MATHEMATICAL MODELLING OF NON-CONDENSIBLE GASES IN HOT DENSE BRINES: THE SYSTEM H_2O-NaCl-CO_2

R. McKIBBIN[1] AND A. McNABB[2]

[1] Dept. of Mathematics, Massey University, Palmerston North, NZ
[2] Maths Physics Research Ltd, Palmerston North, NZ

ABSTRACT – Previous work investigating models which describe the behaviour of brine systems (water + sodium chloride) at high temperatures and pressures is extended to include the presence of non-condensible gases. It is assumed in the model equations that the gases are represented by carbon dioxide. The consequent H_2O-NaCl-CO_2 system is supposed to have the basic characteristics of a brine system as previously studied but with a non-condensible gas added. The phase-space of this ternary system is four-dimensional; however, three-dimensional "cross-sections", imagined as cuts by surfaces of given C02 concentration, can be used to aid in visualising this. The resulting cross-section is a three-dimensional brine T-p-X phase sub-space. The characteristics of the various regions of this 3-D phase-space (McKibbin & McNabb, 1993) are presumed to still apply, but the boundaries are altered in position owing to the presence of the CO_2. Conservation equations are derived; these, together with various thermodynamic relationships and gas laws, are solved for some simple steady vertical flows. The example results provide some insights into the complex relationships between the concentrations of the various components.

1. INTRODUCTION

Our interest in the system H_2O-NaCl-CO_2 arises from questions concerning the nature of geothermal chloride waters at depth in geothermal fields, of the kind of fluid present above cooling volcanic magma releasing chloride-saturated magmatic vapours into groundwater at depth in the Earth's crust (McNabb, 1992), and about convecting hydrothermal systems on the sea floor. Knowledge of how heat is transferred to the base of such geothermal systems and how the fluid phase properties of gassy brines influence the heat transfer and the mineral transport are important for understanding geothermal and mineral deposition processes.

Earlier papers by the present authors (McNabb, 1992; McKibbin & McNabb, 1993, 1995; McNabb, White & McKibbin, 1993) on high-temperature and high-pressure regimes of brines (water + chloride) describe the constraints, the delineation of the various solid, liquid and vapour phases, the compositions of the co-existing phases and their thermodynamic and relevant physical properties. Based on the experimental data of Sourirajan & Kennedy (1962), the complicated phase structure of the brine phase-space (T-p-X) diagrams are described in McKibbin & McNabb (1993) where mathematical descriptions of the boundaries between regimes within the system are given.

The addition of CO_2 adds to the complexity. This paper is our first attempt to fully describe the development of a ternary system where water (H_2O), salts (represented by NaCl) and non-condensible gases (represented by CO_2) co-exist in high-temperature and high-pressure regimes, either as a solution of gas in brine in liquid or gas form, as two fluid phases in equilibrium, or as fluid phases in equilibrium with solid salt precipitate. Conservation equations and gas laws provide a mathematical model which is solved numerically for a few simple cases.

2. THE SYSTEM H_2O-NaCl-CO_2

H_2O-NaCl-CO_2 is a ternary system in which solubility of halite in the gas phase can be considerable. The behaviour of the system at low temperatures and pressures is not of great interest in the applications to be considered here and so the phase complications involving ice are ignored, although our correlations do incorporate the triple point of pure H20 at approximately (0 'C, 0 bars) and that for pure NaCl near (800 'C, 0 bars) as useful reference points [note: pressures are given in bars absolute].

The brine system H_2O-NaCl is used as the basic reference to which CO_2 is added. Clearly, the presence of a non-condensible gas will alter the brine phase boundaries in the state-space. Comprehensive experimental data is not yet available to allow a complete determination of the effect over the wide temperature and pressure ranges being considered here. This study therefore is an attempt to provide a qualitative description, but based on quantitative data which provides a good basis for conclusions drawn from numerical model experiments.

The binary system H_2O-NaCl

The mass fraction of NaCl in the binary system is represented by the dimensionless quantity X, where $X = 0$ corresponds to pure H_2O and $X = 1$ to pure NaCl. Between these limits, the system can exist in a variety of states, corresponding to various combinations of liquid, gas and solid (NaCl).

Correlation formulas for the boundaries in the T-p-X state-space, given in McKibbin & McNabb (1993), were devised so that any chosen state-point could be classified and allocated to one of the eight regions of the state-space by direct calculation rather than by data table interpolation.

The liquid-gas region extends over a large field. It is bounded at low pressures by halite solubility in co-existing liquid and gas (three-phase state), the saturation curve, given by $p = p_{SAT}(T)$, which extends from near (0 ˚C, 0 bars) to a maximum pressure at (600 'C, 392 bars) and then descends to the triple point of pure NaCl near (800 "C, 0 bars).

At high pressures, the two-phase region is bounded by the saturation curve for pure H_2O, given by $p = p_{sat}(T)$, extending from the triple point of H_2O to its critical point (374.15 'C, **221.2** bars), and thence by the H_2O-NaCl critical curve, given by $[p = p_{CRIT}(T), X = X_{CRIT}(T)]$, which terminates at the critical point for pure NaCl at approximately (1075 'C, 930 bars) (Sourirajan & Kennedy, 1962). The saturation curve for pure NaCl is only roughly approximated, by a straight line joining the triple point to the critical point.

Within the two-phase region, for a given value of T and for $p_{SAT}(T) < p < p_{CRIT}(T)$, if the overall chloride mass fraction is in the range $X_{gs}(T, p) < X < X_{\ell s}(T, p)$, there is a mixture of a gas phase and a liquid phase, the properties of which are determined by the NaCl mass fractions $X = X_{gs}(T, p)$ and $X = X_{\ell s}(T, p)$ for the two fluid phases respectively. The gas-phase mass fraction lies between limits which depend on temperature only, $X_{g\ SAT}(T) < X_{gs}(T, p) < X_{CRIT}(T)$, while for the liquid-phase fraction, $X_{CRIT}(T) < X_{\ell s}(T, p) <$ & $_{SAT}(T)$.

Correlations for all of the above functions are provided in McKibbin & McNabb (1993).

The ternary system H_2O-NaCl-CO_2

The addition of a non-condensible gas to the brine system is regarded here as a perturbation to the brine. The equations modelling the system are written in such a way that zero CO_2 concentrations leave the equations for the brine system as studied previously. Extra relationships are need to describe the way dissolved non-condensible gas concentrations affect boiling pressures or temperatures; the basic parameter used is the partial pressure of the CO_2, and Henry's law is used to provide a connection between non-condensible gas fractions in the gas and liquid phases. It is assumed that no CO_2 resides in the solid salt precipitate.

3. CONSERVATION EQUATIONS

In order to follow the evolution of the system, a model mathematical description must be formulated. This can be done by using the equations describing conservation of mass, linear momentum (Darcy's law) and energy. The amounts of the components present are described by the chloride fraction X (the mass fraction of chloride relative to the total mass of water + chloride present) and non-condensible gas fraction Y (the mass fraction of CO_2 relative to the total mass of all fluid components present).

Conservation of mass

The transport behaviour of the fluids is firstly constrained by mass conservation requirements for each chemical ingredient. For our three-component system, these can be expressed as follows:

$$\mathbf{H_2O:} \qquad \frac{\partial A^w_m}{at} + \nabla \cdot \mathbf{Q}^w_m = q^w_m$$

$$\text{NaCl:} \qquad \frac{\partial A^c_m}{at} + \nabla \cdot \mathbf{Q}^c_m = q^c_m$$

$$CO_2: \qquad \frac{\partial A^n_m}{at} + \nabla \cdot \mathbf{Q}^n_m = q^n_m$$

where

$$A^w_m = \phi\, \varepsilon\, [S_\ell(1 - X_\ell)(1 - Y_\ell)\rho_\ell + $$
$$+ (1 - S_\ell)(1 - X_g)(1 - Y_g)\rho_g]$$
$$A^c_m = \phi\, \{(1 - \varepsilon)\rho_c + $$
$$+ \varepsilon\, [S_\ell X_\ell(1 - Y_\ell)\rho_\ell + (1 - S_\ell)X_g(1 - Y_g)\rho_g]\}$$
$$A^n_m = \phi\, \varepsilon\, [S_\ell Y_\ell \rho_\ell + (1 - S_\ell)Y_g\rho_g]\}$$

are the mass per unit volume of formation of the water (superscript w), chloride (c) and non-condensible gas (n) respectively, given in terms of the porosity ϕ, the voidage E (volume fraction of pore space occupied by fluid), the liquid saturation S_ℓ (volume fraction of fluid occupied by liquid), the chloride mass fractions of the brine within each fluid phase X_ℓ and X_g, the C02 mass fractions within each fluid phase Y_ℓ and Y_g, and the phase densities ρ_ℓ, ρ_g and ρ_c, where subscripts ℓ, g and c refer to liquid, gas and solid chloride phases respectively. The terms Q_m and q_m represent, for each component, the mass flux per unit area of the formation (see below) and the rate of injection per unit volume of mass (corresponding to a sink or source) respectively.

The total mass of material per unit volume of formation is given by the sum of the respective quantities for the rock matrix, water, chloride and CO_2:

$$A_m = A^r_m + A^w_m + A^c_m + A^n_m$$
$$= (1 - \phi)\rho_r + \phi\, \{(1 - \varepsilon)\rho_c + \varepsilon\, [S_\ell\rho_\ell + (1 - S_\ell)\rho_g]\}$$

where ρ_r is the density of the solid (rock) matrix. It is assumed that the components, when present, are uniformly **mixed** within each phase.

Note that the mass per unit volume of the chloride within the fluid phases only is given by

$$A^c_{mf} = \phi\, \varepsilon\, [S_\ell X_\ell(1 - Y_\ell)\rho_\ell + (1 - S_\ell)X_g(1 - Y_g)\rho_g]\}$$

When no solid chloride is present, E = 1 and $A_c = A^{-}_{mf}$.

Conservation of momentum (Darcy's law)

The fluid fluxes are assumed to be driven by gravity and pressure, and are governed by Darcy's law for porous media flow. Diffusion within the gas phase is also allowed for in the model equations below, but is assumed small.

The mass fluxes per unit area (specific mass flow rates) are given for each component by the sum of the mass fluxes associated with each fluid phase:

$$
\begin{aligned}
Q_m^w &= Q_{m\ell}^w + Q_{mg}^w \\
&= (1 - X_\ell)(1 - Y_\ell)\, Q_{m\ell} + (1 - X_g)(1 - Y_g)\, Q_{mg} \\
&\qquad - \tau \phi\, (1 - S_\ell)\, \rho_g\, D_w\, \nabla\, [(1 - X_g)(1 - Y_g)] \\
Q_m^c &= Q_{m\ell}^c + Q_{mg}^c \\
&= X_\ell\, (1 - Y_\ell)\, Q_{m\ell} + X_g\, (1 - Y_g)\, Q_{mg} \\
&\qquad - \tau \phi\, (1 - S_\ell)\, \rho_g\, D_c\, \nabla\, [X_g\, (1 - Y_g)] \\
Q_m^n &= Q_{m\ell}^n + Q_{mg}^n \\
&= Y_\ell\, Q_{m\ell} + Y_g\, Q_{mg} - \tau \phi\, (1 - S_\ell)\, \rho_g\, D_n\, \nabla\, [Y_g]
\end{aligned}
$$

The parameters D_w, D_c and D_n are the molecular diffusion constants for each component in the gas phase, with subscripts w, c and n referring to water, chloride and non-condensible gas respectively, while τ is the formation tortuosity. The gravity- and pressure-driven mass fluxes corresponding to each phase, $Q_{m\ell}$ and Q_{mg}, are given by Darcy's law applied to each phase separately, as follows:

$$Q_{m\ell} = Q_{m\ell}^w + Q_{m\ell}^c + Q_{m\ell}^n = k_{r\ell} \frac{k}{\nu_\ell} (-\nabla p + \rho_\ell \mathbf{g})$$

$$Q_{mg} = Q_{mg}^w + Q_{mg}^c + Q_{mg}^n = k_{rg} \frac{k}{\nu_g} (-\nabla p + \rho_g \mathbf{g})$$

Here, k is the solid matrix intrinsic permeability, $k_{r\ell}$ and k_{rg} are the relative permeabilities (permeability reduction factors which are usually assumed, as here, to be dependent on S_ℓ only), ν_ℓ and ν_g are the kinematic viscosities for each fluid phase, p is the total fluid pressure and $\mathbf{g}$ is the gravitational acceleration.

Molecular diffusion of the salt and non-condensible gas is assumed small compared with advection transport and is hereafter ignored. The total fluid mass flux per unit area is then given by

$$Q_m = Q_{m\ell} + Q_{mg}$$

<u>Conservation of energy</u>

The equation of conservation of energy is:

$$\frac{\partial A_e}{\partial t} + \nabla \cdot Q_e = q_e$$

where q_e is a source term and

$$
\begin{aligned}
A_e = {} & (1 - \phi)\rho_r u_r + \\
& + \phi\, \{(1 - \varepsilon)\rho_c u_c + \varepsilon\, [S_\ell \rho_\ell u_\ell + (1 - S_\ell)\rho_g u_g]\}
\end{aligned}
$$

is the energy per unit volume of the fluid-filled formation with u_r, u_c, u_ℓ and u_g being the specific internal energies for the rock matrix, solid chloride, liquid and gas phases. The energy flux per unit area Q_e is given by the sum of the energy fluxes corresponding to the flow of each phase and that due to heat conduction, as follows:

$$Q_e = Q_{m\ell}\, h_\ell + Q_{mg}\, h_g - K\, \nabla T$$

where $Q_{m\ell}$ and Q_m are given above, h_ℓ and h_g are the specific enthalpies of the liquid and gas fluid phases, K is the effective thermal conductivity of the fluid-filled formation and T is the temperature.

<u>Physical and thermodynamic properties of the phases</u>

The above equations require a knowledge of various fluid properties. In particular, the non-condensible gas may be completely dissolved in the single-phase liquid brine, or may contribute a partial pressure when only the gas phase is present, or is otherwise partitioned between the liquid and gas phases in the case where both are present. For small gas concentrations, this partitioning is described approximately by Henry's law.

Densities

In general, the fluid density depends on temperature, pressure and composition, i.e. $\rho = \rho(T, p, X, Y)$. Since Y is small, the density of the liquid phase is given closely by $\rho_\ell = \rho_{b\ell}(T, p, X_\ell)$, which is the density of the brine (combined water + chloride) with salinity X_ℓ. In the gas phase, with total pressure p, and CO_2 partial pressure p_n, Dalton's law gives

$$p = p_w + p_c + p_n = p_b + p_n$$

where $p_b = p_w + p_c$ is the partial pressure of the brine gas, salinity X_g, at temperature T. Assuming that the gas components are nearly ideal (perfect) gases, then each approximately satisfies

$$Pi = \rho_i R_i T \qquad \text{with} \qquad R_i = \frac{R_0}{M_i}$$

where $R_0 = 8.3144$ kJ/kmol K is the universal gas constant and M_i is the g.m.w. of component i in the mixture. For example, $R_{CO_2} = \frac{8.3144}{44.010} \times 10^3 = 188.9$ J/kg K.

Then, $\rho_i = \frac{p_i}{R_i T} = \frac{p_i M_i}{R_0 T}$

and $\rho_g = \rho_{wg} + \rho_{cg} + \rho_{ng} = \rho_{bg} + \rho_{ng}$

where $\rho_{bg} = \rho_{wg} + \rho_{cg}$ is the density of the brine gas. Then

$$Pg = \frac{p_b M_{bg} + p_n M_{CO_2}}{R_0 T}$$

where $M_{bg} = \dfrac{1}{\dfrac{(1 - X_g)}{M_{H_2O}} + \dfrac{X_g}{M_{NaCl}}}$ is the molecular weight of the brine gas, salinity X_g. Using the above,

$$Y_g = \frac{\rho_{ng}}{\rho_g} = \frac{\rho_{ng}}{\rho_{bg} + \rho_{ng}} = \frac{p_n}{p_n + (p - p_n)\dfrac{M_{bg}}{M_{CO_2}}}$$

Table 1: **State** parameters for the eight different **state** regimes in a H_2O-NaCl-CO_2 system, $0 < T \leq 1075\,^\circ C$.

region	system stare	T [°C]	p_b [bars abs]	X	S_ℓ	E	fluid properties required
1	saturated liquid + solid	TI800	$p_b > p_{SAT}(T)$	$X_\ell = X_{\ell\,SAT}(T)$, $X_{\ell\,SAT}(T) \leq X < 1$	1	$0 \leq \varepsilon < 1$	$\rho_{b\ell\,SAT}(T, p_b)$, $h_{b\ell\,SAT}(T, p_b)$, $h_{ng}(T, p_n)$, $h_{n\,sol}(T, p_n)$, $v_{b\ell\,SAT}(T, p_b)$
2	supercritical fluid	T	$p_b \geq p_{CRIT}(T)$	$X = X_f$, $0 < X < X_{\ell\,SAT}(T)$	1	1	$\rho_{b\ell}(T, p_b, X)$, $\rho_{bg}(T, p_b, X)$, $\rho_{ng}(T, p_n)$, $h_{b\ell}(T, p_b, X)$, $h_{bg}(T, p_b, X)$, $h_{ng}(T, p_n)$, $h_{n\,sol}(T, p_n)$, $v_{b\ell}(T, p_b, X)$, $v_{bg}(T, p_b, X)$, $v_{ng}(T, p_n)$
3	saturated gas + solid	$T \leq 800$	$p_b \leq p_{SAT}(T)$	$X_g = X_{g\,sol}(T, p_b)$, $X_{g\,sol}(T, p_b) < X < 1$	0	$0 \leq \varepsilon < 1$	$\rho_{bg\,sol}(T, p_b)$, $\rho_{ng}(T, p_n)$, $h_{bg\,sol}(T, p_b)$, $h_{ng}(T, p_n)$, $v_{bg\,sol}(T, p_b)$, $v_{ng}(T, p_n)$
4	subcritical gas	T	$p_{SAT}(T) < p_b < p_{CRIT}(T)$	$X = X_g$, $0 < X \leq X_{gs}(T, p_b)$	0	1	$\rho_{bg}(T, p_b, X)$, $\rho_{ng}(T, p_n)$, $h_{bg}(T, p_b, X)$, $h_{ng}(T, p_n)$, $v_{bg}(T, p_b, X)$, $v_{ng}(T, p_n)$
5	two-phase gas + liquid	T	$p_{SAT}(T) < p_b < p_{CRIT}(T)$	$X_{gs}(T, p_b) < X < X_{\ell s}(T, p_b)$	$0 < S_\ell < 1$	1	$\rho_{b\ell s}(T, p_b)$, $\rho_{bgs}(T, p_b)$, $\rho_{ng}(T, p_n)$, $h_{b\ell s}(T, p_b)$, $h_{bgs}(T, p_b)$, $h_{ng}(T, p_n)$, $h_{n\,sol}(T, p_n)$, $v_{b\ell s}(T, p_b)$, $v_{bgs}(T, p_b)$, $v_{ng}(T, p_n)$
6	subcritical liquid	T	$p_{SAT}(T) < p_b < p_{CRIT}(T)$	$X = X_\ell$, $X_{\ell s}(T, p_b) \leq X < X_{\ell\,SAT}(T)$	1	1	$\rho_{b\ell}(T, p_b, X)$, $h_{b\ell}(T, p_b, X)$, $h_{ng}(T, p_n)$, $h_{n\,sol}(T, p_n)$, $v_{b\ell}(T, p_b, X)$
7	unsaturated gas $T > 800$	$T > 800$	$p_b \leq p_{SAT}(T)$	$X = X_g$, $0 < X < 1$	0	1	$\rho_{bg}(T, p_b, X)$, $\rho_{ng}(T, p_n)$, $h_{bg}(T, p_b, X)$, $h_{ng}(T, p_n)$, $v_{bg}(T, p_b, X)$, $v_{ng}(T, p_n)$
8	unsaturated gas $T \leq 800$	$T \leq 800$	$p_b \leq p_{SAT}(T)$	$X = X_g$, $0 < X < X_{g\,sol}(T, p_b)$	0	1	$\rho_{bg}(T, p_b, X)$, $\rho_{ng}(T, p_n)$, $h_{bg}(T, p_b, X)$, $h_{ng}(T, p_n)$, $v_{bg}(T, p_b, X)$, $v_{ng}(T, p_n)$

which may be inverted to give

$$p_n = \frac{\dfrac{Y_g}{M_{CO_2}}}{\dfrac{(1 - Y_g)}{M_{bg}} + \dfrac{Y_g}{M_{CO_2}}} \; p$$

Henry's law

The molar fraction of CO_2 in the liquid phase is

$$\frac{\dfrac{Y_\ell}{M_{CO_2}}}{\dfrac{(1 - Y_\ell)}{M_{b\ell}} + \dfrac{Y_\ell}{M_{CO_2}}}$$

where

$$M_{b\ell} = \frac{1}{\dfrac{(1 - X_\ell)}{M_{H_2O}} + \dfrac{X_\ell}{M_{NaCl}}}$$

is the molecular weight of the brine, salinity X_ℓ, and M_{H_2O}, M_{NaCl} and M_{CO_2} are the corresponding values for water, chloride and CO_2. Henry's law relates the partial pressure of C02 in the gas phase to the molar fraction of CO_2 in the liquid phase by

$$p_n = K_H \frac{\dfrac{Y_\ell}{M_{CO_2}}}{\dfrac{(1 - Y_\ell)}{M_{b\ell}} + \dfrac{Y_\ell}{M_{CO_2}}}$$

where $K_H(T, X_\ell)$ is Henry's constant, in this case a function of temperature and the brine salinity. This formula may be inverted to give the brine salinity in terms of the partial pressure p_n of CO_2 in the gas phase, as follows:

$$Y_\ell = \frac{p_n}{p_n + (K_H - p_n)\dfrac{M_{b\ell}}{M_{CO_2}}}$$

Enthalpies

The gas and liquid phase specific enthalpies are given by

$$h_g = (1 - X_g)(1 - Y_g)\, h_{wg} + X_g(1 - Y_g)\, h_{cg} + Y_g\, h_{ng}$$

$$= (1 - Y_g)\, h_{bg} + Y_g\, h_{ng}$$

$$h_\ell = (1 - X_\ell)(1 - Y_\ell)\, h_{w\ell} + X_\ell(1 - Y_\ell)\, h_{c\ell} +$$

$$+ Y_\ell\, (h_{ng} + h_{nsol})$$

$$= (1 - Y_\ell)\, h_{b\ell} + Y_\ell\, (h_{ng} + h_{nsol})$$

where h_{nsol} is the specific energy of dissolution of the C02 in the liquid.

Viscosities

The kinematic viscosities for the two phases are taken to be

$$\nu_\ell = \nu_{b\ell}$$

$$\nu_g = (1 - Y_g)\, \nu_{bg} + Y_g\, \nu_{ng}$$

The independent fluid properties required within each region of the state-space, and their functional dependence, are listed in Table 1.

Determination of the voidage ε and the liquid saturation S_ℓ for the two-phase regimes

The overall mass fraction **X** of chloride within the pore fraction of the system is given by

$$X = \frac{A^c_m}{A^w_m + A^c_m} =$$

$$\frac{(1 - \varepsilon)\rho_c + \varepsilon[S_\ell X_\ell(1 - Y_\ell)\rho_\ell + (1 - S_\ell)X_g(1 - Y_g)\rho_g]}{(1 - \varepsilon)\rho_c + \varepsilon[S_\ell(1 - Y_\ell)\rho_\ell + (1 - S_\ell)(1 - Y_g)\rho_g]}$$

The overall mass fraction **Y** of the non-condensible gas within the fluid fraction of the system is given by

$$Y = \frac{A^n_m}{A^w_m + A^c_{mf} + A^n_m}$$

$$= \frac{S_\ell Y_\ell \rho_\ell + (1 - S_\ell)Y_g\rho_g}{S_\ell\rho_\ell + (1 - S_\ell)\rho_g}$$

In regions 2, **4**, 6, **7** and 8 of the **T-p-X** state-space, $\varepsilon = 1$ and either $S_\ell = 1$ or $S_\ell = 0$, and X and Y are just the mass fractions of chloride and C02 within the liquid or gas (see Table **1**). Within each of regions 1 and 3, the above expression for X can be inverted to give ε as a function of **X.** The corresponding inversion formulas are:

- Region 1 (liquid + solid)

$$\varepsilon = \frac{(1 - X)\rho_c}{(1 - X)\rho_c + (X - X_{\ell SAT})(1 - Y)\rho_{\ell SAT}}$$

where

$$Y = Y_\ell$$

- Region 3 (gas + solid)

$$\varepsilon = \frac{(1 - X)\rho_c}{(1 - X)\rho_c + (X - X_{gsol})(1 - Y)\rho_{gsol}}$$

where

$$Y = Y_g$$

- Region **5** (gas + liquid)

Within the two-phase fluid region, the overall chloride mass fraction **X** is

$$X = \frac{S_\ell X_{\ell s}(1 - Y_\ell)\rho_{\ell s} + (1 - S_\ell)X_{gs}(1 - Y_g)\rho_{gs}}{S_\ell(1 - Y_\ell)\rho_{\ell s} + (1 - S_\ell)(1 - Y_g)\rho_{gs}}$$

This can be inverted to give S_ℓ as a function of X:

$$S_\ell = \frac{(X - X_{gs})(1 - Y_g)\rho_{gs}}{(X_{\ell s} - X)(1 - Y_\ell)\rho_{\ell s} + (X - X_{gs})(1 - Y_g)\rho_{gs}}$$

For a given overall non-condensible gas fraction **Y,** the partition of the CO_2 between the liquid and gas phases can be determined using Henry's law; the appropriate values of Y_g and Y_ℓ are then used, together with **X,** to find the corresponding value of S_ℓ in Region **5.**

In summary, this means that T, p, X and **Y** can be used to determine the state of the system within all regions. The boundaries $X = 0$ and $X = 1$, which correspond to pure H20 and pure NaCl, are not included in the classification.

4. SAMPLE RESULTS

The results of calculations for three examples are presented here. All are solutions of models for steady-state one-dimensional vertical flows.

The method is outlined in McKibbin & McNabb (1995), where special attention is given to the calculations in the two-phase regions (Region **1:** liquid + solid; Region 3: gas + solid; Region **5:** gas + liquid), and in particular to the deposition of solid chloride in Regions 1 and 3. The fluid in Region **2,** where $p_b \geq p_{CRIT}(T)$, is treated as a homogeneous mixture of two components, one gas-like and the other liquid-like, in order that the properties vary smoothly from those of a "gas" at small X-values to those of a "liquid" for $X_{CRIT} < X < X_{\ell\, SAT}$. This ensures that there are no discontinuities in fluid properties as the flow passes from Region 2 to Region **4** (which is gas) or Region 2 to Region 6 (which is liquid), or vice versa. An artificial value of S_ℓ is used to reflect the relative proportions of the contributions to the fluid from the two different sets of properties, although the fluid is neither gas nor liquid in the usual sense. (This can be seen in the z *vs* S_ℓ plots in Cases A and C of the examples presented below.)

For each of the three cases, labelled Case A, Case **B** and Case C, the fluxes are based on a given water flowrate m_w and an energy flux q. The water mass flowrate remains constant throughout the column since water is not "lost" in regions where chloride deposition or dissolution takes place, but q may change slightly there since some energy is released to or removed from the flux by the phase changes. *An* initial state-point is chosen by specifying **a** temperature T, a total pressure p, an overall chloride mass fraction **X** and a CO_2 partial pressure p_n. Mass fluxes of chloride and non-condensible gas can be deduced from these parameters.

With specification of the permeability k, the thermal conductivity K, and the form of the relative permeability functions, the conservation equations are integrated with respect to vertical coordinate z while the state-point of the system can be tracked through calculation of values of T, p, p_b, S_ℓ, X, Y, p_n, and the volumetric strain rate a (labelled "vsrate" in the figures which follow). The volumetric strain rate is the relative rate of expansion $(a = \partial\phi/\partial t)$ of the formation when deposition is taking place in Regions 1 or 3 of the state-space. Dissolution of solid chloride would correspond to negative value of a, although it can be shown that when T decreases with elevation, chloride is deposited and $a > 0$ (see McKibbin & McNabb, 1995).

The results of the calculations are presented graphically, and include state-points from most of the eight distinct state-space regions. Case A describes a brine-only flow (no CO_2) while Cases B and C have non-condensible gas as a component. For each case, the left column contains a set of three views of the track in the brine (water + chloride) state-space from the "top" (T *vs* X), "front" (p_b *vs* X) and the "side" (p_b *vs* T). Below this, in Cases B and C, are the corresponding state-space views from the front (p *vs* X) and from the side (p *vs* T) when the total pressure p is one of the independent variables. The sub-regions through which the trajectory is passing are labelled by their numbers as given in Table 1; the points where the trajectory passes from one sub-region of the state-space to another are indicated by open circles.

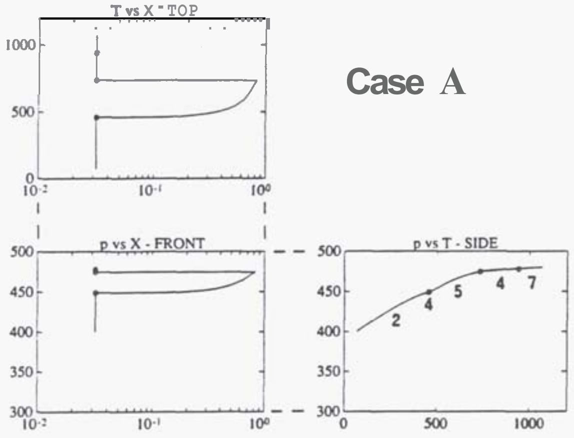
The set of graphs in the right column for each case are depth profiles of some of the calculated parameters, including state-space sub-region number, temperature T, total pressure p, liquid saturation S_ℓ, overall chloride mass fraction X, non-condensible gas mass fraction Y and partial pressure p_n, and volumetric strain rate a ("vsrate"). As mentioned above, the last gives the volumetric rate at which the matrix is expanding due to deposition of solid chloride; outside of Regions 1 and 3, $a = 0$.

For two-phase flows, the relative permeabilities (permeability reduction factors) $k_{r\ell}$ and k_{rg} were calculated from the so-called Corey curves with zero residual liquid and gas saturations. The thermal conductivity in all cases was $K = 2.0$ W m^{-1} K^{-1}. The intrinsic vertical permeability and other parameters used for each case are given in the description attached to each set of graphs.

<u>Case A</u> describes the example of zero net mass flow of a brine (water + chloride only) below an initial point of (T, p, X) = (70 °C, **400** bars, **0.032**). Here, heat flow is mainly conductive, except in the two-phase zone where a small amount of counterflow exists and where the high saturation values indicate a liquid-dominated heat-pipe effect with $S_\ell \approx 1$. The effective X values in this region are generally large, with $X = X_{\ell s}$. Below the two-phase region, the chloride mass fraction is again reduced to the initial value of 3.2 %. Case A reflects the possibility of a magmatic gas with a small NaCl fraction existing at depth, but shielded from a sea-floor discharge with a similarly low salinity by an apparently concentrated brine layer (actually two-phase) at medium depths.

<u>Case B</u> describes the vertical flow of a three-component fluid from depth where there is a gas at high temperature, pressure and salinity (T = 1030 °C, p = **434** bars, X = **46** %), with a small non-condensible gas fraction ($Y = 1.1$ %, which corresponds to $p_n = 2.94$ bars). The gas rises with p and T decreasing, then passes through a two-phase zone for about **300** m where the liquid saturation S_ℓ changes from 0 to 1, and then continues rising as a liquid for about 100 m. The liquid is then cooled enough so that it becomes saturated with respect to chloride; it begins to steadily deposit solid NaCl in the formation at a rate which decreases with height. The salinity continues to decrease as the liquid rises, cooling further, while the CO_2 gas fraction Y of the mixture consequently increases.

Case A

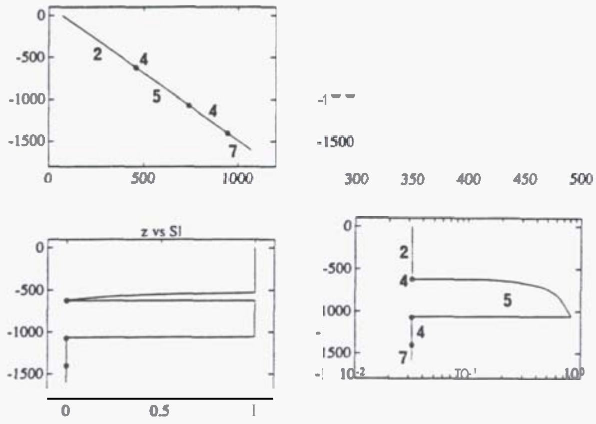


$m_w = 0$ kg s^{-1} m^{-2} $\quad$ $q = 1.25$ W m^{-2}

$k = 2 \times 10^{-15}$ m^2 $\quad$ $Y = 0$

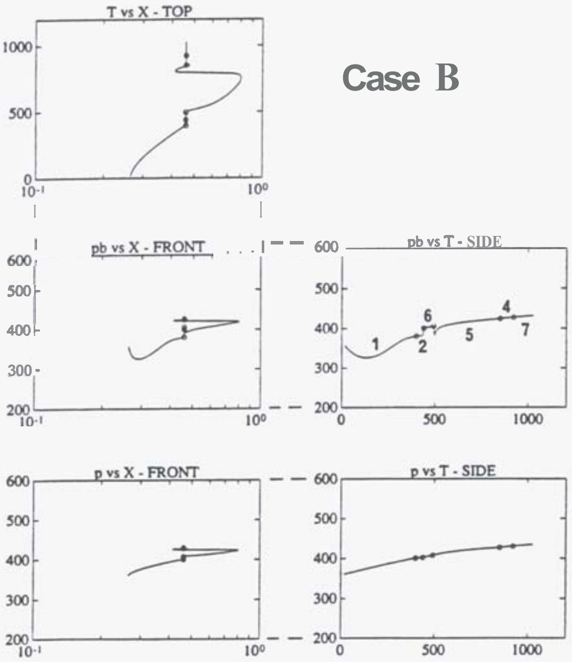
(T, p, X, p_n) = (70 °C, **400** bars, **0.032**, **0** bars) at $z = 0$ m.

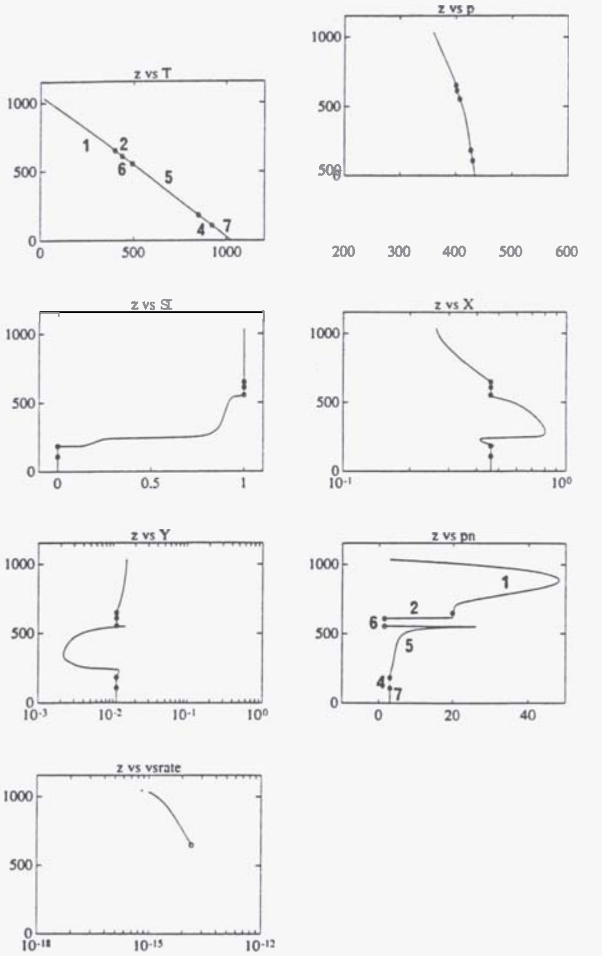
<u>**Left column**</u>: **3** views of the state-space: "top" (T *vs* X), "front" (p *vs* X) and "side" (p *vs* T). Points where the trajectory passes from one sub-region to another are shown by open circles. Subregions through which the trajectory passes are labelled by their numbers as given in Table 1.



<u>**Right column**</u>: Depth profiles of temperature T, pressure p, liquid saturation S_ℓ and chloride mass fraction X. The sub-regions through which the trajectory is passing are labelled on the z *vs* T profile by their numbers as given in Table 1.

Case B



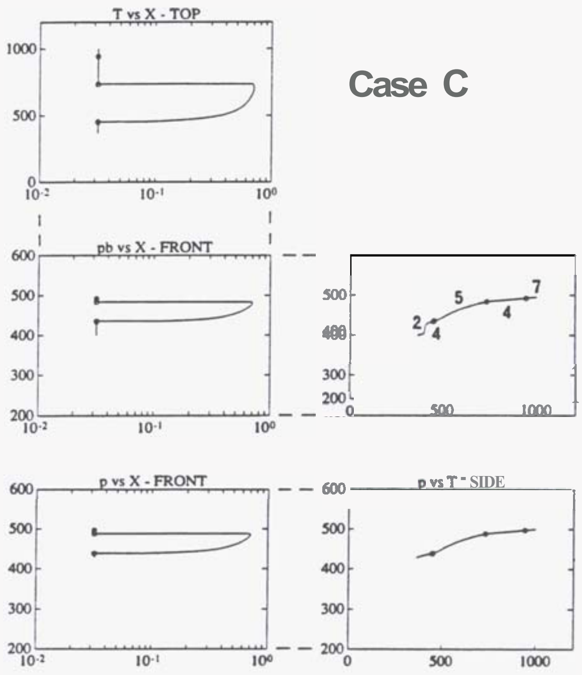


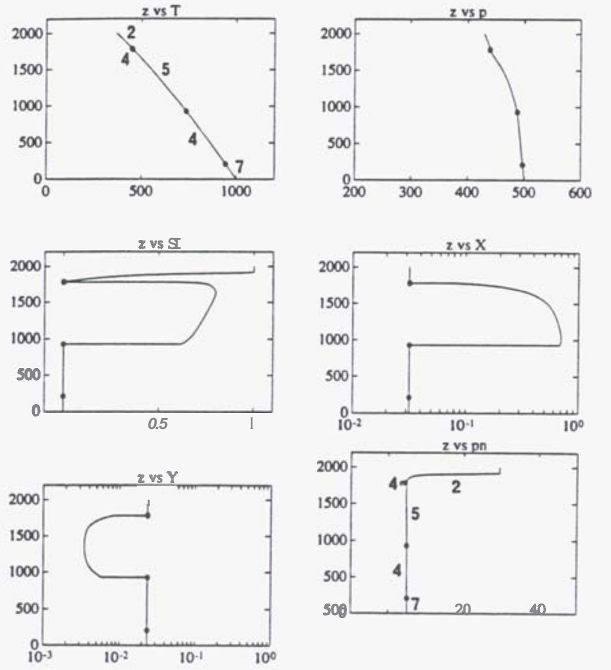
$m_w = 1 \times 10^{-8}$ kg s^{-1} m^{-2} $q = 2$ W m^{-2}
$k = 1 \times 10^{-15}$ m^2
(T, p, X, p_n) = (1030 'C, **434** bars, **0.46, 2.94** bars) at the initial point **(z = 0 m).**

Left column: Projective views of the T-p_b-X and T-p-X state-spaces. Points where the trajectory passes from one sub-region to another are shown by open circles. Sub-regions are labelled by their numbers as given in Table **1**.

Right column: Depth profiles of T, p, S_ℓ, X, **Y**, p_n and vsrate *(a)* .SI units throughout. See text for discussion.

Case C





$m_w = 1 \times 10^{-7}$ kg s^{-1} m^{-2} $q = 1$ W m^{-2}
$k = 1 \times 10^{-15}$ m^2
(T, p, X, p_n) = (1000 'C, *500* bars, 0.032, **5** bars) at the initial point **(z** = 0 **m)** .

Left column: See the caption for Case **B** above.
Right column: Depth profiles of T, p, S_ℓ, X, **Y** and p_n. SI units throughout.
See text for discussion.

The chloride deposition rate is measured by the volumetric strain rate $a = \partial\phi/\partial t$, and is of order $10^{-15} - 10^{-14}\ s^{-1}$, which is equivalent to about 10^{-8} per year. If the formation expands to accommodate the deposition without reducing the effective porosity available for fluid flow, then over 10^6 years the volume of the formation would increase by about 1 %.

Variation of the overall non-condensible gas mass fraction Y with increasing elevation is negligible at depth; it drops then rises through the two-phase zone, is constant again in the unsaturated liquid flow above that, then increases slowly as the chloride is deposited at higher levels. The variation in the CO_2 partial pressure p_n is more dramatic, and reflects the variation in fluid conditions (gas → two-phase → liquid → deposition zone). The relationship between Y and p_n depends strongly on Henry's constant; in this work no extensive data was available for solubility of CO_2 in a brine, so the function $K_H(T, X_\ell)$ was assumed to be that for pure water [a standard correlation for $K_H(T)$ was used].

Case C has some similarities with Case A. Fluid rises from depth where it exists as a low-salinity gas at high temperature and pressure, but with a small partial pressure of CO_2 [$(T, p, X, p_n) = (1000\ ^\circ C, 500\ \text{bars}, 0.032, 5\ \text{bars})$ compared with $(T, p, X) = (1070\ ^\circ C, 480\ \text{bars}, 0.032)$ at depth for Case A]. The trajectory through the T-p-X sub-space is similar to that of Case A, with the same sequence of sub-regions being negotiated. Both T and p decrease steadily with elevation, with the high-temperature gas at depth separated by a two-phase zone from a liquid-like fluid at shallow levels. The lower values of the overall non-condensible gas mass fraction Y in the two-phase zone are similar to those of Case B, but the partial pressure p_n remains almost constant before a significant increase at higher levels in Region 2.

5. SUMMARY

The large number of parameters and thermodynamic relationships that are involved in calculations of the type carried out here do not lend themselves to easy interpretation. The complexity of the brine (water + chloride) problem at high temperatures and pressures, reflected by the intricacies of the T-p-X state-space, make for difficult conceptualisation. Further addition of non-condensible gas increases this complexity, but provides the final fundamental ingredient in the model of a fluid which originates as magmatic vapour and rises to provide the mass and heat input to geothermal systems.

There is much work yet to be done on this problem. In particular, reliable correlations for the fluid properties listed in Table 1 need to be found – only some are known so far, with default values for pure water being used otherwise. Also, a simulator needs to be developed to allow transient calculations for a three-dimensional model to be made.

However, the state-space descriptions and one-dimensional model calculations reported here and in previous papers (McKibbin & McNabb, 1993, 1995) have focused our concentration on the technical problems of describing multi-phase multi-component mass and heat flows below geothermal environments. They have also provided sign-posts for future development of this work.

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REFERENCES

McKibbin, R. and McNabb, A. (1993) Modelling the phase boundaries and properties of the system H_2O-NaCl at high temperatures and pressures. *Proceedings of the 15th New Zealand Geothermal Workshop 1993,* The University of Auckland, 267-273.

McKibbin, R. and McNabb, A. (1995) From magma to groundwater: the brine connection. *Proceedings of the World Geothermal Congress, Florence, May 1995.* International Geothermal Association, 1125-1130.

McKibbin, R. and McNabb, A. Mathematical modelling of heat and mass flows in deep brine systems. *Geothermics.* Submitted.

McNabb, A. The Taupo-Rotorua hot-plate. (1992) *Proceedings of the 14th New Zealand Geothermal Workshop 1992.* The University of Auckland, 111-114.

McNabb, A., White, S.P. and McKibbin, R. (1993) Brine circulation and hot-plate formation. *Proceedings of the 15th New Zealand Geothermal Workshop 1993.* The University of Auckland, 275-277.

Sourirajan, S. and Kennedy, G.C. (1962) The system H_2O-NaCl at elevated temperatures and pressures. *American J. Sci.*, Vol. 260, 115-141.