthalpy wellhead samples

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Key words: excess enthalpy, boiling, geochemical modeling, steam fraction, scale, gas phase composition, liquid phase composition, CHIM-XPT, SOLVEQ-XPT

Abstract

Geochemical modeling of geothermal fluids as they boil, cool, react with wall rocks, precipitate scale, or react with well casing is useful for understanding the chemistry of these processes, which aids in addressing production problems involving scale, corrosion, fluid reinjection, and mixing of fluids from separate wells. Modeling of excess enthalpy well fluids has been challenging because reservoir fluids are difficult to reconstruct from wellhead samples of liquid and gas. To address this problem, we reconstruct the composition of a reservoir liquid-gas mixture, then apply equilibrium calculations at reservoir conditions of pressure and temperature to compute the partitioning of species between gas and liquid, and thereby enable determination of pH, redox state and mineral saturation qualities of the liquid. The computed liquid and gas compositions become the basis for further modeling the process of interest in the system. These modeling calculations are illustrated here for a neutral-pH well in the Mahanagdong System, Philippines.

Introduction

Excess enthalpy geothermal wells produce an amount of steam relative to liquid that exceeds what could have come from boiling of liquid-alone that entered the well at depth. The steam fraction in such wells exceeds the amount produced by isoenthalpic boiling of liquid in the well, starting at the well-bottom temperature. Starting from wellhead samples of steam (gas) and liquid with excess enthalpy, the computation of pH, oxidation state, and mineral saturation characteristics in the geothermal reservoir is complicated because the wellhead steam cannot simply be replaced in the liquid to compute the reservoir liquid properties, as we do for normal enthalpy wells (e.g. Arnorsson *et al.*, 1982; Reed and Spycher, 1984). Further, the particular composition of the steam and liquid at depth cannot be known directly from the compositions at the wellhead because the minor gases partition differentially as a function of pressure and temperature. To address this issue, we use the excess enthalpy steam fraction and compositions of gas and liquid from wellhead samples to compute a single bulk analysis of the two-phase reservoir fluid composition, then compute a gas-liquid equilibrium for the reservoir pressure and temperature (Figure 1). The computed reservoir equilibrium includes the gas phase composition and the liquid composition, thereby enabling assessments of pH, oxidation state, and mineral saturation characteristics in the reservoir.

Reservoir liquid and gas chemical compositions

If the gas and liquid that enters the well are in the same proportions in the well that they are in the reservoir (which may not be true), the reservoir liquid and gas compositions can be computed at the temperature and pressure of the well bottom (T_r, P_r) from the measured wellhead gas fraction (f_s), temperature and pressure (T_s, P_s), as illustrated in Figure 1. This procedure departs from those that assume isoenthalpic boiling in the well of a pure liquid phase that have been used in the past to reconstruct geothermal and sedimentary waters (e.g. Arnorsson *et al.*, 1982; Reed and Spycher, 1984; Pang and Reed, 1998; Palandri and Reed, 2001). The difference for excess enthalpy wells is that the added-back gas phase does not all fit into the liquid at the reservoir conditions of enthalpy, T_r and P_r. Consequently, the particular amount and composition of the gas phase has to be computed for equilibrium with the aqueous phase. Although a knowledge of the wellhead enthalpy alone is enough to determine the steam fraction at depth, and from that the concentrations of dissolved salts in the liquid, the partitioning of minor gases like CO_2, H_2S, H_2, and CH_4 between liquid and gas cannot be known without further calculation. The concentrations of these gas species and their aqueous analogs critically affect pH and aqueous redox state, and thereby affect scale mineral solubilities.

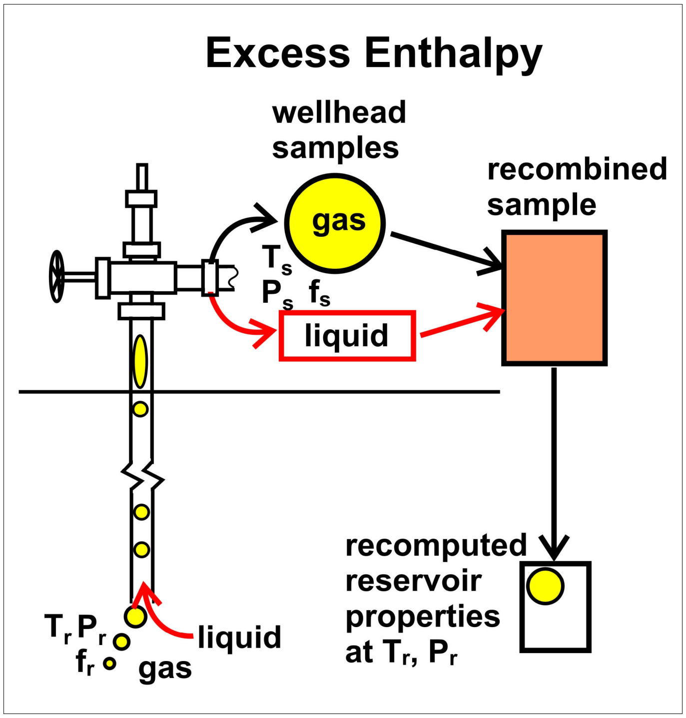

Figure 1. Excess enthalpy wells take in liquid and gas at T_r and P_r with a gas fraction f_r (fraction of gas in total fluid). Wellhead samples are collected at T_s and P_s, with gas fraction f_s, from which the bulk composition of the recombined fluid is computed. The bulk composition is re-computed for gas-aqueous equilibrium at T_r, P_r, to obtain the reservoir liquid and gas properties.

Computation of the reservoir gas and liquid properties as outlined above and in Figure 1 is carried out with computer programs SOLVEQ-XPT and CHIM-XPT (Reed, 1998). To illustrate the procedure, we apply it to a neutral-pH well in the Mahanagdong Geothermal System, Philippines, for which the critical compositional data and calculation results are shown in Table 1. Column A shows the compositions of wellhead samples of liquid and gas. Column B is the total composition of the reservoir fluid expressed in component species (Reed, 1982) obtained by recombining the gas and liquid listed in column A. The computed pH is lower in the recombined mixture (pH 4.54, col B) because the gas phase acidifies the sampled liquid (pH 5.44). Column C shows the computed equilibrium compositions of liquid and gas at the well bottom temperature of 294°C, where the gas fraction is 0.35. The computed well-bottom pH is 6.60, which is higher than pH measured in the 25°C liquid (5.44) owing mostly to lesser dissociation of carbonic acid at 294°C, even though there is more carbonic acid in the liquid at depth (i.e. it is less degassed than it is at the wellhead).

A critical difference in the gas compositions between the wellhead (Column A, Table 1) and the reservoir (Column C) is that the fractions of H_2S and CO_2 are quite different, owing to differences in gas solubilities between the reservoir and wellhead sampling point (T_r 294°C and T_s 176°C). The mole difference in H_2S and CO_2 and the corresponding differences in aqueous sulfide and carbonate species especially affect pH. The difference in gas composition is not a simple function of gas fraction, so it cannot be computed without a complete equilibrium calculation of the reservoir conditions, which are represented in Figure 2 at the high temperature (and high pressure) end of the graph (294°C, 79 bars).

Boiling of the reconstructed fluid

The Mahanagdong gas-liquid mixture in the reservoir (Column C, Table 1) can be numerically boiled in program CHIM-XPT to examine the chemical effects of the fluid depressurizing as it rises in the well and boils further (Figure 2). As the liquid-gas mixture from the reservoir boils, the gas fraction changes from its initial 0.35 at 294°C and 78 bars, to 0.52 at the sampling pressure of 9.1 bars and 176°C. If the water had risen to the surface in a spring, the gas fraction would have become 0.61 at earth surface (1.0 bar and 100°C). From an initial pH at 294°C of 6.6, pH changes to 7.4 at 100°C, i.e. this water boils with increasing pH because the escape of CO_2 to the gas phase drives a decrease in dissolved carbonic acid, as is apparent in Figures 2b and 2c. The increase in pH coupled with decreasing temperature drives precipitation of magnetite, pyrite, and amorphous silica (Figure 2a), which would appear as scale.

Summary and Conclusion

Fluids from excess enthalpy wells include gas in excess of what could have been dissolved in the liquid at reservoir conditions of pressure and temperature (P_r, T_r, Figure 1). Nevertheless, the reservoir liquid and gas compositions can be reconstructed starting from measured gas and liquid compositions and measured gas fraction (and thus enthalpy) in the sampled fluids at T_s, P_s (Figure 1). The recombined gas-liquid mixture is partitioned into calculated gas and liquid at reservoir conditions that takes account of the enthalpy measured at the wellhead. From the reservoir gas-liquid mixture, other processes of interest can be computed, such as scale formation upon boiling, or from mixing in surface pipes of acidic and neutral-pH fluids from separate wells. For the Mahanagdong well fluids, modeling of boiling produces scale of magnetite at high temperature, followed by pyrite then amorphous silica at lower temperatures.

Table 1. Mahanagdong , Philippines

	A	B	C
	Wellhead Samples	Recombined Wellhead Samples	Reservoir (well bottom) liquid & gas
Liquid phase composition (total molality *)			
pH	5.44 (25°)	4.54 (25°)	6.60 (294°)
H^+	0.0006	0.2081	0.0119
Cl^-	0.1226	0.0584	0.0889
SO_4^{2-}	0.0026	0.0024	0.0003
HCO_3^-	0.0009	0.2051	0.0112
HS^-	0.0001	0.0070	0.0014
H_4SiO_4	0.0096	0.0046	0.0064
Ca^{2+}	0.0009	0.0004	0.0004
Mg^{2+}	0.0003	0.0001	0.0000002
Fe^{2+}	0.0001	0.00003	0.00000004
K^+	0.0113	0.0054	0.0082
Na^+	0.1119	0.0533	0.0811
NH_4^+	0.0025	0.0074	0.0001
H_3BO_3	0.0041	0.0019	0.0029
wt.frac.gas			
mol%	gas		gas
H_2O	99.2594		98.9
CH_4	0.002		0.0000007
CO_2	0.6968		1.027
H_2	0.0011		0.011
H_2S	0.0279		0.0435
N_2	0.0083		0.0191
NH_3	0.0046		0.00001
HCl			0.0000003

* Concentrations are total molalities of component species as defined by (Reed and Spycher,1984).

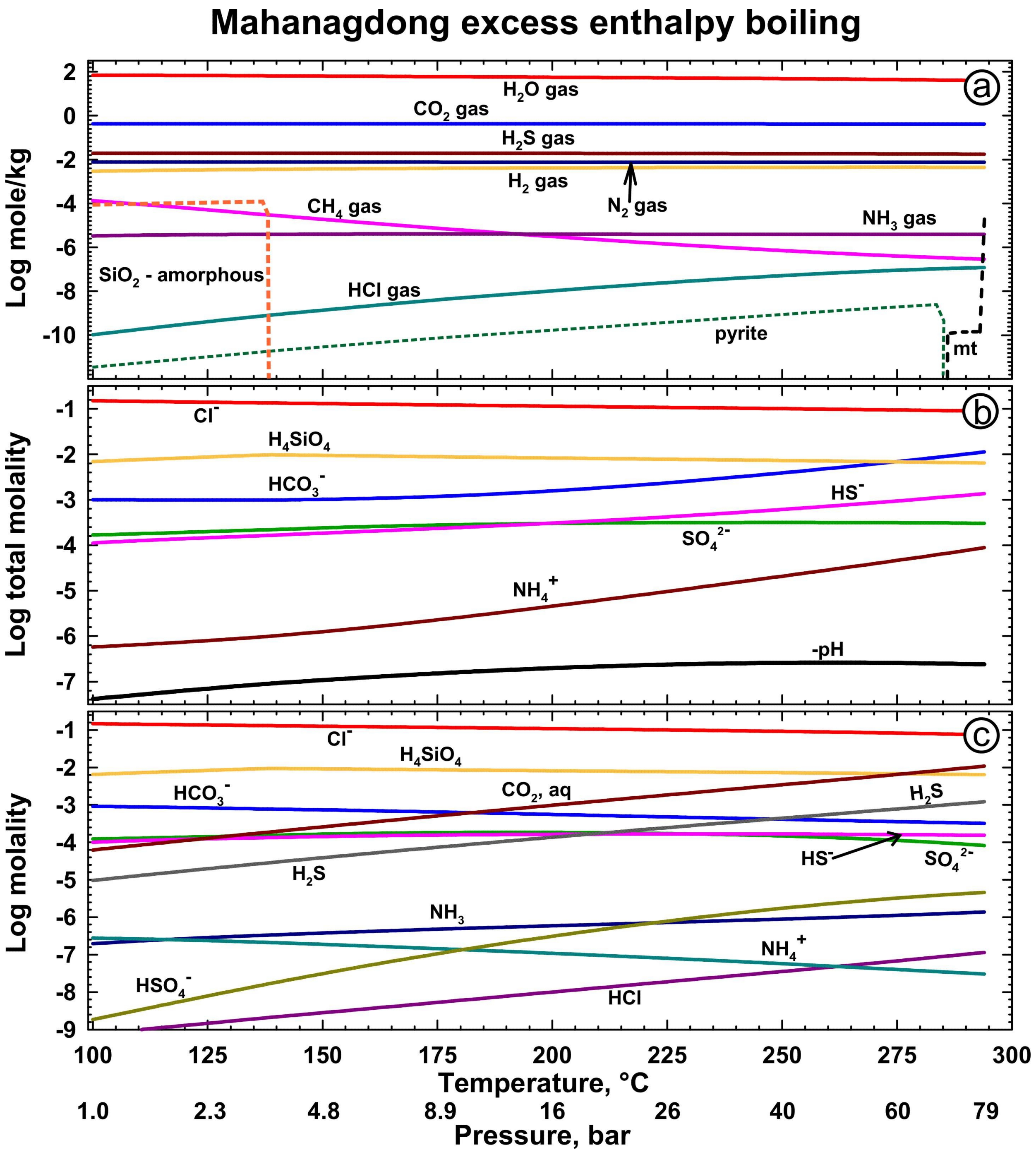

Figure 2. Boiling of the Mahanagdong reservoir liquid, starting from a condition of 0.35 gas fraction, i.e. boiling begins with a gas phase already present. The boiling computation begins at 294°C where the pressure is 79 bars, as shown on the x-axis. (a) Gas phase composition (solid curves) and mineral abundances (dashed curves). For minerals, the y-axis refers to a rate of precipitation in units of log moles per kg of initial water per degree C. The minerals are

fractionated from the liquid and gas as they form, thus are regarded as physically remaining where they precipitated and unable to back-react with the fluids. The gas phase is present at the outset (at 294°C), thus the initially large proportions of CO_2 and H_2S gases relative to H_2O in the first-separated gas are not apparent in this graph. (b) pH and composition of key components in the aqueous phase. The decrease of components HS^- and HCO_3^- reflect their displacement into the gas phase. (c) Concentrations of selected individual species in the aqueous phase that affect pH and precipitation of scale minerals.

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