STEAM AND NITROGEN INJECTION FOR GROUNDWATER REMEDIATION

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ABSTRACT

Groundwater contamination by organic materials and petroleum products is a worrisome problem with environmental, social and health implications constituting a menace to our high-quality groundwater resources. An important remediation technique is steam injection, modelled by a system of balance equations that takes into account mass interchange between different phases. Despite the presence of these source terms, we have developed techniques to solve the Riemann problem. As an example we consider a one-dimensional porous medium filled initially with water, where steam and nitrogen are injected; we neglect compressibility, heat losses and capillarity effects and present a physical model based on the mass balance and energy conservation equations. An interesting feature is that we can calculate the mass transfer directly from the model, independently of the expression for the mass transfer.

1. INTRODUCTION

The frequent and widespread occurrence of contamination due to spills and leaks of organic materials, such as petroleum products, that occurs during their transport, storage and disposal constitute a menace to our high-quality ground-water resources. In spite of increased awareness of the environmental impacts of oil spills, it appears to be impossible to avoid these accidents, so it is necessary to develop techniques for groundwater remediation. Traditional clean up methods for these spills such as pump-and-treat can be very expensive and slow. So removal of contaminants with steam is considered an alternative. One disadvantage of steam is the ecological impact of high temperatures, see [5]. This can be alleviated if we co-inject nitrogen leading to a lower temperature. We refer to [4], [3] and [6]. This theory was studied initially in [4] and extended in [6]. The complete class of equations is considered in [6].

We present a physical model for steam and nitrogen injection based on mass balance and energy conservation equations. We study the three possible physical phase mixture situations: the single-phase gas situation, spg; the two-phase situation, tp; and the single-phase liquid situation, spl. For each physical situation, we reduce the four balance equations system presented in Section 2 to a system of conservation laws of type:

$$\frac{\partial}{\partial t}G(V) + \frac{\partial}{\partial x}uF(V) = 0, \tag{1}$$

supplemented by appropriate thermodynamical constraints between variables, such that Raoult and Clausius-Claperyon laws. Here $V = (V_1, V_2)$ is a subset of the variables:

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gas saturation s_g, steam composition ψ_{gw} and the temperature T and it represents the unknowns in each physical situation; $G = (G_1, G_2, G_3)$ and $F = (F_1, F_2, F_3)$ are the accumulation vector and the flux vector, respectively; u is a total velocity. The state of the general system is represented by (s_g, ψ_{gw}, T, u). Eq. (1) has an important feature, the variable u does not appear in the accumulation term, it appears isolated in the flux term, thus this equation has an infinite speed mode associated to u; nevertheless we are able to solve the Riemann problem for Eq. (1), which is a mathematical novelty.

In Section 2, we present the physical model that describes the injection of steam and nitrogen in a one-dimensional horizontal porous rock filled with water. In Section 3, we present the model equations for balance of water, steam, nitrogen and temperature. The full system is not a system of conservation equations, since there is a water mass source term $q_{q \longrightarrow a,w}$, which is the condensation rate between the water and steam phases. In Section 4, we describe three physical situations in which the balance system reduces to conservation systems of type (1). In Section 5, we study the type of waves that appear in the solution. It is remarkable that in the two phase situation there is an evaporation rarefaction wave. In Section 6, we show an example of the Riemann solution for a mixture of steam and nitrogen in the *spg* into a rock filled with water.

2. Physical model

We consider the injection of steam and nitrogen in a one dimensional horizontal porous rock core filled with water. The core consists of rock with constant porosity φ and absolute permeability k. We assume that the fluids are incompressible and that the pressure changes are so small that they do not affect the physical properties of the fluids. We are interested in scales dictated by field reservoirs. The effect of spatial second derivative terms (capillary pressure, heat conductivity, etc) is to widen the heat condensation front, while the convergence of the characteristics tries to sharpen it. The balance of these effects yields the width of the condensation front. In the field this width is typically a few tenth of centimeters; on the other hand, the distance between injection and production wells is of the order of 1000 meters. Thus this widths is negligible, so we can set it to zero and simplify our analysis with no error of practical importance, thus we disregard the diffusive terms, so that the Riemann solution can be found.

Darcy's law relates pressure gradient in each fluid phase with its seepage speed:

$$u_w = -\frac{k k_{rw}}{\mu_w} \frac{\partial p}{\partial x}, \qquad u_g = -\frac{k k_{rg}}{\mu_g} \frac{\partial p}{\partial x}. \tag{2}$$

The fractional flow functions for water and steam are given by:

$$f_w = \frac{k_{rw}/\mu_w}{k_{rw}/\mu_w + k_{rg}/\mu_g}, \qquad f_g = \frac{k_{rg}/\mu_g}{k_{rw}/\mu_w + k_{rg}/\mu_g}. \tag{3}$$

Using Darcy's law (2) and (3) we can write u_w and u_g as:

$$u_w = u f_w, \qquad u_g = u f_g, \quad \text{where} \quad u = u_w + u_g \tag{4}$$

is the *total* or *Darcy velocity*; s_w and s_g are the water and gas saturation.

3. The model equations

Using (4), we write the equations of mass balance for liquid water, gaseous steam and gaseous nitrogen as:

$$\frac{\partial}{\partial t}\varphi\rho_W s_w + \frac{\partial}{\partial x}u f_w \rho_W = +q_{g\longrightarrow a,w}, \tag{5}$$

$$\frac{\partial}{\partial t}\varphi\rho_{gw} s_g + \frac{\partial}{\partial x}u f_g \rho_{gw} = -q_{g\longrightarrow a,w}, \tag{6}$$

$$\frac{\partial}{\partial t}\varphi\rho_{gn} s_g + \frac{\partial}{\partial x}u f_g \rho_{gn} = 0, \tag{7}$$

where $q_{g\longrightarrow a,w}$ is the water mass source term (the condensation rate between the water and steam phases); ρ_W is the constant water density, ρ_{gw} (ρ_{gn}) denote the concentration of steam (nitrogen) in the gaseous phase (mass per unit gas volume); in the presence of liquid water thermodynamic considerations specify how these concentrations depend on temperature, see [6]. The saturations s_w and s_g add to 1. By (3), the same is true for f_w and f_g.

The equation of energy conservation is based on an enthalpy formulation see [1], [2]. We neglect heat conduction, so the energy conservation is given by:

$$\frac{\partial}{\partial t}\varphi\left(\hat{H}_r + s_w H_W + s_g H_g\right) + \frac{\partial}{\partial x}\left(u f_w H_W + u f_g H_g\right) = 0. \tag{8}$$

Here $H_W = \rho_W h_W$, $H_g = \rho_{gw} h_{gW} + \rho_{gn} h_{gN}$, H_r is the rock enthalpy per unit volume and $\hat{H}_r = H_r/\varphi$; h_W, h_{gW} and h_{gN} are the enthalpies per unit mass of water in the liquid aqueous phase, of water in the gaseous phase and of nitrogen in the gaseous phase; these enthalpies depend on temperature, see [6].

4. Physical situations

There are three regions in different physical situations. Initially, there is only water in the core in the single-phase liquid situation, *spl*. Injecting a superheated gas a region containing only gaseous steam and nitrogen forms in the single-phase gaseous situation, *spg*. Another situation is the two phase, *tp*, where there is a mixture of liquid water, gaseous nitrogen and steam at boiling temperature. The latter depends on the concentration of nitrogen in the gas. We assume that each region is in thermodynamic equilibrium, so we use Gibbs' phase rule $f = c - p + 2$, where f represents the number of thermodynamic degrees of freedom, c is the number of components and is p the number of phases.

4.1. **Single-phase gaseous situation - *spg*.** Since we fix the pressure, by Gibb's rule we have two other thermodynamic unknowns: temperature and gas composition. We assume that nitrogen and steam in the gaseous phase behave as ideal gases with densities denoted by ρ_{gN} and ρ_{gW}. We also assume that there are no volume effects due to mixing:

$$\rho_{gN} = \frac{M_N p_{atm}}{RT}, \quad \rho_{gW} = \frac{M_W p_{atm}}{RT}, \quad \frac{\rho_{gw}}{\rho_{gW}(T)} + \frac{\rho_{gn}}{\rho_{gN}(T)} = 1, \tag{9}$$

where the p_{atm} is the atmospheric pressure, R is the gas constant; M_W, M_N are the nitrogen and water molar masses. From Eq. (9), we define the steam and nitrogen gas

composition, as:

$$\psi_{gw} = \rho_{gw}/\rho_{gW}(T) \qquad \text{and} \qquad \psi_{gn} = \rho_{gn}/\rho_{gN}(T), \quad \text{so} \quad \psi_{gw} + \psi_{gn} = 1. \qquad (10)$$

The compositions ρ_{gw} and ρ_{gn} are functions of temperature only that can be obtained from (10.a) and (10.b). Using Eqs. (9.a), (9.b), (10.a) and (10.b), eq. (5)-(8) become:

$$\frac{\partial}{\partial t}\varphi\theta_W\psi_{gw}T^{-1} + \frac{\partial}{\partial x}u\theta_W\psi_{gw}T^{-1} = 0, \qquad (11)$$

$$\frac{\partial}{\partial t}\varphi\theta_N\psi_{gn}T^{-1} + \frac{\partial}{\partial x}u\theta_N\psi_{gn}T^{-1} = 0, \qquad (12)$$

$$\frac{\partial}{\partial t}\varphi\left(\hat{H}_r + \psi_{gw}H_{gW} + \psi_{gn}H_{gN}\right) + \frac{\partial}{\partial x}u(\psi_{gw}H_{gW} + \psi_{gn}H_{gN}) = 0; \qquad (13)$$

we have substituted ρ_{gW} and ρ_{gN} from Eqs. (9.a), (9.b), defined $H_{gW} = M_W p_{atm} h_{gW}/RT$ and $H_{gN} = M_N p_{atm} h_{gN}/RT$, where h_{gW} and h_{gN} are functions of T, see [6]. We have three variables to determine: temperature, gas composition and Darcy speed.

4.2. **Two-phase situation - tp.** There is only one thermodynamic variable, which is the temperature, since the pressure is fixed. The compositions in Eq. (10) depend on temperature. When pure steam is injected the condensation temperature is constant, $T_b = 373.15$ at atmospheric pressure. We have three variables to be determined: temperature, saturation and total Darcy velocity. We add (5) and (6) and replace (5)-(8) by:

$$\frac{\partial}{\partial t}\varphi\left(\rho_W s_w + \rho_{gw}s_g\right) + \frac{\partial}{\partial x}u\left(\rho_W f_w + \rho_{gw}f_g\right) = 0, \qquad (14)$$

$$\frac{\partial}{\partial t}\varphi\left(\rho_{gn}s_g\right) + \frac{\partial}{\partial x}u(\rho_{gn}f_g) = 0, \qquad (15)$$

$$\frac{\partial}{\partial t}\varphi\left(\hat{H}_r + H_W s_w + H_g s_g\right) + \frac{\partial}{\partial x}u(H_W f_w + H_g f_g) = 0. \qquad (16)$$

4.3. **Single-phase liquid situation - spl.** Again, there is only one thermodynamic variable, which is the temperature. Since $s_w = 1$ and $s_g = 0$, we have $f_w = 1$ and $f_g = 0$. From Eq. (6), $q_{g\longrightarrow a,w}$ vanishes. One can prove that the total Darcy velocity u is independent of position. We assume that rock and water enthalpy depend linearly on temperature, see [6], so Eqs. (5)-(8) become:

$$\frac{\partial}{\partial t}T + \lambda_T^W\frac{\partial T}{\partial x} = 0, \quad \text{where} \quad \lambda_T^W = u_W\frac{C_W}{\varphi C_W + C_r}, \qquad (17)$$

where we use u_W to indicate that the velocity is spatially constant in the spl, V is the temperature T; C_W and $\hat{C}_r$ are water and rock capacity.

Fig. 1.b shows the three physical situations in the variables $V = (T, \psi_{gw}, s_w)$.

5. The Riemann Problem

We are interested in the Riemann problem associated to (5)-(8), which is the solution of these equations with initial data

$$\begin{cases} (s_L, \psi_L, T_L, u_L) & \text{if } x > 0 \\ (s_R, \psi_R, T_R, \cdot) & \text{if } x < 0, \end{cases} \qquad (18)$$
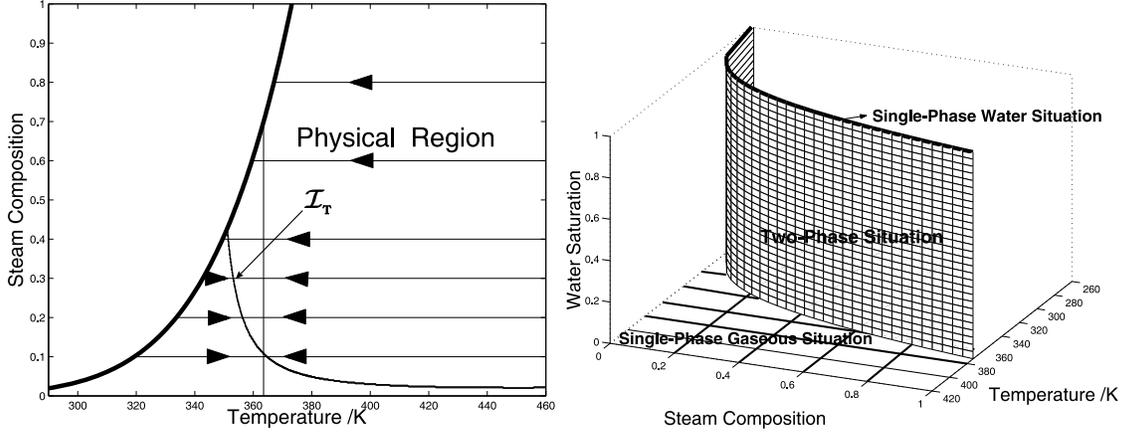
FIGURE 1. *a) Left:* The physical region in the $\{T, \psi_{gw}\}$ plane where the *spg* occurs satisfying thermodynamical constraints, see [6]. The wide curve represents the temperature saturation for a mixture of water an nitrogen. The horizontal rarefaction curves are associated to λ_T; the arrows indicate the direction of increasing speed. The vertical lines are contact discontinuity curves associated to λ_c, in which ψ_{gw} changes, T and u are constant. $\mathcal{I}_T$ is the thermal inflection manifold.*b) Right:* Phase space for $V = (s_W, \psi_{gw}, T)$ and physical situations in admissible regions.

where $s = s_w$ is the water saturation and $\psi = \psi_{gw}$ is the steam composition. The speed u is specified at the injection side. The general solution of the Riemann problem associated to Eq. (1) consists of a sequence of elementary waves, namely shocks and rarefactions.

5.1. **Shock waves.** Discontinuities or shocks appear in solution of the Riemann problems and need to satisfy the Rankine-Hugoniot conditions (RH), see [6], which can be written as:

$$v^s \left(G^+(V^+) - G^-(V^-) \right) = u^+ F^+(V^+) - u^- F^-(V^-), \tag{19}$$

where (V^+, u^+) is the state on the right of the shock and (V^-, u^-) is the state on the left of the shock; v^s is the shock speed; G^+ (G^-) and F^+ (F^-) are the accumulation and flux terms on the right (left) of the shock, which in general have different expressions in each physical situation. We specify the left conditions for the variables V and u, but the right conditions are specified only for V. The speed u^+ is always obtained from the RH condition (19). For a given state (V^-, u^-), the set of states (V^+, u^+) that satisfies the RH condition (19) forms the Hugoniot curve, which is denoted by $\mathcal{H}(V^-, u^-; V^+, u^+)$. This locus in V does not depend on the Darcy speed u. The expressions for the RH curve, the shock speed v^s and u^+, for $[G_i] = G_i^+ - G_i^-$ for $i = 1, 2$ are [6]:

$$det \begin{pmatrix} [G_1] & -F_1^+ & -F_1^- \\ [G_2] & -F_2^+ & F_2^- \\ [G_3] & -F_3^+ & F_3^- \end{pmatrix} = 0, \quad v^s = \frac{u^-}{\varphi} \frac{F_2^+ F_1^- - F_1^+ F_2^-}{F_1^+[G_2] - F_2^+[G_1]}, \quad u^+ = \frac{u^-}{\varphi} \frac{F_1^-[G_2] - F_2^-[G_1]}{F_1^+[G_2] - F_2^+[G_1]}.$$

5.2. **Characteristic speeds.** In each physical situation a system of conservation laws in different forms must be used to find the characteristic speeds.

If we assume that the solution is sufficiently smooth, we differentiate all equations in (1) with respect to their variables, obtaining a system of the form:

$$B\frac{\partial}{\partial t}\begin{pmatrix} V \\ u \end{pmatrix} + A\frac{\partial}{\partial x}\begin{pmatrix} V \\ u \end{pmatrix} = 0, \tag{20}$$

where the matrices B and A (which depend on V) are the derivatives of $G(V)$ and $uF(V)$ with respect to the variables V and u. Since $G(V)$ does not depend on u, the last column in matrix B is zero. The characteristic values λ and vectors $\vec{r}_i$, (where i is the label of each eigenvector) for the following system are the rarefaction wave speeds and directions:

$$A\vec{r}^i = \lambda B\vec{r}^i \quad \text{where } \lambda \text{ is obtained by solving} \quad det(A - \lambda B) = 0. \tag{21}$$

For each i, the rarefaction waves in the $\{x, t\}$ plane are solutions of

$$\left(\frac{dV}{d\xi}, \frac{du}{d\xi}\right) = \vec{r}, \quad \text{with increasing } \xi \text{ satisfying} \quad \xi = x/t = \lambda(V(\xi), u(\xi)). \tag{22}$$

It is remarkable that in V the rarefaction curves do not depend on the Darcy speed u and that u does not change sign on the rarefaction waves. From this property, which is valid also to shocks, it is possible to show that the Riemann solution can be solved only in the space of variables V; then u can be calculated as a function of V, see [6]. It is also remarkable that in the tp situation there is an evaporation rarefaction wave.

6. The Riemann problem for steam and nitrogen injection

We consider the injection of a mixture of steam and nitrogen in the spg below boiling temperature of pure water at prevailing pressure into a rock saturated with water:

$$\begin{cases} (0, \psi_L, T_L, \cdot) & \text{if } x = 0 \text{ (the injection point)}, \\ (1, \psi_{gw}(T_R), T_R, \cdot) & \text{if } x > 0. \end{cases} \tag{23}$$

6.1. Waves in the solution.

6.1.1. *Single-phase gaseous situation.* There are two waves: a thermal and a compositional wave. On the thermal wave, the temperature and speed change while the gas composition is constant. The characteristic speed is denoted by λ_T. On the compositional wave, the gas composition changes while the temperature and speed are constant. This wave has speed denoted by λ_c. The characteristic speeds are positive and $\lambda_c > \lambda_T$.

6.1.2. *Two-phase situation.* There are two waves: an evaporation rarefaction wave and a saturation (Buckley-Leverett) wave, both isothermal. On the evaporation rarefaction wave, the saturation, temperature and speed change. The characteristic speed is denoted by λ_e. The condensation shock is denoted by S_c and its speed is v_c. On the saturation wave, the water saturation changes, but the saturation and speed are constant. The characteristic speed is denoted by λ^{BL} (Buckley-Leverett); this rarefaction wave is represented by R_{BL}. The shock is the Buckley-Leverett shock S_{BL} and its speed is denoted by v^{BL}.

6.1.3. *Shock between regions.* Between the spg and tp situations, there is a condensation shock with speed v^{GT}, which is denoted by S_{GT}.
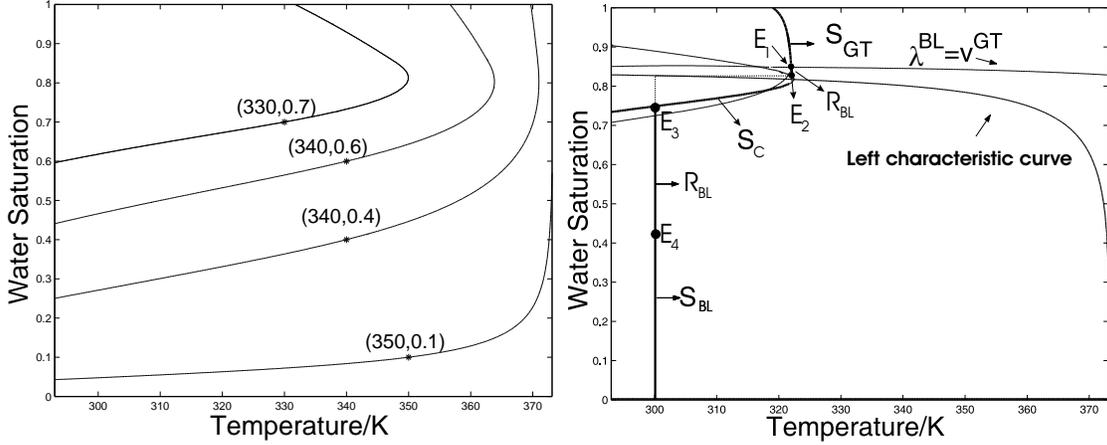
FIGURE 2. *a) Left:* The condensation shocks S_c in the *tp* situation. The state indicate in each curve is the initial point for S_c. The Buckley-Leverett curves are in the vertical lines with constant temperature. *b) Right:* The states and curves in the *tp* situation.

6.1.4. *Riemann Solution.* We consider the Riemann problem with left and right states in the form (23): L has $\psi_L = 0.1$, $T_L = 340K$ and R has $T_R = 300K$.

Since L is in the *spg* situation, see Fig. 1, we propose a shock S_{GT} connecting L and an intermediate state E_1. This state is obtained on the S_{GT} shock where $v^{GB}(L; E_1) = \lambda^{BL}(E_1)$. This state is obtained by the intersection of Hugoniot curve S_{BL} from L with the coincidence curve between v^{BL} and λ^{BL}. We can verify that $v^{GB}(L; E_1) < \lambda_T(L)$.

From E_1 there exists an isothermal rarefaction R^{BL} up to E_2, with fixed temperature T_{E_1}. The state E_2 is obtained using the "left characteristic shock curve".

The "left characteristic shock curve" is constructed by the coincidence between the state P_1 on the R^{BL} (from E_1) and the state P_2. The state P_2 belongs to the evaporation shock S_c (from P_1) and the vertical line from the right state R, in which the equality $v_c(P_1; P_2) = \lambda^{BL}(P_1)$ is satisfied. The vertical lines represent isothermal Buckley-Leverett shock and rarefaction curves.

Thus the state E_2 is obtained from the intersection between the vertical line starting at the right state R and the "left characteristic shock curve", see Figure (2.*b*).

The state E_3 is obtained from the intersection between the S_c starting at E_2 and the vertical line from the right state R. From E_3 there is an isothermal rarefaction up to E_4. The state E_4 is obtained as to satisfy the equality $\lambda^{BL}(E_4) = v^{BL}(E_4; R)$. The solution is summarized in the Figures (2.*b*) and (3).

Condensation of water occurs in the shocks S_{GT} and S_c between the states L-E_1 and E_2-E_3.

7. SUMMARY AND CONCLUSIONS

We have described a solution of the Riemann problem for the injection of a mixture of nitrogen and steam into a porous rock filled with water and sketched a systematic theory for the Riemann solution. The set of solutions depends L^1 continuously on the Riemann
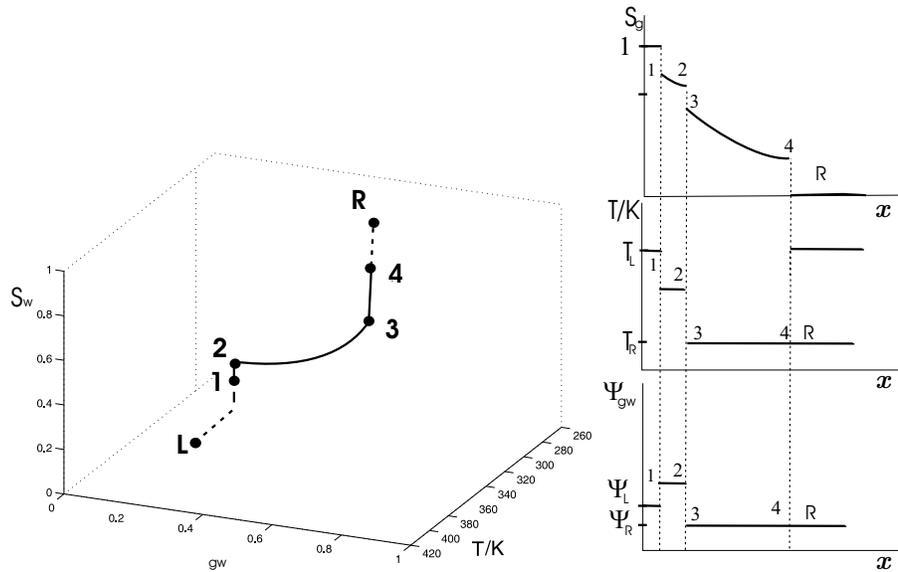
FIGURE 3. *a) Left:* Riemann solution in phase space V, described in Section 6.1.4. In the Riemann solution, we have removed the surface in the phase space of Fig. 1. *b) Right:* The saturation, temperature and gas composition profiles for some $t > 0$. In both Figures, the numbers 1 to 4 indicate the intermediate states E_1 to E_4.

data. It is a step towards obtaining a general method for solving Riemann problems for a wide class of balance equations with phase changes, [6].

Practically, this solution shows that in principle it is possible to clean up NAPL's from soil with a mixture of nitrogen and steam at moderate temperatures, $(67^{o}C)$.

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