

Wet-Steam Well Discharges. II. Assessment of Aquifer Fluid Compositions

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ABSTRACT

The discharge enthalpy of wells drilled into liquid-dominated high-temperature geothermal reservoirs is often elevated, i.e. higher than that of steam saturated water at the aquifer temperature. Sometimes wells drilled into such reservoirs discharge steam only. The discharged steam largely forms by depressurization boiling, but a fraction may form by conductive heat transfer from the reservoir rock to the fluid in the aquifer or be present initially in the reservoir. Two processes are considered to be responsible for generating well discharge enthalpy which is higher than that of the parent fluid. They are phase segregation and the mentioned conductive heat transfer. Phase segregation may occur in the depressurization zone around discharging wells as a consequence of the effects of capillary forces, relative permeability and the difference in the flow properties of water and steam. Production of elevated discharge enthalpy by heat transfer from the aquifer rock does not cause the chemical composition of the total well discharge to deviate from that of the initial aquifer fluid. By contrast, when phase segregation occurs, the total well discharge chemical composition differs from that of the initial aquifer fluid. Methods are outlined, which permit calculation of initial aquifer fluid compositions of wet-steam wells with elevated discharge enthalpy from analytical data on water and steam samples collected at the wellhead.

1. INTRODUCTION

Two geochemical methods have been developed to assess the initial steam fraction in aquifers producing into wet-steam wells (D'Amore and Celati, 1983; D'Amore and Truesdell, 1985; Arnórsson et al., 1990). The first method, that of D'Amore and co-workers, is based on the assumption of specific gas-gas equilibria. Both methods assume that all the steam and gas of the initial aquifer fluid, which boils, is discharged from the well. Instead of gas-gas equilibria, however, in the latter method specific mineral equilibria are considered to control the concentrations of the reactive gases (CO_2 , H_2S and H_2) used to obtain values for initial steam fractions. Arnórsson and D'Amore (2000) present a summary of these methods. Neither method presents procedures for calculation of initial aquifer water or aquifer steam compositions.

Wet-steam wells and their producing aquifers may be defined as isolated, closed or open systems between initial (undisturbed) conditions in the aquifer and wellhead. In the case of an isolated system boiling is adiabatic and the chemical composition of the total well discharge is the same as that of the initial aquifer fluid. In the case of a closed system, the chemical composition of the total well discharge is also the same as that of the initial aquifer fluid but the enthalpy is not. For the open system model, both chemical composition and enthalpy differ between initial aquifer fluid and the total well discharge. Each of the three

models are first dealt with separately and then combined. Procedures are given for calculating initial aquifer water and steam compositions for the three models mentioned and for the combined model.

2. BOILING IN PRODUCING AQUIFERS AND WELL DISCHARGE ENTHALPY

The discharge enthalpy of wells producing from liquid dominated geothermal reservoirs may be the same as that of the aquifer fluid but often it is evidently higher, and it is not uncommon that wells drilled into liquid dominated geothermal reservoirs discharge dry steam. Wells with discharge enthalpy higher than that of steam saturated water at the aquifer temperature have been termed "excess enthalpy wells".

There may be several reasons for excess enthalpy of wet-steam well discharges. One is the presence of a significant steam fraction in the initial aquifer fluid. Another is that the discharge has multiple feeds, shallow vapour dominated feeds and deep liquid dominated feeds. Further, excess enthalpy could be the consequence of processes in the depressurization zone around discharging wells.

When wet-steam wells have both liquid and steam feeds, the cause is the existence of a steam cap over liquid dominated reservoirs. Such steam caps form by gravity segregation of water and steam. Sub-vertical fracture permeability is characteristic of many drilled geothermal reservoirs. Production from liquid dominated reservoirs, such as Wairakei, New Zealand (Cloworthy, 2000) and Svartsengi, Iceland (Ármannsson, 2003), is known to have enhanced gravity segregation as evidenced by enhanced fumarole activity and the formation of shallow steam caps.

Pressure drawdown in high-temperature, liquid-dominated geothermal reservoirs, which occurs as a consequence of production, leads to extensive depressurization boiling in producing aquifers. Depressurization boiling causes cooling of the aquifer fluid, thus creating a temperature difference between the aquifer rock and that fluid. This in turn favours conductive heat transfer from rock to fluid, thus increasing the fluid enthalpy. As the fluid is two-phase, such heat transfer will not cause a change of fluid temperature but enhance boiling of the water. In this way it causes an increase in the steam to water ratio of the fluid.

Excess discharge enthalpy can also be produced in the depressurization zone by phase segregation. Such segregation is the consequence of the effects of capillary forces, the different flow properties of water and steam, and relative permeability. The mass flow rate of each phase is determined by the relative permeability and the pressure gradient, which generally is different for the two phases, as well as the densities and viscosities of water and steam. Adhesive forces between mineral surfaces and fluid, which are the cause of capillary pressure, are stronger for water than for steam, thus reducing the mobility of the liquid phase. The effect of capillary pressure becomes stronger in formations of small pores and fractures, i.e. when

permeability is low. Typical relative permeability functions are depicted in Fig. 1. They show the relationship between liquid saturation (fraction of water by volume) and relative permeability. From this figure one can read that water is immobile when water saturation is below about 0.6.

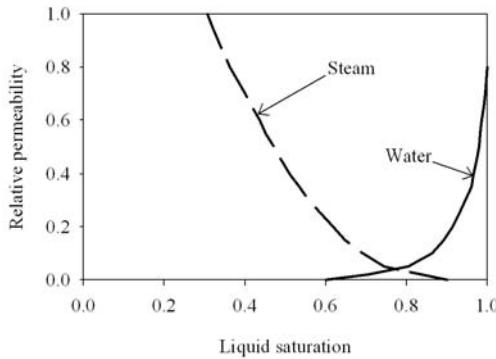


Fig. 1. Typical relative permeability functions. From Pruess (2002).

Glover et al. (1981) used the chemistry of well discharges to obtain information about the processes responsible for the development of excess enthalpy. If the concentration of a non-volatile, conservative component, like Cl, in the total well discharge stays constant, despite changes in discharge enthalpy, the cause of the enthalpy increase is heat transfer from rock to fluid in the depressurization zone (closed system model in this contribution). If the Cl concentration stays constant in the total discharge, it will approach infinity in the water phase as the discharge enthalpy approaches that of dry steam assuming, of course, that the Cl is only found in the liquid phase (Fig. 2). If, on the other hand, the concentration of a conservative component stays constant in either the water or the steam phases, despite changes in discharge enthalpy, the cause is phase segregation (open system model in this contribution). Constant concentration of a conservative non-volatile component in water at a particular vapour separation pressure means that the concentration in the total discharge approaches zero as the discharge enthalpy approaches that of dry steam (Fig. 3). The above interpretation assumes that no changes occur in the concentration of the conservative component in the fluid of the source aquifer. The approach of Glover and co-workers, which is very clear, involves the approximation that the steam to water ratio of a fluid sensing depressurization does not affect the extent to which the water boils. Such is not the case. However, in the range 10-55 bar-a vapour pressure, the enthalpy of steam stays about constant (Fig. 4) so in this range variable steam to water ratio does not affect the extent of depressurization boiling but at higher and lower pressures it will.

Changes with time in the degree of phase separation, which are reflected in changes in discharge enthalpy and cause changes in the chemical composition of total well discharges, can mask changes in the composition of the aquifer fluid that occur as a consequence of recharge into the producing aquifers. This masking effect needs to be assessed when interpreting data on well discharge compositions with respect to the type and extent of water recharge into producing aquifers. Production of excess enthalpy by phase segregation or conductive heat transfer from the rock at vapour pressure above about 55 bar-a may lead to steam condensation upon depressurization to vapour pressure between about 55 and 10 bar-a. In the same way,

production of excess enthalpy at vapour pressures between about 55 and 10 bar-a will enhance depressurization boiling below 10 bar-a. To demonstrate this, let us assume that a well discharge has developed a discharge enthalpy of 2500 kJ kg^{-1} at 320°C (112.9 bar-a vapour pressure). From steam tables and equation (1) in Arnórsson and Stefánsson (2005) one obtains a steam fraction value of 0.836 at this temperature. Depressurization to 240°C (33.5 bar-a vapour pressure) causes the steam fraction to decrease a little (by

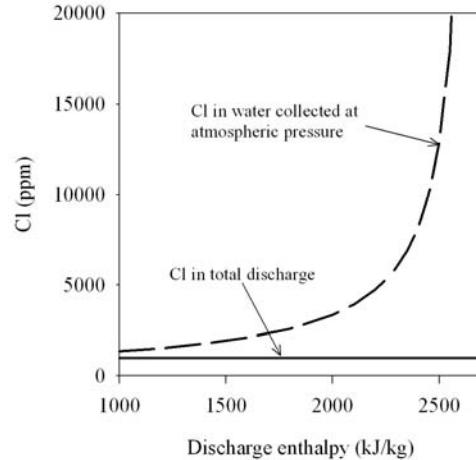


Fig. 2. Theoretical variation with discharge enthalpy in the Cl content of total discharge (solid line) and water discharged at atmospheric pressure (broken line) when excess enthalpy is produced by enhanced water evaporation due to conductive heat transfer from aquifer rock to fluid.

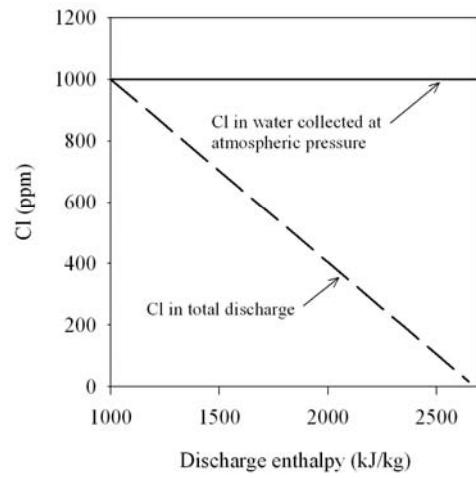


Fig. 3. Theoretical variation with discharge enthalpy in the Cl content of water sampled at atmospheric pressure (solid line) and total discharge (broken line) when excess discharge enthalpy is caused by phase segregation in producing aquifers.

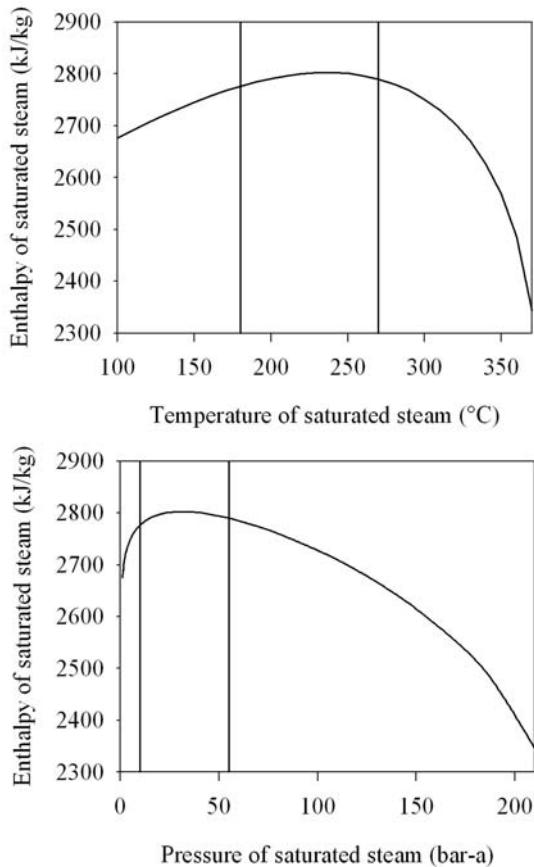


Fig. 4. Relationship between enthalpy, temperature and pressure of saturated steam. The enthalpy of steam is about constant within the ranges marked by the vertical lines, 180-270°C and 10-55 bar-a, respectively.

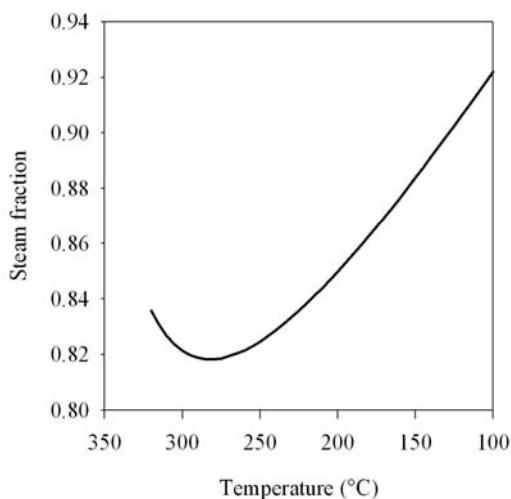


Fig. 5. Variation in steam fraction with temperature of saturated steam. Fluid enthalpy 2500 kJ kg⁻¹. Initial conditions: vapour pressure 112.9 bar-a (320°C).

condensation) to 0.829. Depressurization to atmospheric pressure (1 bar-a vapour pressure) has caused the steam fraction to increase to 0.922 (Fig. 5).

In this contribution we summarize models which allow calculation of aquifer fluid compositions for excess enthalpy wells from data collected at the wellhead. In another presentation (Arnórsson and Stefánsson, 2005), a detailed account is given of calculation of total well discharge compositions for different sampling conditions.

3. EVALUATION OF AQUIFER FLUID COMPOSITIONS

Three models are considered. The first model corresponds to an isolated system so boiling is adiabatic. In this model, the enthalpy and the total well discharge composition is the same as that of the parent aquifer fluid. The second model corresponds to a closed system. In this model the fluid flowing into wells can gain heat from the aquifer rock with the result that the enthalpy of the well discharge is higher than that of the parent aquifer fluid but the chemical composition of the total well discharge is the same as that of this fluid. The third model treats the system between well and undisturbed aquifer as open, so both the enthalpy and the composition of the total well discharge differ from that of the parent aquifer fluid. The cause of this difference is considered to be phase segregation in the depressurization zone around the well.

3.1 Isolated system model

In an isolated system, the enthalpy of the well discharge is that of the aquifer fluid. If this enthalpy equals liquid enthalpy, only liquid water is present in the aquifer but, if it is higher, steam is present in the aquifer. In the first instance the system is sub-boiling but in the second it is two-phase. For a single liquid aquifer phase, the following equation gives the concentration of component *i*, m_i^t , in the aquifer water.

$$m_i^t = m_i^{vc} X^c + m_i^{lc} (1 - X^c) \quad (1)$$

m_i^{vc} and m_i^{lc} denote the concentrations of component *i* in steam and water samples collected at vapour pressure P^c , respectively. The steam fraction, X^c , is given by

$$X^c = \frac{h^{fl} - h^{lc}}{L^c} \quad (2)$$

where h^{fl} represents the enthalpy of the aquifer water and h^{lc} and L^c the enthalpy of steam saturated water at vapour pressure P^c and its latent heat of vaporization, respectively.

Equation (1) assumes that both water and steam samples are collected at the same pressure. It is, however, common to collect water and steam samples at different pressures, i.e. steam samples at elevated pressure and water samples from the weirbox at atmospheric pressure. When this is the case, the reader is referred to Table 1 in Arnórsson and Stefánsson (2005) for calculation of m_i^t .

If steam forms part of the initial aquifer fluid, some of the chemical components will be present in significant concentrations in both phases, namely components which exist at least partly as gaseous species. The distribution of such gaseous species between the water and the steam phases is described by the distribution coefficient, D , defined as

$$D_s = \frac{n_s^v}{n_s^l} \quad (3)$$

where n_s^v and n_s^l designate the mole fractions of gaseous species s in the steam and water phases, respectively. D for such species equals $55.51/(P^t \cdot K_s)$ (see Arnórsson and Stefánsson, 2005) where P^t is the total pressure in the system (vapour pressure plus gas partial pressures) and K_s the solubility constant for gaseous species s expressed in moles $\text{kg}^{-1} \text{bar}^{-1}$. The factor 55.51 is to convert mole fraction into moles kg^{-1} .

From conservation of mass, it follows that the relationship between the concentrations of component i in the aquifer fluid (the total well discharge) and in the initial aquifer steam and the initial aquifer water are given by

$$m_i^f = m_i^t = m_i^{fv}Y + m_i^{fl}(1-Y) \quad (4)$$

where m_i^f , m_i^{fv} and m_i^{fl} designate the concentrations of component i in the aquifer fluid, the initial aquifer steam and the initial aquifer water, respectively, and Y is the initial steam fraction in the aquifer fluid.

The concentration of component i , which partly exists as a gaseous species s in both the water and steam phases, can be expressed as the sum of the concentrations of individual chemical species containing this component, i.e.

$$m_i^{fv} = m_{i,s}^{fv} + \sum_j m_{i,j}^{fv} \quad (5)$$

and

$$m_i^{fl} = m_{i,s}^{fl} + \sum_j m_{i,j}^{fl} \quad (6)$$

Here, $m_{i,s}^{fv}$ and $m_{i,s}^{fl}$ represent the concentrations of gaseous species s in the initial aquifer steam and the initial aquifer water and $\sum_j m_{i,j}^{fv}$ and $\sum_j m_{i,j}^{fl}$ are the sums of the concentrations in the initial aquifer steam and water, respectively, of all other species of this component.

Combining equations (3) and (4) yields

$$m_{i,s}^f = m_{i,s}^{fl} \left(Y \left(\frac{55.51}{P^t \cdot K_s} - 1 \right) + 1 \right) \quad (7)$$

If it is assumed that the mass of gaseous species s of component i is for all practical purposes present only in the steam under sampling conditions, it follows that $m_{i,s}^f = m_{i,s}^{vc}X^c$ so

$$Y = \left(\frac{m_{i,s}^{vc}X^c}{m_{i,s}^{fl}} - 1 \right) \left(\frac{55.51}{P^t \cdot K_s} - 1 \right)^{-1} \quad (7a)$$

where $m_{i,s}^{vc}$ denotes the concentration of gaseous species s of component i in a steam sample collected at vapour pressure P^t . X^c is defined by equation (2).

For a non-volatile component i , which does not partition significantly into the initial aquifer steam, i.e. $m_i^{fv} = 0$, it follows from equation (4) that

$$m_i^{fl} = \frac{m_i^t}{1-Y} \quad (4a)$$

For a volatile species s of component i , which is present in significant concentrations in both the initial aquifer water and steam phases, we have from equation (7) since $m_{i,s}^f = m_{i,s}^{vc}X^c$ that

$$m_{i,s}^f = m_{i,s}^{vc}X^c \left(Y \left(\frac{55.51}{P^t \cdot K_s} - 1 \right) + 1 \right)^{-1} \quad (7b)$$

Equation (7b) can be used to derive $m_{i,s}^{fl}$ for volatile species other than that used to calculate Y . Having obtained $m_{i,s}^f$, $m_{i,s}^{fv}$ can be obtained from equation (4):

$$m_{i,s}^{fv} = \frac{m_{i,s}^t - m_{i,s}^f(1-Y)}{Y} \quad (4b)$$

In deriving equation (7), the approximation was made that $D_s = m_s^v/m_s^l$, i.e. the mole fraction ratio is taken to be equal to the molal ratio (moles kg^{-1} H_2O). This approximation is reasonable for dilute aqueous solutions and for steam low in gaseous components.

The value of Y , as defined by equation (7), assumes chemical equilibrium between the initial aquifer steam and the initial aquifer water. To solve equation (7a) to obtain a value for Y it must further be assumed that the aqueous concentration of gaseous species s of component i in the reservoir water, $m_{i,s}^f$, is fixed by a specific temperature dependent chemical equilibrium, such as with a mineral buffer.

Exact solution of equation (7a) requires an aqueous speciation program, which calculates individual species concentrations and their distribution between the water and steam phases. A reasonably accurate solution of equation (7a) can, however, be obtained by assuming that the reactive volatile components (CO_2 , H_2S , H_2), which are considered to be controlled by equilibrium with mineral buffers (see e.g Arnórsson et al., 1990; 1998), form gaseous species only and that they are, for all practical purposes, present only in the steam phase under sampling conditions. In this case analysis of the steam phase gives the concentrations of these gaseous species in the total discharge.

Equations describing the aqueous concentrations of H_2S and H_2 for two minerals buffers are given in Table 1. These equations are based on thermodynamic data on the minerals from Holland and Powell (1998) except for pyrite and pyrrhotite, which are from Helgeson et al. (1978). The data on the gases are based on Hemingway and Robie (1995) and Fernandez-Prini et al. (2003). The respective reactions are:

- 1 pyrr + pyr + 2pre + 2 H_2O_l = 2epi + 3 H_2S_{aq}
- 2 4pyrr + 2pre + 2 H_2O_l = 2pyr + 2epi + 3 $\text{H}_{2,qaq}$
- 3 pyr + mag + 2 H_2O_l = 2hem + 2 H_2S_{aq}
- 4 2mag + H_2O_l = 3hem + $\text{H}_{2,qaq}$

(pyrr = pyrrhotite, pyr = pyrite, pre = prehnite, epi = epidote, mag = magnetite, hem = hematite) The equations in Table 1 are valid for one mole of gas.

It is considered best to use H_2 to calculate Y , rather than CO_2 or H_2S because these latter gases are more soluble in water than H_2 . Consequently, their concentrations in the

well discharge are less sensitive to the value of Y than that of the less soluble H_2 .

Care must be taken when selecting a temperature equation to describe the equilibrium concentration of a particular gas in the initial aquifer water. The equations in Table 1 are based on the most recently published thermodynamic data on the respective minerals and gases. Such data are under constant revision and new experimental data on the minerals are being generated at times. Equations 1 and 2 are expected to apply to waters of low salinity, such as those occurring in basalt (<500 ppm Cl), but equations 3 and 4 to higher salinity waters (>500 ppm Cl). However, this needs to be assessed for each geothermal field.

Table 1. Temperature equations describing the aqueous concentrations (moles kg⁻¹) of H_2S and H_2 at equilibrium with selected mineral buffers.

gas	Buffer	Equation: logK(gas) (T in K)
H_2S	1	$13.47 - 3375.53/T + 0.01299 \times T - 5.958 \times \log T$
H_2	2	$22.94 - 1753.24/T + 0.01750 \times T - 11.540 \times \log T$
H_2S	3	$28.31 - 4271.94/T + 0.01189 \times T - 10.751 \times \log T$
H_2	4	$50.79 - 4382.50/T + 0.02373 \times T - 20.863 \times \log T$

3.2 Closed system model

In this model, the enthalpy of the total well discharge is higher than that of the initial aquifer fluid but the chemical composition is the same. The cause of the enthalpy increase is conductive heat transfer from the aquifer rock to the aquifer fluid. This occurs in the depressurization zone around wells where depressurization boiling has caused cooling of the fluid. The steam fraction relative to the total well discharge, which forms as a consequence of conductive heat flow from the rock and those formed by depressurization boiling and initially present in the aquifer are equal to the total steam fraction of the discharge (X^c) at vapour pressure P^c , all fractions referring to the total well discharge.

$$X^c = U^e + Z^c \quad (8)$$

U^e designates the steam fraction formed by heat transfer from the rock. Z^c is the mass fraction of the aquifer fluid that exists as steam at vapour pressure P^c due to depressurization boiling. Z^c incorporates Y and is defined by

$$Z^c = \frac{h^f - h^{lc}}{L^c} \quad (9)$$

A value for Y can be obtained from equation (7a), if it is assumed that the steam formed by conductive heat transfer is free of gas. On the basis of this assumption, which seems reasonable, it follows that

$$m_i^f = m_i^t = m_i^{vc} X^c \quad (10)$$

The enthalpy of the initial aquifer fluid, h^f is given by

$$h^f = h^{fv} \cdot Y + h^{fl} (1 - Y) \quad (11)$$

and the enthalpy added to the fluid by heat transfer from the rock, h^d , by

$$h^t = h^d + h^f \quad (12)$$

where h^t is the total discharge enthalpy. Equation (8) may be written as

$$\frac{h^t - h^{lc}}{L^c} = U^e + \frac{h^f - h^{lc}}{L^c} \quad (8a)$$

so

$$U^e = \frac{h^t - h^f}{L^c} \quad (8b)$$

From knowledge of Y (from equation (7a)) and selection of initial aquifer temperature (vapour pressure), which fixes the enthalpy of the initial aquifer steam (h^{fv}) and the initial water (h^{fl}), the enthalpy of the initial aquifer fluid, h^f can be obtained from equation (11) and U^e subsequently from equation (8b).

As for the isolated system model, equation (7a) is valid for calculating Y . Also, equations (4a), (7b) and (4b) are valid for obtaining values for m_i^f (the concentration of a non-volatile component in the initial aquifer water), m_{is}^f (the concentration of a volatile species s of component i in the initial aquifer water) and m_{is}^{fv} (the concentration of a volatile species s of component i in the initial aquifer steam).

3.3 Open system model

To account for excess enthalpy of well discharges, this model assumes that the water and steam phases in the depressurization zone separate, at least partly, due to their different flow properties, the steam moving preferentially into the well. When excess well discharge enthalpy is the product of such phase segregation, the total discharge composition differs from that of the initial aquifer fluid; the total discharge is enriched in gaseous components but depleted in aqueous solutes.

By the open system model, the mass flow rate of water and steam from a wet-steam well, M^d , can be divided into two components

$$M^d = M^f - M^{lr} \quad (13)$$

where M^f and M^{lr} denote the masses of the aquifer fluid, which has boiled to produce steam flowing into a well, and boiled water retained in the aquifer, respectively. Converting mass into mass fraction relative to the total well discharge yields

$$1 = V^f - V^{lr} \quad (13a)$$

where V^f denotes the mass fraction of the reservoir fluid, which has boiled by depressurization to yield steam flowing into the well and V^{lr} the mass fraction of boiled water retained in the aquifer.

In the discussion below, it is assumed that phase segregation occurs at a specific vapour pressure, symbolized as P^g . The mass fractions of the aquifer fluid at this pressure relative to the total well discharge are expressed by the three terms in the equation

$$1 = V^f Z^g + V^f (1 - Z^g) - V^{lr} \quad (14)$$

The first term ($V^f Z^g$) denotes the initial steam fraction plus that formed by depressurization boiling to pressure P^g , the second term ($(V^f (1 - Z^g))$) is the boiled water fraction and the third (V^{lr}) the fraction of boiled water retained in the aquifer. By further depressurization boiling, to vapour pressure P^c at which a sample is collected, the mass fraction of steam (X^c) in the flowing fluid is given by

$$X^c = V^f Z^g + [V^f (1 - Z^g) - V^{lr}] Z^{gc} \quad (15)$$

Z^g is given by

$$Z^g = \frac{h^f - h^{lg}}{L^g} \quad (16)$$

and Z^{gc} by

$$Z^{gc} = \frac{h^t - h^{lc}}{L^c} - \frac{h^t - h^{lg}}{L^g} \quad (17)$$

Z^{gc} represents the steam fraction formed by depressurization boiling of the remaining flowing water fraction (the term in brackets in equation (15)) from vapour pressure P^g to vapour pressure P^c .

For a component i , which is present for all practical purposes only as gaseous species, s , in the steam phase at sampling conditions, we have $m_i^t = m_i^{vs} X^c$. Assuming that practically all of the gaseous species in the initial reservoir fluid occupies the steam phase at vapour pressure P^g , m_i^t is also equal to the concentration of this gaseous species in the initial aquifer fluid multiplied by the fraction of that fluid that has been converted into steam, or

$$m_i^t = m_{is}^{vs} X^c = m_{is}^f V^f \quad (18)$$

Combination of equations (7) and (18) by eliminating m_{is}^f yields

$$\frac{V^f}{X^c} = \frac{m_{is}^{vs}}{m_{is}^f} \left\{ Y \left(\frac{55.51}{K_s P^t} - 1 \right) + 1 \right\}^{-1} \quad (19)$$

For any particular steam sample collected at vapour pressure P^c , both X^c and V^f must be constants. Let us define this ratio of constants as R , i.e. the right hand side of equation (19). Equation (19) has two unknowns, V^f and Y . It can, however, be solved by considering simultaneously two gases, such as H_2 and H_2S . We have

$$\frac{m_{H2}^{vs}}{m_{H2}^f} \left\{ Y \left(\frac{55.51}{K_{H2} P^t} - 1 \right) + 1 \right\}^{-1} = \frac{m_{H2S}^{vs}}{m_{H2S}^f} \left\{ Y \left(\frac{55.51}{K_{H2S} P^t} - 1 \right) + 1 \right\}^{-1} \quad (20)$$

Isolating Y and rearranging yields

$$Y_{HS} = \frac{A_H - A_S}{55.51/P^t \left(\frac{A_S}{K_{H2}} - \frac{A_H}{K_{H2S}} \right) + (A_H - A_S)} \quad (20a)$$

where $A_H = m_{H2}^{vs}/m_{H2}^f$ and $A_S = m_{H2S}^{vs}/m_{H2S}^f$. The subscript HS in Y_{HS} indicates that the Y value was derived from data

on H_2 and H_2S . Having obtained a value for Y and therefore also R , V^f can be obtained from

$$R = V^f/X^c \quad (21)$$

and V^{lr} (the boiled and degassed aquifer water retained in the aquifer) subsequently from equation (13a).

It should be noted that in the case of the isolated and closed system models a single gas only is needed to obtain a value for Y as the concentration of a gas species in the aquifer fluid equals that in the total discharge; $m_{is}^f = m_{is}^t = m_{is}^{vs} X^c$. It corresponds to $V^f = 1$ (see equation (18)).

By the open system model, the concentration of a non-volatile component i in the initial aquifer fluid (m_i^f) is given by

$$m_i^f = m_i^{lc} (1 - Z^g) (1 - Z^{gc}) \quad (22)$$

We also have

$$m_i^f = m_i^{fl} (1 - Y) \quad (23)$$

Combination of equations (22) and (23) by elimination of m_i^f yields

$$m_i^{fl} = m_i^{lc} \frac{(1 - Z^g) (1 - Z^{gc})}{1 - Y} \quad (24)$$

Equation (24) allows calculation of the concentration of a non-volatile component i in the initial aquifer water according to the open system model. To obtain a value for m_i^{fl} , Y , Z^g and Z^{gc} must be obtained from equations (20a), (16) and (17), respectively.

As the concentrations of the reactive gases, H_2 and H_2S , in the initial aquifer water (m_{is}^{fl}) are assumed to be fixed by equilibrium with a specific mineral buffer for the derivation of Y , their concentrations in the aquifer steam is given by an equation analogous to equation (4):

$$m_{is}^{fv} = \frac{m_{is}^{vs} X^c - m_{is}^{fl} (1 - Y)}{Y} \quad (25)$$

because, in the open system model, the mass of all gaseous species present in the initial aquifer fluid is discharged from the well and all the gas is present in the steam at the sample collection vapour pressure P^c . The concentration of other gases (not used to obtain Y) in the initial aquifer water can be obtained from equation (7b) and subsequently m_{is}^{fv} for these gases from equation (25).

Some components, such as carbonate carbon, do not only form gaseous species, which are present in significant concentrations in both the aquifer water and steam phases, but many other species. An aqueous speciation program is necessary to calculate the concentrations of such components in each phase.

3.4 Combined models

The processes described by the closed system and open systems models above are both potentially operative in the depressurization zone around discharging wet-steam wells. These models can be combined in two ways. The first involves enhanced vaporization of mobile water flowing

into the well by conductive heat transfer from the aquifer rock. The second combination assumes that water held immobile on the surfaces of minerals by capillary forces, evaporates to yield steam that flows into the well. In the discussion below it is assumed that the steam formed by evaporation of capillary water is free of gas as well as the steam which forms by conductive heat transfer from the aquifer rock to the flowing fluid. It is further assumed that both phase segregation and conductive heat transfer from the rock occurs at a specific vapour pressure, symbolized below as P^g .

3.4.1 Enhanced boiling of flowing water

When the heat transfer from the aquifer rock leads to steam formation by enhanced evaporation of mobile water, the steam fraction (X^c) in the well discharge at vapour pressure P^c is given by the following modification of equation (15)

$$X^c = V^f (Z^g + U^g) + \left[V^f (1 - (Z^g + U^g)) - V^{lr} \right] Z^{gc} \quad (15a)$$

V^f , Z^g and Z^{gc} are defined by equations (13a), (16) and (17), respectively. U^g represents the steam fraction relative to the total well discharge which is produced by conductive heat transfer from the aquifer rock to the flowing fluid. Since $V^{lr} = V^f - 1$ (equation (13a)) and $V^f = RX^c$ (equation (21)), rearrangement of equation (15a) and isolation of U^g yields

$$U^g = \frac{X^c \cdot Z^{gc}}{RX^c(1 - Z^{gc})} - Z^g \quad (26)$$

To retrieve U^g from equation (26), it is necessary to calculate R , X^c , Z^g and Z^{gc} from various previous equations, i.e. R from (20a), (19) and (21), Z^g and Z^{gc} from equations (16) and (17), respectively, and X^c from an equation analogous to equation (2)

$$X^c = \frac{h^t - h^{lc}}{L^c} \quad (27)$$

The concentration of a non-volatile component i in the initial aquifer fluid, which is found in insignificant concentration in steam at vapour pressure P^g equals its concentration in the water at vapour pressure P^g multiplied by the water fraction at this pressure. This water fraction is equal to 1 minus the fraction which has been converted into steam at P^g , or $(Z^g + U^g)$, so

$$m_i^f = m_i^{lg} (1 - (Z^g + U^g)) \quad (28)$$

Upon further depressurization boiling to the sampling pressure (P^c) subsequent to phase segregation and conductive heat transfer from the aquifer rock to the flowing fluid, which has raised the enthalpy of the flowing fluid (the enthalpy of the well discharge) to h^t , the concentration of a non-volatile component in the water at vapour pressure P^g has been increased by steam formation corresponding to Z^{gc} , or

$$m_i^{lg} = m_i^{lc} (1 - Z^{gc}) \quad (29)$$

From equation (28) and (29) it follows that

$$m_i^f = m_i^{lc} (1 - (Z^g + U^g)) (1 - Z^{gc}) \quad (30)$$

The concentration of a non-volatile component i in the initial aquifer steam is taken to be zero so

$$m_i^f = m_i^{fl} (1 - Y) \quad (31)$$

Combining equations (30) and (31) yields

$$m_i^{fl} = \frac{m_i^{lc} (1 - (Z^g + U^g)) (1 - Z^{gc})}{1 - Y} \quad (32)$$

Equation (32) permits calculation of the concentration of a non-volatile component i in the initial aquifer water by the open system model when transfer of heat from the aquifer rock enhances boiling of the flowing water.

The concentration of gaseous species s of component i in the initial aquifer fluid is related to its concentration in the initial aquifer water and steam by

$$m_{is}^f = m_{is}^{fv} Y + m_{is}^{fl} (1 - Y) \quad (33)$$

The concentration in the total well discharge equals both $m_{is}^{vc} X^c$ and $m_{is}^f V^f$ (see equation (18)) so

$$\frac{m_{is}^{vc} X^c}{V^f} = m_{is}^{fv} Y + m_{is}^{fl} (1 - Y) \quad (33a)$$

For H_2 and H_2S , m_i^f is selected for derivation of Y assuming that the concentrations of these gases are fixed by equilibrium with a specific mineral buffer. For these gases m_i^{fv} can be obtained from

$$m_{is}^{fv} = m_{is}^{fl} \frac{55.51}{P^t K_s} \quad (34)$$

For other gases m_i^f can be obtained by combining equations (33a) and (34). This gives

$$m_{is}^f = \frac{m_{is}^{vc} X^c}{V^f} \left[Y \left(\frac{55.51}{P^t K_s} - 1 \right) + 1 \right]^{-1} \quad (35)$$

Having obtained m_i^f for a gaseous species s , m_i^{fv} can be obtained as before from equation (34). Equation (35) permits calculation of the concentration of gaseous species, other than those used to retrieve Y (H_2 and H_2S) in the initial aquifer water.

3.4.2 Enhanced boiling of capillary water

When some steam forms by conductive heat transfer to immobile capillary water, equation (13a) becomes modified as follows:

$$1 = V^f - V^{lr} + U^g \quad (13b)$$

and equation (15) becomes

$$X^c = V^f Z^g + \left[V^f (1 - Z^g) - V^{lr} \right] Z^{gc} + U^e \quad (15b)$$

We symbolize the steam formed by vaporization of capillary water as U^e to distinguish it from the vapour fraction which forms as a consequence of vaporization of the flowing water by conductive heat transfer from the aquifer rock (U^g). Common solution of equations (21), (13b) and (15b) and isolation of U^g yields

$$U^e = X^c \left\{ \frac{1}{1-Z^{gc}} - RZ^g \right\} - \frac{Z^{gc}}{1-Z^{gc}} \quad (26a)$$

The concentration of a non-volatile component i in the boiled aquifer water at pressure P^g , i.e. the vapour pressure at which both phase segregation and conductive heat transfer from the rock to the immobile capillary water is assumed to take place is given by

$$m_i^f = m_i^{lg} (1-Z^g) \quad (36)$$

At P^c , the pressure at which a water sample is collected we have

$$m_i^f = m_i^{lc} (1-Z^g)(1-Z^{gc}) \quad (37)$$

As the concentration of the non-volatile component in the initial aquifer steam is taken to be zero, equation (31) is valid so it follows from equation (37) that

$$m_i^f = \frac{m_i^{lc} (1-Z^g)(1-Z^{gc})}{1-Y} \quad (37a)$$

Equation (37a) permits calculation of the concentration of a non-volatile component in the initial aquifer water by the open system model when both evaporation of capillary water and phase segregation cause an increase in the total well discharge enthalpy.

As for the combined model, which assumes that conductive heat transfer from the rock enhances evaporation of the flowing water, equation (20a) is valid for obtaining Y . Hence, V^f can be retrieved from equation (21) and X^c from equation (27).

As m_{is}^f for H_2 and H_2S are taken to be fixed by equilibrium with specific mineral buffers to retrieve Y , m_{is}^{fv} for these gases can be obtained from equation (34). For other gases, the concentration in the initial aquifer water (m_{is}^f) can be obtained from equation (35) and their concentration in the initial aquifer steam (m_{is}^{fv}) subsequently from equation (34).

4. SELECTION OF AQUIFER TEMPERATURE

The value of a gas solubility constant (K_s) is temperature dependent and so are the values of m_i^f for H_2 and H_2S which are assumed, for the derivation of Y , to be controlled by temperature dependent equilibria with a specific mineral buffer. Further, P^t depends on temperature; it is approximately equal to the pressure of saturated vapour. Therefore, a temperature value must be selected for solution of equations (7a) and (20a). This temperature is that considered to prevail in the source aquifer under initial conditions, i.e. beyond the depressurization zone around producing wells. There are essentially two ways of selecting this value. Firstly, one may use a geothermometer temperature or a measured temperature downhole in a thermally stabilized well at the depth level of the main pro-

Table 2. Isolated and closed system models - Equations for calculation of initial steam fraction in the aquifer fluid (Y), the steam fraction in the total well discharge generated by heat flow from the rock (U^e) and component concentrations in the initial aquifer water and the initial aquifer steam.

A ^a	Equation
1	$m_i^t = m_i^{vc} X^c + m_i^{lc} (1-X^c)$ (1)^b
2	$Y = \left(\frac{m_{is}^{vc} X^c}{m_{is}^{f1}} - 1 \right) \left(\frac{55.51}{P^t \cdot K_s} - 1 \right)^{-1}$ (7a)^c
3	$m_i^{f1} = \frac{m_i^t}{1-Y}$ (4a)^d
4	$m_{is}^{f1} = m_{is}^{vc} X^c \left(Y \left(\frac{55.51}{P^t \cdot K_s} - 1 \right) + 1 \right)^{-1}$ (7b)
5	$m_{is}^{fv} = \frac{m_i^t - m_{is}^{f1} (1-Y)}{Y}$ (4b)

^aTerm to be calculated. 1: Concentration of component i in total well discharge, 2: Steam fraction in initial reservoir fluid, 3: Concentration of non-volatile component in initial reservoir water, 4: Concentration of gaseous species s of component i in initial aquifer water, 5: Concentration of gaseous species s of component i in initial aquifer steam.

^bIf water and steam samples are collected at different pressures, use the appropriate equation in Table 1 of Arnórsson and Stefánsson (2005) to obtain m_i^t .

^cTo obtain a value for m_{is}^f use equation (2) or (4) in Table 1 or another equation considered to be more appropriate.

^dValid for a non-volatile component.

ducing horizon. In the first case, it is assumed that no chemical reactions occur in the depressurization zone with respect to those components which constitute the respective geothermometer. In the second case, it is assumed that the measured temperature downhole in a thermally stabilized well provides the aquifer temperature. Evaluation of aquifer temperature by both methods is only an approximation at best. In the case of a two-phase reservoir with an inclined aquifer, such as a fault or fracture, the temperature in the aquifer varies with depth as dictated by pressure. The discharging well may withdraw fluid from deeper and hotter or shallower and cooler levels of the producing aquifer. The use of geothermometers, which are based on component ratios, such as the Na/K geothermometer, is straight forward because the ratio is not affected by the boiling processes. This is, on the other hand, not so for geothermometers based on component concentrations, such as the quartz geothermometer. An iterative process is required to obtain the geothermometer temperature for these. Besides, some re-equilibration involving the geo-

Table 3. The open system model - Equations for calculation of initial steam fraction in the aquifer fluid (Y), the fraction of boiled water retained in the aquifer (V^{lr}) and the concentrations of non-volatile components (m_i^{f1}) in the initial aquifer water and gaseous species in the initial aquifer water (m_{is}^f) and steam (m_{is}^{fv}).

A ^a	Equation
1	$Y_{HS} = \frac{A_H - A_S}{55.51 \left(\frac{A_s}{K_{H2}} - \frac{A_H}{K_{H2S}} \right) + (A_H - A_S)} \quad (20a)$
2	$V^f = \frac{m_{i,s}^{v,c} X^c}{m_{i,s}^{f,l}} \left\{ Y \left(\frac{55.51}{K_s P^t} - 1 \right) + 1 \right\}^{-1} \quad (19)$
3	$V^{l,r} = V^f - 1 \quad (13a)$
4	$m_i^{f,l} = m_i^{l,c} \frac{(1 - Z^g)(1 - Z^{g,c})}{1 - Y} \quad (24)$
5	$m_{i,s}^{f,l} = m_{i,s}^{v,c} X^c \left(Y \left(\frac{55.51}{P^t \cdot K_s} - 1 \right) + 1 \right)^{-1} \quad (7b)$
6	$m_{i,s}^{f,v} = \frac{m_{i,s}^{v,c} X^c - m_{i,s}^{f,l} (1 - Y)}{Y} \quad (25)$
	^a Term to be calculated. 1: initial aquifer steam fraction, 2: fraction of aquifer water relative to total well discharge which has boiled to yield steam into well, 3: fraction of boiled water retained in aquifer relative to total well discharge, 4: concentration of non-volatile component i in initial aquifer water, 5: concentration of gaseous species s in initial aquifer water (does not apply to the gases H ₂ and H ₂ S which should be used to derive a value for Y), 6: concentration of gaseous species s in initial aquifer steam.

thermometer components may occur in the depressurization zone.

Most drilled geothermal reservoirs in the world have anisotropic permeability. For such reservoirs, it is inevitable that the fluid flowing into a well is a mixture of many components that have travelled different distances at different velocities from their point of origin to the wells. For this reason, it is an approximation to select a single aquifer temperature for the aquifer fluid of a well discharge. Mixing of source fluids of significantly different temperatures results in discrepancies between geothermometer temperatures. Indeed such discrepancies may be used to recognize inflow into a well from aquifers of significantly different temperatures.

It is important to be aware of the approximations made in selecting a temperature value to retrieve Y (the initial steam fraction in the aquifer). It is advisable always to carry out a sensitivity study by calculating Y for a range of temperatures around the temperature considered to be the best choice of aquifer temperature.

Table 4. Combined closed and open system models – Equations for calculation of initial steam fraction in the aquifer fluid (Y), fraction of boiled water retained in aquifer ($V^{l,r}$), steam fraction formed by enhanced boiling of water by conductive heat transfer from aquifer rock and concentrations of non-volatile components ($m_i^{f,l}$) in initial aquifer water and gaseous species in initial aquifer water ($m_{i,s}^{f,l}$) and steam ($m_{i,s}^{f,v}$).

A ^a	Equation
	Equations valid for both versions of combined model
1	$Y_{HS} = \frac{A_H - A_S}{55.51 \left(\frac{A_s}{K_{H2}} - \frac{A_H}{K_{H2S}} \right) + (A_H - A_S)} \quad (20a)$
2	$V^f = \frac{m_{i,s}^{v,c} X^c}{m_{i,s}^{f,l}} \left\{ Y \left(\frac{55.51}{K_s P^t} - 1 \right) + 1 \right\}^{-1} \quad (19)$
3	$m_{i,s}^{f,v} = m_{i,s}^{f,l} \frac{55.51}{P^t K_s} \quad (34)$
4	$m_{i,s}^{f,l} = \frac{m_{i,s}^{v,c} X^c}{V^f} \left[Y \left(\frac{55.51}{P^t K_s} - 1 \right) + 1 \right]^{-1} \quad (35)$
	Equations valid for version involving enhanced boiling of flowing water
5	$U^g = \frac{X^c - Z^{g,c}}{R X^c (1 - Z^{g,c})} - Z^g \quad (26)$
6	$V^{l,r} = V^f - 1 \quad (13a)$
7	$m_i^{f,l} = \frac{m_i^{l,c} (1 - (Z^g + U^g)) (1 - Z^{g,c})}{1 - Y} \quad (32)$
	Equations valid for version involving boiling of capillary water
8	$U^e = X^c \left\{ \frac{1}{1 - Z^{g,c}} - R Z^g \right\} - \frac{Z^{g,c}}{1 - Z^{g,c}} \quad (26a)$
9	$V^{l,r} = V^f + U^g - 1 \quad (13b)$
10	$m_i^{f,l} = \frac{m_i^{l,c} (1 - Z^g) (1 - Z^{g,c})}{1 - Y} \quad (37a)$
	^a Term to be calculated. 1: initial aquifer steam fraction, 2: fraction of aquifer water relative to total well discharge which has boiled to yield steam into well, 3: concentration of gaseous species s in initial aquifer steam, 4: concentration of gaseous species s in initial aquifer water, 5: fraction of steam in total well discharge formed by vaporization of flowing water by conductive heat transfer from rock, 6 and 9: fraction of boiled water retained in aquifer, 7 and 10: concentration of non-volatile component i in initial aquifer water, 8: fraction of steam in total well discharge formed by vaporization of capillary water by conductive heat transfer from rock.

5. DISCUSSION

The methodology described in this contribution to calculate the initial aquifer water and initial aquifer steam compositions for wells with excess discharge enthalpy involves various simplifying assumptions. Phase segregation and transfer of heat from the aquifer rock to the aquifer fluid, when they occur, are assumed to take place at one temperature, i.e. at one pressure. In reality both must occur over a range of pressures in the depressurization zone around wells.

As already pointed out, all waters in nature are mixtures of many components. This also holds for fluids flowing into wet-steam wells. For this reason, selection of a single temperature to calculate Y (the initial steam fraction in the aquifer) should be regarded as an approximation, which is only acceptable if a well discharge largely derives its fluid from aquifers of similar temperature.

Geothermal systems are open systems. For this reason, it is always questionable how closely chemical equilibria between phases are approached. The methodology described here to obtain values for the initial aquifer steam fraction assumes certain gas-mineral buffer equilibria. The thermodynamic databases used to retrieve the equilibrium constants for such equilibria carry some error and they are under constant re-assessment and improvement by new experiments. Also, the chemical composition of some of the minerals participating in these equilibria display variable composition and information in this respect is lacking for many geothermal fields under exploitation.

Measurement of the discharge enthalpy of wet-steam wells is not very precise ($\pm 10\%$), at least when using the Russel James critical lip pressure method. For wells with only slight enthalpy excess it is advisable to measure temperature and pressure downhole in a discharging well to determine if the first level of boiling is within the well or not. If within the well, it is clear that the enthalpy of the discharge should be taken to be equal to that of steam saturated water at the temperature prevailing in the well just below the first level of boiling.

An approach that would be of interest to develop is to model the composition of well discharges rather than to assess aquifer water and aquifer steam compositions from data on water and steam samples collected at the wellhead. It is envisaged that modeling of this kind would involve the selection of several components of a specific chemical composition and temperature and their mixing in different proportions until the mixture matched the well discharge composition and enthalpy. It would be appropriate to select the minimum number of components needed to match the well discharge characteristics. The selection of component compositions should be based on a combination of arbitrary selection of conservative component concentrations and concentrations for reactive components based on specific mineral-solution equilibria in a way similar to that used in many computer codes for reaction progress modeling. It remains to be seen whether assumptions of specific mineral-solution equilibria will yield acceptable results.

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8. NOMENCLATURE

D_s Distribution coefficient for gaseous species s between water and steam; defined by equation (3).

h^d Enthalpy contribution to well discharge caused by heat transfer from rock (kJ kg^{-1}).

h^f Enthalpy of initial aquifer fluid (kJ kg^{-1}).

h^{f,l} Enthalpy of initial aquifer water (kJ kg^{-1}).

h^{f,v} Enthalpy of initial aquifer steam (kJ kg^{-1}).

h^{lc}	Enthalpy of steam saturated water at vapour sampling pressure, P^c (kJ kg ⁻¹).	m_i^{vc}	Concentration of component i in steam at vapour pressure P^c (moles kg ⁻¹)
h^{lg}	Enthalpy of water at vapour pressure P^g , the pressure at which heat transfer from rock, which enhances vaporization and/or phase segregation is assumed to have occurred.	n_s^l	Mole fraction of component i in water (moles gaseous species s / moles H ₂ O + moles all solutes)
h^t	Enthalpy of total well discharge (kJ kg ⁻¹).	n_s^v	Mole fraction of component i in steam (moles gaseous species s / moles H ₂ O + moles all solutes)
K_s	Solubility constant for gaseous species s (moles kg ⁻¹ bar ⁻¹).	P^c	Vapour pressure at which samples are collected (bar-a)
L^c	Latent heat of vapourization at sampling pressure P^c (kJ kg ⁻¹).	P^g	Vapour pressure at which heat transfer from rock, which enhances vaporization and/or phase segregation is assumed to have occurred
L^{fl}	Latent heat of vaporization of initial aquifer water (kJ kg ⁻¹).	P^t	Total pressure (bar-a)
L^g	Latent heat of vaporization at vapour pressure P^g (kJ kg ⁻¹).	R	Constant, defined by equations (18) and (20)
M^d	Mass flow of water and steam from wet-steam well (kg s ⁻¹).	U^e	Mass fraction of steam in well discharge formed by enhanced vaporization of the flowing water due to conductive heat transfer from aquifer rock.
M^f	Mass flow of aquifer fluid which has boiled to yield steam flowing into well (kg s ⁻¹).	U^g	Mass fraction of steam in well discharge formed by vaporization of immobile capillary water due to conductive heat transfer from aquifer rock.
M^{lr}	Mass flow of boiled aquifer water which separates from steam flowing into well (kg s ⁻¹)	V^f	Mass fraction of aquifer fluid which boils to yield steam into well
m_i^f	Concentration of component i in initial aquifer fluid (moles kg ⁻¹)	V^{lr}	Mass fraction of boiled water retained in the aquifer
m_i^l	Concentration of component i in initial aquifer water (moles kg ⁻¹)	X^c	Mass fraction of steam in well discharge at vapour pressure, P^c
m_i^{fv}	Concentration of component i in initial aquifer steam (moles kg ⁻¹)	Y	Initial steam fraction in aquifer relative to aquifer fluid.
m_i^{lc}	Concentration of component i in water sample collected at vapour pressure P^c (moles kg ⁻¹)	Z^c	Mass fraction of initial reservoir fluid which has vaporized by depressurization boiling to vapour pressure P^c .
m_s^l	Concentration of gaseous species s in water (moles kg ⁻¹)	Z^g	Mass fraction of initial reservoir fluid which has vaporized by depressurization boiling to vapour pressure P^g .
m_i^t	Concentration of component i in total well discharge (moles kg ⁻¹)	Z^{gc}	Mass fraction of water which has vaporized by depressurization boiling from aquifer vapour pressure to vapour pressure P^c .
m_s^v	Concentration of gaseous species s in steam (moles kg ⁻¹)		