

Derivation of basic equations of mass transport in porous media, Part 2. Generalized Darcy's and Fick's laws

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This is the second part of a series of two papers on the development of a general thermodynamic basis for the study of transport phenomena in porous media. The porous medium is modelled as a superposition of one solid continuum coexisting and interacting with an N -component fluid-phase continuum. Macroscopic balance laws derived in Part 1 provide the equations of mass and momentum for the mean motion of the fluid phase and diffusive motions of individual components. The Coleman and Noll's method of exploitation of the entropy inequality is applied to restrict a rather general set of constitutive equations. Gradients of the fluid-phase density and concentrations of $N-1$ components are included among independent variables to account for buoyancy and cross-coupling effects properly. Extensions of certain classical relations for fluid-phase pressure, solid stress tensor, and components' chemical potentials are obtained as results of the constitutive theory. Further simplifications and linearizations of constitutive equations and balance laws yield a general extension of Darcy's and Fick's laws, applicable to cases where the fluid has more than one main component. It is found out that both relations have to be modified to account for the effect of high concentrations. It is shown that classical forms of those laws are valid only if fluid components exist at low concentrations. All assumptions are carefully and explicitly stated during the course of development. As an illustration of the theory, proper forms of Darcy's and Fick's laws for the flow and transport of concentrated brine in porous media are given. The development here also provides a fundamental basis to equations used in the description of chemico-osmosis effects.

Key Words: species transport, dispersion, Fick's law, Darcy's law, mixtures, multi-component fluid, porous medium, Coleman and Noll method.

INTRODUCTION

In recent years, there has been growing interest in the modelling of mass transport processes which take place during the flow of contaminated concentrated brine in soil formations. An important case of practical interest arises in the study of transport or radionuclides released from a repository in a rock-salt formation. In most scenarios about the potential pathways of release of radionuclides to the biosphere, transport of species via the groundwater plays an important role¹. In such cases, the polluted water always contains a high salt concentration. Another example is the exploitation of geothermal reservoirs which in some situations involves the flow of groundwater with a high salt concentration². Note that in the latter case, high temperatures are also encountered.

Despite the complex nature of such problems, current approaches adopted for their solution often employ the same approximations and assumptions that have been adopted in less extreme situations. For instance, almost all existing models employ Darcy's law and Fick's law

which, at best, are valid at low solute concentrations and isothermal conditions. Although more research needs to be conducted, there are some experimental evidence that movement of high-concentration chloride cannot be properly explained by classical Fick's and Darcy's laws. In the measurements of breakthrough curves, it is noticed that the centre of mass of chloride travels more than two times faster than that of a lithium tracer³. Another example is the use of certain boundary conditions which are commonly employed in species transport problems (as well as in heat problems), but are not admissible in the cases that high concentrations are involved. Also, it has been shown that some numerical schemes which work satisfactorily at low solute concentrations, yield unacceptable results for high-concentration situations⁴.

These considerations indicate that equations, ideas, and methodologies currently employed in the study of low-concentration transport phenomena, may lead to incorrect results if they are simply assumed to be equally applicable to high-concentration situations. Instead, one has to start from basic principles and develop a general framework which avoids undesirable restrictive assumptions. The present work, prepared in two parts, is an attempt in that direction.

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In Part 1⁵, using the averaging technique, we developed a macroscopic description of a porous medium composed of a rock skeleton and a multi-component fluid. Macroscopic balance laws for fluid components and rock aggregates were developed and a general formulation of the second law of thermodynamic was provided. In this Part, we develop a constitutive theory which takes the material properties of rock and fluid into considerations. The main objective is to construct a framework within which theories of mass, momentum, and energy transport in porous media can be advanced.

First, we review macroscopic balance equations and some of the definitions provided in Part 1 and supplement them by kinematic relations for the rock. Next, starting with a general set of constitutive postulates, the Coleman and Noll method of exploitation of entropy inequality is employed to arrive at a number of relations for thermodynamic properties. Those equations are then linearized and combined with mass and momentum balance laws to arrive at generalized Fick's and Darcy's laws applicable to mass transport in a deforming porous medium under nonisothermal conditions. Finally, several cases of practical interest are considered and various assumptions needed to arrive at classical forms of Darcy's law and Fick's law are discussed.

KINEMATICS

Consider a porous medium composed of a deformable rock skeleton and a compressible fluid. The fluid phase consists of N miscible components which may interact with each other (in the molecular level) and with the rock (through solid-fluid interfaces) to exchange mass, momentum, and energy. A macroscopic description of the system was developed in Part 1. Here, we simply employ the macroscopic quantities and balance laws which were defined and/or derived in Part 1. Because all quantities used in this part pertain to the macroscopic situation, we will drop all the averaging signs such as overbar and angular brackets, unless confusion with microscopic variables may arise. Thus, for example $\langle \rho^\alpha \rangle^f$ becomes ρ^α and \bar{E}^α becomes E^α . In this section, we reintroduce some of the basic variables and provide kinematics relations for the rock phase.

The (macroscopic) mass density function for a fluid component, ρ^α , is defined as the mass of component α present in a unit volume of the fluid phase. Then, the total mass of fluid phase per its unit volume, ρ^f , is given by:

$$\rho^f = \sum_{\alpha} \rho^\alpha \quad (1)$$

The mass fraction of a component α is denoted by C^α and defined by

$$C^\alpha = \rho^\alpha / \rho^f \quad (2a)$$

subject to

$$\sum_{\alpha} C^\alpha = 1 \quad (2b)$$

Throughout this work, \sum_{α} denotes a summation from $\alpha=1$ to N (i.e. $\sum_{\alpha=1}^N$), and α (or other Greek indices) always ranges from 1 to N , unless otherwise specified. Note that repetition of Greek indices does not imply a summation. A rather comprehensive list of symbols is given at the end of paper. The mass density function of

rock phase, ρ^r , is defined as the mass of solid per unit volume of aggregates. Porosity of the porous medium, n , is defined to be that fraction of a unit volume of porous medium that is occupied by the fluid phase. Because fluid components are miscible, they all have the same volume fraction n . Then, the volume fraction of solid phase will be simply $1-n$. Note that ρ^f and ρ^r are equivalents to true densities of the fluid and the solid, respectively, when they exist separately. In particular, ρ^r may be approximated by the average density of rock grains. The bulk density of porous medium, denoted by ρ^m , is defined as

$$\rho^m = n\rho^f + (1-n)\rho^r \quad (3)$$

As a result of thermodynamic processes, the rock phase as well as each of the fluid components undergo an independent motion. In particular, one could assign a reference configuration to the rock phase which will be altered by its motion. Thus, a typical particle of the solid phase occupying the position X_K at time $t=0$, is carried to a new position x_k at time t . Then, the solid phase motion is given by a function $F_k^r(X_K, t)$ such that

$$x_k = F_k^r(X_K, t) \quad (4)$$

Throughout this Part, standard indicial notation will be used. Upper case Latin indices refer to the reference position (i.e., material coordinates), while lower case Latin indices refer to the deformed position (i.e., spatial coordinates). Greek indices are used to indicate a component of the fluid phase. Superscripts f, r , and m will be used to designate the fluid phase, the solid phase (the rock), and the porous medium, respectively.

A measure of deformation of the solid is the Lagrangian strain tensor E_{KL}^r , defined by

$$E_{KL}^r = \frac{1}{2} (F_{kK}^r F_{kL}^r - \delta_{KL}) \quad (5)$$

where δ_{KL} is the Kronecker delta, and F_{kK}^r is the displacement gradient tensor:

$$F_{kK}^r = \frac{\partial F_k^r}{\partial X_K} \quad (6)$$

The velocity and acceleration of the solid are defined, respectively, as

$$v_k^r = \left. \frac{\partial F_k^r}{\partial t} \right|_{x_K} = v_k^r(x_k, t) \quad (7)$$

$$a_k^r = \left. \frac{\partial v_k^r}{\partial t} \right|_{x_K} = \left. \frac{\partial^2 F_k^r}{\partial t^2} \right|_{x_K} = a_k^r(x_k, t) \quad (8)$$

In writing v_k^r and a_k^r as functions of x_k rather than X_K , it is assumed that the functional relationship of (4) is invertible. This will be true if the jacobian of motion, defined by $J^r = \det F_{kK}^r$, will be nonzero; which is a common assumption in continuum mechanics^{6,7}.

The material derivative of a function following the motion of the solid (i.e., with fixed X_K) will be denoted by D^r/Dt and defined as follows:

$$\frac{D^r \Psi(x_k, t)}{Dt} = \left. \frac{\partial \Psi(x_k, t)}{\partial t} \right|_{x_K} = \left. \frac{\partial \Psi}{\partial t} \right|_{x_k} + \left. \frac{\partial \Psi}{\partial x_k} \frac{\partial x_k}{\partial t} \right|_{x_K} \quad (9a)$$

which, by using the definition of v_k^r becomes,

$$\frac{D^r \Psi}{Dt} = \frac{\partial \Psi}{\partial t} + \Psi_{,k} v_k^r \quad (9b)$$

Similarly, denoting the velocity of component α of the fluid phase by v_k^α , the derivative of a function following the motion of that component is given by:

$$\frac{D^\alpha \Psi}{Dt} = \frac{\partial \Psi}{\partial t} + \Psi_{,k} v_k^\alpha \quad (10)$$

A useful relation between $D^\alpha \Psi / Dt$ and $D^r \Psi / Dt$ is easily obtained from (9) and (10):

$$\frac{D^\alpha \Psi}{Dt} = \frac{D^r \Psi}{Dt} + \Psi_{,k} v_k^{\alpha r} \quad (11)$$

where $v_k^{\alpha r}$ is the velocity of component α relative to the solid phase:

$$v_k^{\alpha r} = v_k^\alpha - v_k^r \quad (12)$$

The average velocity of the fluid phase as a whole is related to those of its components by:

$$v_k^f = \sum_\alpha C^\alpha v_k^\alpha \quad (13)$$

Then, the diffusion-dispersion velocity of a component α , denoted by u_k^α , is defined to be:

$$u_k^\alpha = v_k^\alpha - v_k^f \quad (14)$$

subject to

$$\sum_\alpha C^\alpha u_k^\alpha = 0 \quad (15)$$

The time rate of change of a quantity following the motion of fluid phase is defined analogous to equation (10). Thus, the following relations will hold.

$$\frac{D^f \Psi}{Dt} = \frac{D^r \Psi}{Dt} + u_k^f \Psi_{,k} \quad (16a)$$

and

$$\frac{D^r \Psi}{Dt} = \frac{D^f \Psi}{Dt} + v_k^{fr} \Psi_{,k} \quad (16b)$$

where

$$v_k^{fr} = v_k^f - v_k^r \quad (17a)$$

Also, we have:

$$v_k^{\alpha r} = u_k^\alpha + v_k^{fr} \quad (17b)$$

Finally, let the deformation rate tensor d_{kl}^a ($a = f$ for the fluid and r for the rock) be defined by:

$$d_{kl}^a = v_{(k,l)}^a = \frac{1}{2} (v_{k,l}^a + v_{l,k}^a) \quad (18)$$

where parenthesis in the subscript of $v_{(k,l)}^a$ denote the symmetric part of $v_{k,l}^a$, as defined in equation (18). Then,

the following relation may be established for the derivative of E_{KL}^r (Ref. 7):

$$\frac{D^r E_{KL}^r}{Dt} = d_{kl}^r F_{(kK}^r F_{lL)}^r \quad (19)$$

where parenthesis in the subscripts of $F_{kK}^r F_{lL}^r$ denote its symmetric part with respect to indices k and l :

$$F_{(kK}^r F_{lL)}^r = \frac{1}{2} (F_{kK}^r F_{lL}^r + F_{lK}^r F_{kL}^r) \quad (20)$$

BALANCE LAWS

Equations of balance of mass, momentum, energy, and entropy for individual fluid components and the solid phase were derived in Part 1. In practical problems of species transport in porous media, one is interested in the mean motion of fluid phase and the diffusive motion of $N-1$ components. Also, equations of state are always given in terms of fluid pressure, fluid density, and concentrations of $N-1$ components. Therefore, we choose to employ balance laws for $N-1$ of the components, for the fluid phase, and for the rock. In writing the balance equations for fluid components, we recast them in a form that ensures the redundancy of equations for the N th component. Thus, with the help of equation (2a), balance of mass for components is written in terms of C^α . Balance of linear momentum for components is obtained by subtracting the momentum balance of the N th component from those of the remaining $N-1$ components; so that $N-1$ independent equations are obtained.

As explained in Part 1, because we assume that fluid components always attain a state of thermal equilibrium, balance of energy is given only for the fluid phase and the rock. Further note that using definitions (9) and (10), the time derivative terms and convective flux terms can be written in terms of the total derivative D/Dt . Equations of balance will read as follows:

Mass:

$$\frac{D^f n \rho^f}{Dt} + n \rho^f d_{kk}^f = n \rho^f \hat{R}^f \quad (21a)$$

$$\frac{D^r (1-n) \rho^r}{Dt} + (1-n) \rho^r d_{kk}^r = (1-n) \rho^r \hat{R}^r \quad (21b)$$

$$n \rho^f \frac{D^f C^\beta}{Dt} + J_{k,k}^\beta = n \rho^f C^\beta (\hat{R}^\beta - \hat{R}^f) \quad \beta = 1 \text{ to } N-1 \quad (21c)$$

where equations (1), (2), (10), (16a), and (21a) have been used in obtaining (21c), and J_k^β is the diffusive-dispersive mass flux of component β , defined by:

$$J_k^\beta = n \rho^f C^\beta u_k^\beta \quad \beta = 1 \text{ to } N \quad (22)$$

and subject to:

$$\sum_\beta J_k^\beta = 0 \quad (23)$$

Momentum:

$$n\rho^f \frac{D^f v_k^f}{Dt} - \sigma_{kl,l}^f - n\rho^f g_k^f = n\rho^f \hat{T}_k^f \quad (24a)$$

$$(1-n)\rho^r \frac{D^r v_k^r}{Dt} - \sigma_{kl,l}^r - (1-n)\rho^r g_k^r = (1-n)\rho^r \hat{T}_k^r \quad (24b)$$

$$n\rho^f C^\beta \left(\frac{D^\beta v_k^\beta}{Dt} - \frac{D^N v_k^N}{Dt} \right) - (\sigma_{kl,l}^\beta - (C^\beta/C^N)\sigma_{kl,l}^N) - n\rho^f C^\beta (g_k^\beta - g_k^N) = n\rho^f C^\beta (\hat{T}_k^\beta - \hat{T}_k^N) \quad (24c)$$

Energy:

$$n\rho^f \frac{D^f E^f}{Dt} - \sigma_{kl}^f v_{l,k}^f - q_{k,k}^f - n\rho^f h^f = n\rho^f \hat{Q}^f$$

$$(1-n)\rho^r \frac{D^r E^r}{Dt} - \sigma_{kl}^r v_{l,k}^r - q_{k,k}^r - (1-n)\rho^r h^r = (1-n)\rho^r \hat{Q}^r \quad (25b)$$

where σ_{kl}^f , σ_{kl}^r , and σ_{kl}^β are symmetric second order tensors. All the variables are defined in the Nomenclature. Once again note that in using equations of balance derived in Part 1, we have dropped all averaging signs. Quantities \hat{R}^β , and \hat{T}_k^β account for the exchange of mass and momentum between the component α and all other components and the solid phase as defined in Part 1. It is possible to partition them into separate terms, each accounting for one of the effects such as chemical reaction and mutual drag between components, chemical reaction and viscous drag between components and solid grains, sorption of components on solid grains and solution/dissolution processes. As a case of practical interest, such a partitioning is given for the mass exchange term in the Appendix B. Above-mentioned exchange terms are subject to the following restrictions derived in Part 1.

$$(1-n)\rho^r \hat{R}^r = -n \sum_\alpha \rho^\alpha \hat{R}^\alpha = -n\rho^f \hat{R}^f \quad (26a)$$

$$(1-n)\rho^r \hat{T}_k^r = -n \sum_\alpha \rho^\alpha (\hat{T}_k^\alpha + \hat{R}^\alpha v_k^{\alpha r}) = -n\rho^f (\hat{T}_k^f + \hat{R}^f v_k^{fr}) \quad (26b)$$

$$(1-n)\rho^r \hat{Q}^r = -n \sum_\alpha \rho^\alpha \left(\hat{Q}^\alpha + \hat{T}_k^\alpha v_k^{\alpha r} + \hat{R}^\alpha \left(\frac{1}{2} v_k^{\alpha r} v_k^{\alpha r} + E^\alpha - E^r \right) \right) - n\rho^f \left(\hat{Q}^f + \hat{T}_k^f v_k^{fr} + \hat{R}^f \left(\frac{1}{2} v_k^{fr} v_k^{fr} + E^f - E^r \right) \right) \quad (26c)$$

Further, we recall from Part 1 that fluid bulk properties are related to those of its components by the following equations.

$$g_k^f = \sum_\alpha C^\alpha g_k^\alpha \quad (27)$$

$$\sigma_{kl}^f = \sum_\alpha (\sigma_{kl}^\alpha - n\rho^\alpha u_k^\alpha u_l^\alpha) \quad (28)$$

$$E^f = \sum_\alpha C^\alpha \left(E^\alpha + \frac{1}{2} u_k^\alpha u_k^\alpha \right) \quad (29)$$

$$q_k^f = \sum_\alpha \left[q_k^\alpha + t_{kl}^\alpha u_l^\alpha - n\rho^\alpha \left(E^\alpha + \frac{1}{2} u_l^\alpha u_l^\alpha \right) u_k^\alpha \right] \quad (30)$$

$$S^f = \sum_\alpha C^\alpha S^\alpha \quad (31)$$

SECOND LAW OF THERMODYNAMICS

According to the second law, the rate of net entropy production of the system must be nonnegative. This requirement may be expressed in the following form⁵:

$$\Gamma^m = n \sum_\alpha \rho^\alpha \Gamma^\alpha + (1-n)\rho^r \Gamma^r \geq 0 \quad (32)$$

In part 1, using the balance equations, this relation was put in the following expanded form.

$$\Gamma^m = \frac{1}{\theta^f} \sum_\alpha \left\{ -n\rho^\alpha \left(\frac{D^\alpha A^\alpha}{Dt} + S^\alpha \frac{D^\alpha \theta^f}{Dt} \right) + \sigma_{kl}^\alpha v_{k,l}^\alpha + \frac{q_k^\alpha}{\theta^f} \theta_{f,k}^\alpha + \theta^f \left(\frac{q_k^\alpha}{\theta^f} - \phi_k^f \right)_{,k} + n\rho^\alpha \hat{Q}^\alpha \right\} + \frac{1}{\theta^r} \left\{ -(1-n)\rho^r \left(\frac{D^r A^r}{Dt} + S^r \frac{D^r \theta^r}{Dt} \right) + \sigma_{kl}^r v_{k,l}^r + \frac{q_k^r}{\theta^r} \theta_{r,k}^r + \theta^r \left(\frac{q_k^r}{\theta^r} - \phi_k^r \right)_{,k} + (1-n)\rho^r \hat{Q}^r \right\} \geq 0 \quad (33)$$

where A is the Helmholtz free energy function defined by:

$$A = E - \theta S \quad (34)$$

and θ^f and θ^r , defined in Part 1, are identified as the absolute temperature functions of fluid and rock, respectively.

At this point, certain simplifying assumptions are made. In continuum mechanics, it is normally assumed that the entropy flux, ϕ_k , is proportional to the heat flux, q_k , such that:

Assumption 1:

$$\phi_k^f = q_k^f / \theta^f \quad (35a)$$

$$\phi_k^r = q_k^r / \theta^r \quad (35b)$$

In the remainder of this work, attention will be confined to cases where local thermal equilibrium exists between the fluid phase and rock aggregates so that a common function $\theta(x, t)$ gives the temperature of the fluid or the solid phase at a given point and time. Therefore,

Assumption 2:

$$\theta^f(x, t) \equiv \theta^r(x, t) \equiv \theta(x, t) \quad (36)$$

Now, by the aid of relations (35) and (36), it is possible to further simplify the entropy inequality (33). However,

first we like to recast it in terms of the fluid phase bulk properties. To do so, the following identity is needed. It can be deduced from equations (1), (2), (10), (16), (21a), (21c), and (26a).

$$\begin{aligned} \sum_{\alpha} \rho^{\alpha} \frac{D^{\alpha} A^{\alpha}}{Dt} &= \rho^f \frac{D^f A^f}{Dt} + \sum_{\alpha} ((\rho^f C^{\alpha} A^{\alpha} u_k^{\alpha})_{,k} - \rho^f C^{\alpha} A^{\alpha} (\hat{R}^{\alpha} - \hat{R}^f)) \\ &= \rho^f \frac{D^f A^f}{Dt} + \sum_{\alpha} (\rho^f C^{\alpha} (A^{\alpha} - A^N) u_k^{\alpha})_{,k} \\ &\quad - \sum_{\alpha} \rho^f C^{\alpha} A^{\alpha} (\hat{R}^{\alpha} - \hat{R}^f) \end{aligned} \quad (37)$$

where A^f is the inner part of Helmholtz free energy of the fluid phase defined by:

$$A^f = \sum_{\alpha} C^{\alpha} A^{\alpha} \quad (38)$$

Then, by the aid of relations (37), (14), (17), (26), (28), (30), and (31), and after some tedious algebraic manipulations, the entropy inequality (33) is transformed into the following form.

$$\begin{aligned} \theta \Gamma^m &= -n \rho^f \frac{D^f A^f}{Dt} + \left(\sigma_{kl}^f + n \rho^f \sum_{\alpha} C^{\alpha} u_k^{\alpha} u_l^{\alpha} \right) d_{kl}^f \\ &\quad - (1-n) \rho^r \frac{D^r A^r}{Dt} + \sigma_{kl}^r d_{kl}^r - n \rho^f \hat{T}_k^f v_k^{fr} \\ &\quad - n \rho^f \left((A^f - A^r) + 12 v_k^{fr} v_k^{fr} \right) \hat{R}^f \\ &\quad + \sum_{\alpha} \left[\left(\sigma_{kl}^{\beta} - \frac{C^{\beta}}{C^N} \sigma_{kl}^N \right) - n \rho^f C^{\beta} (A^{\beta} - A^N) \delta_{kl} \right] u_{k,l}^{\beta} \\ &\quad - \sum_{\beta} \left\{ n \rho^f C^{\beta} (\hat{T}_k^{\beta} - \hat{T}_k^N) + n \rho^f C^{\beta} (A^{\beta} - A^N)_{,k} \right. \\ &\quad \quad \left. + (A^{\beta} - A^N) (n \rho^f C^{\beta})_{,k} + \sigma_{kl}^N \left(\frac{C^{\beta}}{C^N} \right)_{,l} \right\} u_k^{\beta} \\ &\quad - \frac{1}{2} n \rho^f \sum_{\beta} C^{\beta} u_k^{\beta} u_k^{\beta} \hat{R}^{\beta} - \rho^m S^m \frac{D^r \theta}{Dt} \\ &\quad - \left(\frac{q_k^m}{\theta} - n \rho^f \sum_{\alpha} C^{\alpha} S^{\alpha} v_k^{\alpha r} \right) \theta_{,k} > 0 \end{aligned} \quad (39)$$

where S^m and q_k^m are the internal entropy and the inner part of heat vector of the porous medium, respectively. They are defined by:

$$\rho^m S^m = (n \rho^f S^f + (1-n) \rho^r S^r) \quad (40a)$$

$$q_k^m = q_k^f + q_k^r \quad (40b)$$

It is noticed that in equation (39), terms related to the motion of components have the same form as they appear in the equation of momentum conservation (24c).

Before closing this section, it must be noted that, because fluid and solid are assumed to attain a common temperature at all times, it suffices to solve only one of the two energy equations (25). The other equation simply prescribes certain interdependence between thermal properties of the two coexisting continua. In practice, usually the energy equation for the porous medium, as a whole, is employed. We will follow the same formulation. The energy equation for the porous medium is obtained by summation of equations (25a) and (25b), and repeated

use of equations of mass conservation, relations (14)–(17), and restrictions (26). After a lengthy manipulation, we arrive at the following:

$$\begin{aligned} \rho^m \frac{D^r E^m}{Dt} &+ (n \rho^f E^f v_k^{fr})_{,k} - \sigma_{kl}^f v_l^f - \sigma_{kl}^r v_l^r - q_{k,k}^m \\ &\quad - n \rho^f h^f - (1-n) \rho^r h^r \\ &\quad + n \rho^f \left(\hat{T}_k^f v_k^{fr} + \frac{1}{2} \hat{R}^f v^{fr^2} \right) = 0 \end{aligned} \quad (41)$$

where E^m is the internal energy of the porous medium defined similarly to S^m in equation (40a).

CONSTITUTIVE EQUATIONS

Examination of equations (21), (24), (41), and the entropy inequality (39) reveals that we have $4N + 5$ equations in terms of $16N + 17$ unknowns which are enumerated below.

$n,$	$\theta,$	$\rho^f,$	$\rho^r,$	$C^{\beta},$	$v_k^f,$	$u_k^{\beta},$	$F_k^f,$	$A^f,$	$A^r,$	$(A^{\beta} - A^N),$	$S^{\alpha},$	S^m
(1)	(1)	(1)	(1)	($N-1$)	(3)	($3N-3$)	(3)	(1)	(1)	($N-1$)	(N)	(1)
$\sigma_{kl}^f,$	$\sigma_{kl}^r,$	$(\sigma_{kl}^{\beta} - (C^{\beta}/C^N) \sigma_{kl}^N),$	$\hat{T}_k^f,$	$(\hat{T}_k^{\beta} - \hat{T}_k^N),$	$\hat{R}^{\beta},$	$\hat{R}^f,$	q_k^m					
(6)	(6)	($6N-6$)	(3)	($3N-3$)	($N-1$)	(1)	(3)					

All other quantities appearing in balance laws are related to above-listed variables according to kinematic relations, by their own definitions, and/or because of restrictions (26).

It is apparent that we are short of $12N + 12$ equations. This should be expected as we have said nothing yet about the behaviour of components of the porous medium. Therefore, general balance laws of previous section must be supplemented by constitutive relations which account for material properties of fluid and solid phases under consideration, and also remove the deficit in the number of equations. To start with, we postulate a rather general form of constitutive functions for our unknowns. We shall restrict ourselves only in the choice of the set of independent variables as will be explained farther below. The entropy inequality, the objectivity principle, and material symmetries will be utilized in order to restrict the general postulates. The unknowns, chosen as dependent variables are members of the set $\{\Psi_{\Lambda}\}$ given below.

$$\begin{aligned} \{\Psi_{\Lambda}; \Lambda = 1 \text{ to } 12N + 11\} &= \left\{ A^f, A^r, (A^{\beta} - A^N), S^{\alpha}, S^m, \right. \\ &\quad \left. \sigma_{kl}^f, \sigma_{kl}^r, \left(\sigma_{kl}^{\beta} - \left(\frac{C^{\beta}}{C^N} \right) \sigma_{kl}^N \right), \hat{T}_k^f, (\hat{T}_k^{\beta} - \hat{T}_k^N), \hat{R}^{\beta}, \hat{R}^f, q_k^m \right\} \\ &\quad \alpha = 1 \text{ to } N; \quad \beta = 1 \text{ to } N - 1 \end{aligned} \quad (42)$$

These variables are not directly measurable and they will be determined as functions of directly measurable variables, hereby called independent variables. The choice of independent variables is made in accordance with the expected behaviour of fluid components, the

fluid phase, and the solid phase, as well as the type of phenomena to be encountered. In this work, the following constraints are imposed.

Assumptions 3:

The solid grains are incompressible, i.e., $\rho^r = \rho_o^r(X_K)$.

Assumption 4:

The solid phase is a thermoelastic material.

Assumption 5:

All components of the fluid are macroscopically nonviscous.

Incorporating Assumption 3 in the mass conservation equation (21b), one obtains the following relations:

$$\frac{D^r \rho^r}{Dt} = 0 \tag{43a}$$

$$\frac{D^r n}{Dt} = (1-n) d_{kk}^r + n \frac{\rho^f}{\rho_o^f} \hat{R}^f \tag{43b}$$

Assumption 3 is adopted here in order to provide us with the necessary closure equation (for a thorough discussion of the problem of the closure equation see Bedford and Drumheller⁸). It is a simple, yet practically nonrestrictive assumption which was first adopted by Hassanizadeh and Gray⁹.

From equation (43b) and by the aid of kinematic relations, one can establish a relation for n in terms of J^r (the jacobian of the rock motion) and \hat{R}^r ¹⁰; this means that the three quantities are not independent. On the other hand, J^r is expressible in terms of invariants of the strain tensor E_{KL}^r ⁷. Therefore, in the postulation of constitutive relations, if E_{KL}^r and \hat{R}^r (or \hat{R}^f) are among the list of variables, n will not be treated as an unknown.

Acknowledging these considerations, the following constitutive relations are postulated for dependent variables.

Assumption 6:

$$A^f = A^f(\rho^f, C^\gamma, E_{KL}^r, \theta) \tag{44a}$$

$$A^r = A^r(\rho^f, E_{KL}^r, \theta) \tag{44b}$$

$$A^\beta - A^N = \hat{A}^\beta(\rho^f, C^\gamma, E_{KL}^r, \theta) \tag{44c}$$

$$\Psi_\Lambda = \Psi_\Lambda(\rho^f, C^\gamma, \rho_{,k}^f, C_{,k}^\gamma, n_{,k}, E_{KL}^r, \theta, \theta_{,k}, u_k^f, v_k^{fr})$$

$$\beta, \gamma = 1 \text{ to } N-1; \quad \Lambda = N+2 \text{ to } 12N+11 \tag{44d}$$

In these relations, $n_{,k}$, $C_{,k}^\gamma$, $\rho_{,k}^f$, u_k^f , and v_k^{fr} are included to account for buoyancy as well as diffusion effects; E_{KL}^r accounts for effects of elasticity of the rock; and θ and $\theta_{,k}$ allow for modelling of thermal effects and heat transfer. Note that, as explained above, as long as E_{KL}^r is among the list of independent variables, n need not be included in the list. Constitutive relations given for A^f , A^r , and A^β are not the most general that one can postulate. However, it can be shown that this choice is merely an early simplification, which will be eventually obtained from a more general set of constitutive relations.

Equations (44) must obey principles of objectivity and admissibility. According to the principle of objectivity,

constitutive relations shall remain unchanged under an orthonormal transformation of the frame of reference. It is for the satisfaction of this principle that relative velocities u_k^f and v_k^{fr} , instead of absolute velocities v_k^f and v_k^r , and stain tensor E_{KL}^r , instead of the displacement gradient F_{kK}^r , are selected as independent variables. The principle of admissibility requires that constitutive equations shall not violate balance laws and the second law of thermodynamics. This requirement reveals much information on constitutive functions and will be fully explored here. For an exposition of principles of objectivity and admissibility, one may consult Eringen⁷ for single-phase media and Hassanizadeh¹¹ for ultiphase systems.

Restrictions imposed by the principle of admissibility, and in particular by the second law of thermodynamics, are explored by the Coleman and Noll's method¹². Details of the procedure are given in Appendix A and lead to the following simplifications of constitutive equations.

$$A^\gamma = A^\gamma(\rho^f, C^\gamma, \theta) \quad \gamma = 1 \text{ to } N-1 \tag{45a}$$

$$A^r = A^r(\rho^f, E_{KL}^r, \theta) \tag{45b}$$

$$A^\beta - A^N = \hat{A}^\beta(\rho^f, C^\gamma, \theta) \quad \gamma = 1 \text{ to } N-1 \tag{45c}$$

$$\rho^m S^m = -n \rho^f \frac{\partial A^f}{\partial \theta} - (1-n) \rho^f \frac{\partial A^r}{\partial \theta} \tag{45d}$$

$$\sigma_{kl}^f = -n \rho^f \delta_{kl} - n \sum_\alpha C^\alpha u_k^\alpha u_l^\alpha \tag{46a}$$

$$\sigma_{kl}^r = -(1-n) p^f \delta_{kl} + e \sigma_{kl}^r \tag{46b}$$

$$\hat{\sigma}_{kl}^{\beta} = \sigma_{kl}^\beta - (C^\beta/C^N) \sigma_{kl}^N = -n \rho^f C^\beta (\hat{\mu}^\beta - \hat{A}^\beta) \delta_{kl} \tag{46c}$$

$$n \rho^f \hat{T}_k^f = n \rho^f \hat{t}_k^f + p^f n_{,k} \tag{47a}$$

$$n \rho^f C^\beta (\hat{T}_k^\beta - \hat{T}_k^N) = n \rho^f C^\beta \hat{t}_k^\beta + (n \rho^f C^\beta (\hat{\mu}^\beta - \hat{A}^\beta))_{,k} - n \rho^f C^\beta \hat{\mu}_{,k}^\beta - \sigma_{kl}^N (C^\beta/C^N)_{,l} \tag{47b}$$

where,

$$p^f = p^f(\rho^f, C^\gamma, E_{KL}^r, \theta) = \rho^f \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^f \frac{\partial A^r}{\partial \rho^f} \right) \tag{48a}$$

$$\hat{\mu}^{\beta} = \mu^\beta - \mu^N = \frac{\partial A^f}{\partial C^\beta} = \hat{\mu}^\beta(\rho^f, C^\gamma, \theta) \quad \gamma = 1 \text{ to } N-1 \tag{48b}$$

$$\mu^f = \sum_\alpha C^\alpha \mu^\alpha = \frac{p^f}{\rho^f} + A^f \tag{48c}$$

$$e \sigma_{kl}^r = (1-n) \rho_o^r \frac{\partial A^r}{\partial E_{KL}^r} F_{(kK}^r F_{lL}^r \tag{48d}$$

$\hat{\mu}^\beta$ is the relative chemical potential of component β with respect to a reference – here being the chemical potential of the N th component, p^f is the thermodynamic pressure of fluid phase, and $e \sigma_{kl}^r$ is the effective stress acting on solid grains. It is noted that the stress tensor for fluid components do not have any dissipating part. This result is a consequence of Assumption 5 which prescribes the fluid components as macroscopically nonviscous. In fact,

from comparison of (46a) and (28), it is easily found that the sum of partial stresses of components is equal to the fluid-phase pressure:

$$\sum_{\alpha} \sigma_{ki}^{\alpha} = -np^f \delta_{ki} \quad (48e)$$

This is in accordance with classical thermodynamics of mixtures. Also it is interesting to note that relation (48b), which is a classical result for species transport in fluids, is proved here to be equally valid for species transport in porous media.

Remaining quantities in the set of independent variables, Ψ_{Λ} , retain their dependence on the full list of independent variables. They are, however, restricted by the residual entropy inequality quoted here from Appendix A.

$$\begin{aligned} \theta \Gamma^m = & \left[\frac{q_k^m}{\theta} - n\rho^f \sum_{\alpha} C^{\alpha} S^{\alpha} u_k^{\alpha} - n\rho^f \left(\frac{\partial A^f}{\partial \theta} + S^f \right) v_k^{fr} \right] \theta_{,k} \\ & - n\rho^f \sum_{\alpha} C^{\beta} \hat{t}_k^{\beta} u_k^{\beta} - n\rho^f \hat{t}_k^{fr} v_k^{fr} \\ & - n\rho^f \sum_{\beta} C^{\beta} \left[\hat{\mu}^{\beta} + \frac{1}{2} u_k^{\beta} u_k^{\beta} \right] \hat{R}^{\beta} \\ & - n\rho^f \left[(G^f - G^r) + \frac{1}{2} v_k^{fr} v_k^{fr} - \hat{\mu}^f \right] \hat{R}^f \geq 0 \end{aligned} \quad (49)$$

where $\hat{\mu}^f$ is the chemical potential of fluid phase relative to that of the N th component and G^f and G^r are Gibb's free energy functions of fluid and solid defined below.

$$G^f = \frac{p^f}{\rho^f} + A^f \quad (50a)$$

$$G^r = \frac{p^r}{\rho_o^r} + A^r \quad (50b)$$

Further information on constitutive functions are obtained by examining the entropy inequality at equilibrium states

EQUILIBRIUM RESTRICTIONS

The state of thermodynamic equilibrium is defined to be the state at which the following independent variables are all zero.

$$\{Z_{\Lambda}; \Lambda = 1 \text{ to } 3N + 3\} = \{\theta_{,k}, v_k^{fr}, u_k^{\alpha}; \alpha = 1 \text{ to } N - 1\} \quad (51)$$

Furthermore, the additional conditions for equilibrium, commonly given in thermodynamics and thermochemistry^{1,3}, is adopted here that,

$$\hat{\mu}^{\beta}|_e = 0 \quad (52a)$$

$$G^f|_e = G^r|_e \quad (52b)$$

where, '|_e' denotes evaluation of the preceding term at equilibrium. It is readily verified that $\theta \Gamma^m$ goes to zero at equilibrium; i.e., it attains its minimum value. The necessary and sufficient conditions to ensure that $\theta \Gamma^m$ is a minimum at equilibrium are,

$$\frac{\partial \Gamma}{\partial Z_{\Lambda}}|_e = 0; \quad \Lambda = 1, \dots, 3N + 3 \quad (53a)$$

$$\left\| \frac{\partial^2 \Gamma}{\partial Z_{\Lambda} \partial Z_{\Pi}} \right\| \text{ is positive semi-definite; } \Lambda, \Pi = 1 \text{ to } 3N + 3 \quad (53b)$$

Application of restriction (53a) to the residual entropy inequality (49) yields the following:

$$q_k^m|_e = 0 \quad (54a)$$

$$\hat{t}_k^f|_e = 0 \quad (54b)$$

$$\hat{t}_k^{\beta}|_e = 0 \quad (54c)$$

Also, from equation (46a), it immediately follows that

$$\sigma_{ki}^f|_e = -np^f \delta_{ki} \quad (54d)$$

Conclusions drawn out of these equations are: (i) at equilibrium there is no flow of heat into or out of the porous medium, (ii) \hat{T}_k^f and \hat{T}_k^{β} consist of an equilibrium and a dissipative part, the latter being zero at equilibrium. From equations (47), it is apparent that the equilibrium part of \hat{T}_k^f is due to buoyancy forces arising from the existence of the solid phase, while the equilibrium part of \hat{T}_k^{β} , in addition to this effect, also receives contribution from buoyancy effects arising from the existence of other components. The requirement (53b) places further restrictions on the form of constitutive functions, specially on material coefficients when linear approximations are employed.

So far as we are interested, exploitation of the entropy inequality for extracting information about constitutive functions is accomplished. It can be verified that the combination of constitutive functions (44) – subject to restrictions (45) to (48) and (52) to (54), with conservation equations (21), (24), and (41) – subject to restrictions (26) and (43b), provide $4N + 5$ equations in terms of $4N + 5$ unknowns, namely $n, p^f, C^{\beta}, u_k^{\beta}, v_k^{fr}, F_k^r$, and θ . In particular, substitution of equations (47a) and (46a) into (24a), equations (47a) and (46b) into (24b), and equations (46c) and (46b) into (24c), yield the following equations of motion for the fluid phase, the rock phase, and fluid components, respectively.

$$\rho^f a_k^f + \left(\sum_{\alpha} C^{\alpha} u_k^{\alpha} u_i^{\alpha} \right)_{,i} + p_{,k}^f - \rho^f g_k^f = \rho^f \hat{t}_k^f + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \rho_{,k}^f \quad (55a)$$

$$\rho_o^r a_k^r + p_{,k}^f - \rho_o^r \sigma_{ki,l}^r - \rho_o^r g_k^r = -\frac{n}{1-n} \rho^f (\hat{t}_k^f + \hat{R}^f v_k^{fr}) \quad (55b)$$

$$(a_k^{\beta} - a_k^N) + \hat{\mu}_{,k}^{\beta} - (g_k^{\beta} - g_k^N) = \hat{t}_k^{\beta} \quad (55c)$$

where a_k^{α} is the acceleration term equal to $D^{\alpha} v_k^{\alpha} / Dt$ (also a_k^f and a_k^r). Equations (55a) and (55b) have familiar forms and except for the apparent stress tensor due to diffusion effects, they are identical to the ones derived by Hassanizadeh and Gray⁹ for flow of a (single-component) fluid in a porous elastic solid. It was shown there that, employing a linearized constitutive function for \hat{t}_k^f , neglecting acceleration terms, and under isothermal conditions, equation (55a) reduces to Darcy's law.

Equation (55c), as presented here has not been derived before for components of a fluid flowing in a porous medium. Bowen⁶ has established a similar relation but for a miscible mixture of fluids (or a multi-component solution). The rest of this work concerns itself with the derivation of generalized Fick's law and Darcy's law from equations(55).

DERIVATION OF GENERALIZED FICK'S AND DARCY'S LAWS

First, constitutive functions of previous section are linearized in terms of the following variables.

$$\{\chi_\Lambda; \Lambda=1 \text{ to } 6N+13\} = \{\rho_{,k}^f, C_{,k}^\gamma, n_{,k}, e_{kl}^r, T, T_{,k}, v_k^{fr}, u_k^\gamma; \gamma=1 \text{ to } N-1\} \quad (56a)$$

where e_{kl}^r is the infinitesimal strain tensor approximating E_{KL}^r in the linear theory⁷, and T is the deviation of temperature θ from a reference value T_o , such that

$$T = \theta - T_o \quad (56b)$$

Thus, constitutive relations (44), restricted by equations (45) to (48) and (52) to (54), are expanded in a Taylor series around the state ($\chi_\Lambda=0; \Lambda=1 \text{ to } 6N+13$). For example, for $\hat{\tau}_k^f$ one obtains

$$\begin{aligned} \hat{\tau}_k^f = & \left. \frac{\partial \hat{\tau}_k^f}{\partial \rho_{,l}^f} \right|_o \rho_{,l}^f + \sum_\gamma^{N-1} \left. \frac{\partial \hat{\tau}_k^f}{\partial C_{,l}^\gamma} \right|_o C_{,l}^\gamma + \left. \frac{\partial \hat{\tau}_k^f}{\partial n_{,l}} \right|_o n_{,l} + \left. \frac{\partial \hat{\tau}_k^f}{\partial e_{lm}^r} \right|_o e_{lm}^r \\ & + \left. \frac{\partial \hat{\tau}_k^f}{\partial \theta} \right|_o T + \left. \frac{\partial \hat{\tau}_k^f}{\partial \theta_{,l}} \right|_o T_{,l} + \left. \frac{\partial \hat{\tau}_k^f}{\partial v_l^{fr}} \right|_o v_l^{fr} + \sum_\gamma^{N-1} \left. \frac{\partial \hat{\tau}_k^f}{\partial u_l^\gamma} \right|_o u_l^\gamma + 0(\Delta^2) \end{aligned} \quad (57)$$

where, $|_o$ denotes evaluation at $\chi_\Lambda=0$, and Δ^2 is defined by

$$\begin{aligned} \Delta^2 = & \rho_{,k}^f \rho_{,k}^f + \sum_\gamma^{N-1} C_{,k}^\gamma C_{,k}^\gamma + n_{,k} n_{,k} + e_{kl}^r e_{kl}^r + T^2 \\ & + T_{,k} T_{,k} + v_k^{fr} v_k^{fr} + \sum_\gamma^{N-1} u_k^\gamma u_k^\gamma \end{aligned} \quad (58)$$

Now the following assumption is adopted

Assumption 7:

Quantities of order Δ^2 are small and can be neglected.

Further note that according to restriction (54b), $\hat{\tau}_k^f$ must vanish at equilibrium. Hence, realizing that $\rho_{,l}^f, C_{,l}^\gamma, n_{,l}, e_{kl}^r$, and T are independent variables which are nonzero at equilibrium, their coefficients in equation (57) must vanish identically such that we get:

$$\hat{\tau}_k^f = -R_{kl}^f v_l^{fr} + \sum_\gamma^{N-1} S_{kl}^{\gamma f} u_l^\gamma + T_{kl}^f T_{,l} \quad (59)$$

where $R_{kl}^f, S_{kl}^{\gamma f}$, and T_{kl}^f stand for coefficients of v_l^{fr}, u_l^γ and

$T_{,l}$ in equation (57), respectively. They are called material coefficients and are functions of ρ^f, C^γ, n , and T_o . Appearance of v_l^{fr} and u_l^γ ($\gamma=1 \text{ to } N-1$) in this equation indicates that the force exerted on the fluid, as it moves through the solid, depends not only on the mean motion of the fluid, but also on the diffusive motion of its components. Contribution of an individual component may be negligible only if it exists at a low concentration such that it comprises a small portion of the fluid phase as compared to other components. Such presumptions will be referred to later in the discussion of results.

In an analogous manner, the following linear constitutive relations is obtained for $\hat{\tau}_k^\beta$.

$$\hat{\tau}_k^\beta = R_{kl}^\beta v_l^{fr} - \sum_\gamma^{N-1} S_{kl}^{\beta \gamma} u_l^\gamma + T_{kl}^\beta T_{,l} \quad (60)$$

Here also, $R_{kl}^\beta, S_{kl}^{\beta \gamma}$, and T_{kl}^β are material coefficients depending on n, ρ^f, C^γ , and T_o . Note that the dependence on the porosity n is resumed, because in the linear theory dependence on E_{kl}^r vanishes. The R - S - T coefficients are subject to the second condition of equilibrium (53b). It can be verified that to fulfill (53b), R_{kl}^f and $S_{kl}^{\beta \beta}$ must be positive semi-definite tensors. Before substitution of above relations into equations of motion, two more simplifying assumptions are made.

Assumption 8:

Inertial terms in equations (55) are small and may be neglected.

Assumption 9:

Dependence of the rock free energy on the fluid-phase density can be neglected; i.e., $\partial A^r / \partial \rho^f \approx 0$.

Assumption (8) is equivalent to the assumption of 'creeping flow', commonly adopted in the study of flow in porous media. Assumption (9) is not necessary for the derivation given here; it is merely adopted to reduce subsequent algebra.

Hence, substitution of equations (59) and (60) into (55a) and (55c), respectively, under the light of Assumptions 7 to 9, yield,

$$\frac{1}{\rho^f} (p_k^f - \rho^f g_k^f) = -R_{kl}^f v_l^{fr} + \sum_\gamma^{N-1} S_{kl}^{\gamma f} u_l^\gamma - T_{kl}^f T_{,l} \quad (61)$$

$$\hat{\mu}_{,k}^\beta - (g_k^\beta - g_k^N) = R_{kl}^\beta v_l^{fr} - \sum_\gamma^{N-1} S_{kl}^{\beta \gamma} u_l^\gamma - T_{kl}^\beta T_{,l} \quad (62)$$

We now solve these equations to find v_l^{fr} and u_l^γ in terms of other variables. To be able to do so, one has to assume the following:

Assumption 10:

Tensorial quantities R_{kl}^f, R_{kl}^β , and $\hat{R}_{kl}^{\beta \gamma} = (R_{km}^\beta)^{-1} S_{lm}^{\beta \gamma} - (R_{km}^f)^{-1} S_{lm}^{\gamma f}$ have an inverse. The inverse of the latter quantity is denoted by $\pi_{mk}^{\alpha \beta}$ such that $\sum_\beta^{N-1} \pi_{mk}^{\alpha \beta} \hat{R}_{kl}^{\beta \gamma} = \delta_{ml}^{\alpha \gamma}$ where $\delta_{mi}^{\alpha \gamma} = \delta_{mi}$ if $\alpha = \gamma$ and zero otherwise.

Then, one will find the following relations for v_k^{fr} and J_k^β (or u_k^β). Note that $\hat{\mu}_{,k}^\beta$ has been expanded in terms of $\rho_{,k}^f, C_{,k}^\gamma$, and $T_{,k}$. It is also possible to expand p_k^f in terms of the same set of variables. However, we have chosen to keep it in a more familiar form which makes the comparison with

existing theories easier.

$$v_k^{f,r} = -K_{kl}^f(p_{,l}^f - \rho^f g_l^f) - \left[B_{kl}^f \rho_{,l}^f + \sum_{\gamma}^{N-1} D_{kl}^{f,\gamma} C_{,\gamma}^f \right] - \sum_{\beta} L_{kl}^{f,\beta} (g_l^{\beta} - g_l^N) - M_{kl}^f T_{,l} \quad (63)$$

$$J_k^z = n \rho^f C^z u_k^z = -K_{kl}^z (p_{,l}^f - \rho^f g_l^f) - \left(B_{kl}^z \rho_{,l}^f + \sum_{\gamma}^{N-1} D_{kl}^{z,\gamma} C_{,\gamma}^f \right) - \sum_{\beta} L_{kl}^{z,\beta} (g_l^{\beta} - g_l^N) - M_{kl}^z T_{,l} \quad (64)$$

where,

$$B_{kl}^f = \sum_{\beta} L_{kl}^{f,\beta} \left(\frac{\partial \mu^{*\beta}}{\partial \rho^f} \right)_{C^{\gamma}, T} \quad (65a)$$

$$D_{kl}^{f,\gamma} = \sum_{\beta} L_{kl}^{f,\beta} \left(\frac{\partial \mu^{*\beta}}{\partial C^{\gamma}} \right)_{\rho^f, T, C^{\delta} (\delta \neq \gamma)} \quad (65b)$$

$$B_{kl}^z = \sum_{\beta} L_{kl}^{z,\beta} \left(\frac{\partial \mu^{*\beta}}{\partial \rho^f} \right)_{C^{\gamma}, T} \quad (66a)$$

$$D_{kl}^{z,\gamma} = \sum_{\beta} L_{kl}^{z,\beta} \left(\frac{\partial \mu^{*\beta}}{\partial C^{\gamma}} \right)_{\rho^f, T, C^{\delta} (\delta \neq \gamma)} \quad (66b)$$

where $()_{C^{\gamma}, T}$ denotes that the differentiation is carried out with C^{γ} and T being held constant. Tensors K , L , and M are material coefficients depending on ρ^f , C^{γ} , n , and T_o . They are related to R - S - T tensors of equations (59) and (60) in a complicated way. In particular, for $L_{kl}^{f,\beta}$ and $L_{kl}^{z,\beta}$, we have,

$$L_{kl}^{f,\beta} = \sum_{\gamma}^{N-1} (R_{nk}^{f,\gamma})^{-1} S_{nm}^{f,\gamma} \pi_{mp}^{\gamma\beta} (R_{lp}^{\beta})^{-1} \quad (67a)$$

$$L_{kl}^{z,\beta} = n \rho^f C^z \pi_{km}^{\alpha\beta} (R_{lm}^{\beta})^{-1} \quad (67b)$$

Among these coefficients, K_{kl}^f and $D_{kl}^{z,\gamma}$ may be identified as the coefficients of permeability and dispersion, respectively. Clearly, all of them have to be determined by direct measurements or empirical methods.

It is important to note that in the foregoing development, we assumed a linear relationship in terms of $v_k^{f,r}$ in order to keep the level of algebra to a minimal. However, it is known that in general the dispersion coefficient is a function of the flow velocity. This means that our development shall allow for a dependence of material coefficients on $v_k^{f,r}$. Such a modification can be achieved in the following manner. In equation (57), we do not linearize in terms of $v_k^{f,r}$. Rather, we shall assume that $\hat{\tau}_k^f$ (and $\hat{\tau}_k^{\beta}$) can be expanded in a finite-order polynomial in terms of $v_k^{f,r}$. Then, it can be shown¹⁴ that the polynomial is reduceable to a first degree polynomial with coefficients depending on the invariant(s) of $v_k^{f,r}$ (i.e., $|v_k^{f,r}|$). Hence, in equations (59) and (60), as well as in (63) and (64), we shall consider all coefficients to be dependent on $|v_k^{f,r}|$ as well as n , ρ^f , C^{γ} , and T_o .

DISCUSSION OF RESULTS

Equations (63) and (64) may be regarded as the generalized Darcy's law and Fick's law, respectively. An

equation similar to (64) but for diffusion in a multi-component solution has been suggested by Bird *et al.*¹⁵ on intuitive grounds. Equation (63), however, is quite new. Note that the symmetry in the form, of these equations is typical of cases where coupling effects exist. In these equations, four groups of terms can be distinguished. In other words, transport of each individual component, or the fluid as a whole, may be caused by four different effects:

- (i) a pressure gradient and gravity force acting upon the whole fluid (we call it pressure-induced transport),
- (ii) density gradients of the whole fluid and/or its individual components (density-induced transport),
- (iii) the difference in response of individual components to external force fields (force-induced transport), and
- (iv) a temperature gradient established in the medium (temperature-induced transport).

The third effect will be of importance only in those ionic systems where there exists an external electric magnetic field. The second effect, i.e., the effect of concentration gradients on the fluid flow in porous media is new here. It is, however, reminiscent of chemico-osmosis effects in clay formations where water moves through clay in response to a salt concentration gradient (there is a voluminous literature on the subject, e.g., see Mitchell¹⁶). In those situations, an equation similar to (63) (without g - and T -terms) is employed to describe the flow. Thus, our development provides a thermodynamic foundation for equations of chemico-osmosis as well. The effect of temperature gradient on the flow as given by equation (63), is in agreement with those obtained for a single-component fluid in earlier works⁹. Also, a discussion of its relevance and significance is provided elsewhere¹¹.

Significance of above-mentioned effects in a particular thermodynamic process depends, in the first place, on their relative magnitude. Moreover, material properties of the medium under consideration, reflected in its material coefficients and equations of state, will further determine the possible contribution of each effect. Note that in general, $p_{,k}^f$ may be expanded in terms of $\rho_{,k}^f$, $n_{,k}$, and $T_{,k}$; so that the first effect may appear not to be independent of the other three. However it will be shown later that there are situations where terms containing density gradients may be neglected, while the pressure term will persist.

Equations (63) and (64) along with equations of mass conservations (equations (34a), (34c), and (43b)), energy balance equation (37), the rock momentum balance equation (55b), and constitutive relations of previous section, provide a determinant system of equations to solve for n , ρ^f , C^{β} , F_k^r , $v_k^{f,r}$, and T , in terms of x_k and t . Further manipulations are necessary, however, in order to put solid momentum equation and energy equation into a workable form. Required steps to be followed can be established within the framework of present approach.

In order to appreciate the effect of various terms in generalized Darcy's and Fick's laws, in the remainder of this section, equations (63) and (64) are discussed under a number of situations of practical interest. In each case, additional assumptions which allow for certain simplifications are clearly stated.

Case (a)

Absence of force fields other than gravity

A common case of practical interest is when no electric

or magnetic force fields prevail in the system so that the only external force is gravity. Note than even if ions are formed as result of dissociation, still the electric forces established thereof are important only in the molecular range. Hence, we can assume that the principle of electric neutrality holds at the macroscopic as well as microscopic level so that in the absence of an electric field, no macroscopic separation of pairing ions will take place. Thus, the following assumption is imposed here.

Assumption 11:

The only external supply of momentum is provided by the gravity, whose density is denoted by g_k , so that

$$g_k^{\alpha} = g_k^f = g_k^s = g_k \quad (68)$$

Imposition of this assumption on equations (63) and (64) yields:

$$v_k^{fr} = -K_{ki}^f(p_{,i}^f - \rho^f g_i) - \left[B_{ki}^f \rho_{,i}^f + \sum_{\gamma}^{N-1} D_{ki}^{f\gamma} C_{,i}^{\gamma} \right] - M_{ki}^f T_{,i} \quad (69a)$$

$$J_k^{\alpha} = -K_{ki}^{\alpha}(p_{,i}^f - \rho^f g_i) - \left[B_{ki}^{\alpha} \rho_{,i}^f + \sum_{\gamma}^{N-1} D_{ki}^{\alpha\gamma} C_{,i}^{\gamma} \right] - M_{ki}^{\alpha} T_{,i} \quad (69b)$$

As compared to classical Darcy's law and Fick's law, these equations contain two additional terms: a concentration-gradients term in the Darcy's law and a pressure-gradient term in the Fick's law. They are most probably important when high species concentrations and high pressure gradients are established in the medium. The significance of the first effect is discussed in case (c) below. The second effect, called 'pressure diffusion', is known to exist in a multi-component solution even at low concentrations but only under unusually high pressure gradients¹⁵. However, it is perceivable that pressure diffusion may be effective even at normal pressure gradients when high concentrations exist. Whether or not such effects are actually important, should be investigated by means of further analysis, physical experiments, and field observations.

Case (b)

Fluid containing components at low concentrations

Most often, one or more fluid components may exist at very low concentrations. Here, first we consider a situation where the fluid phase consists of one main component, say component N , and $N-1$ other components existing at low concentrations, such that

$$\rho^{\beta} \ll \rho^f \quad \text{or} \quad C^{\beta} \ll 1 \quad \beta = 1 \text{ to } N-1 \quad (70a)$$

$$\rho^N \approx \rho^f \quad \text{or} \quad C^N \approx 1 \quad (70b)$$

Under these conditions, one may expect that some of the material coefficients attain limiting values. In this regard, we adopt the following assumption.

Assumption 12:

At low concentrations, the fluid pressure, p^f , will not be dependent on C^{γ} 's while $\hat{\mu}^{*\beta}$ will depend but only on C^{β} .

Then, from definitions of p^f and $\hat{\mu}^{*\beta}$, one can show the following:

$$\begin{aligned} \left(\frac{\partial \hat{\mu}^{*\beta}}{\partial \rho^f} \right)_{C^{\gamma}, T} &= \left\{ \frac{\partial}{\partial \rho^f} \left(\frac{\partial A^f}{\partial C^{\beta}} \right)_{\rho^f, T, C^{\delta}} \right\}_{C^{\gamma}, T} \\ &= \left\{ \frac{\partial}{\partial C^{\beta}} \left(\frac{\partial A^f}{\partial \rho^f} \right)_{C^{\gamma}, T} \right\}_{\rho^f, T, C^{\delta}} \\ &= \left(\frac{\partial}{\partial C^{\beta}} \left(\frac{p^f}{(\rho^f)^2} \right) \right)_{\rho^f, T, C^{\delta}} \cong 0 \end{aligned} \quad (71a)$$

$$\left(\frac{\partial \hat{\mu}^{*\beta}}{\partial C^{\gamma}} \right)_{\rho^f, T, C^{\delta}} \cong 0 \quad \text{if } \gamma \neq \beta \quad (71b)$$

Substituting these results into equations (65) and (66), one will find that

$$B_{ki}^f = B_{ki}^{\alpha} \cong 0 \quad (73a)$$

$$D_{ki}^{f\beta} = \sum_{\gamma} L_{ki}^{f\gamma} \left(\frac{\partial \hat{\mu}^{*\gamma}}{\partial C^{\beta}} \right)_{\rho^f, T, C^{\delta}} \cong L_{ki}^{f\beta} \left(\frac{\partial \hat{\mu}^{*\beta}}{\partial C^{\beta}} \right)_{\rho^f, T} \quad (73b)$$

$$D_{ki}^{\alpha\beta} = L_{ki}^{\alpha\beta} \left(\frac{\partial \hat{\mu}^{*\beta}}{\partial C^{\beta}} \right)_{\rho^f, T} \quad (73c)$$

Thus, equations (68) and (69) reduce to the following forms

$$v_k^{fr} = -K_{ki}^f(p_{,i}^f - \rho^f g_i) - \sum_{\beta} \left(L_{ki}^{f\beta} \frac{\partial \hat{\mu}^{*\beta}}{\partial C^{\beta}} \right) C_{,i}^{\beta} - M_{ki}^f T_{,i} \quad (74)$$

$$J_k^{\alpha} = - \sum_{\beta} \left(L_{ki}^{\alpha\beta} \frac{\partial \hat{\mu}^{*\beta}}{\partial C^{\beta}} \right) C_{,i}^{\beta} - K_{ki}^{\alpha}(p_{,i}^f - \rho^f g_i) - M_{ki}^{\alpha} T_{,i} \quad (75)$$

It is possible to further simplify these equations if additional assumptions are imposed. Returning to equation (57), we conjecture that the force applied by the solid phase on low-concentration components is only a small fraction of the total force exerted on the whole fluid phase. Furthermore, mutual effects of low-concentration components on each others' motions may be assumed negligible, compared to the effect of high concentration components (including component N). In terms of constitutive coefficients, we may state the following:

Assumption 13:

If a component γ exists at a low concentration, its contributions to the fluid-solid interaction forces, $\hat{\tau}_k^f$ and $\hat{v}_k^{*\beta}$ will be small such that, in equations (59) and (60) we will have

$$S_{ki}^{f\gamma} \approx 0 \quad (76a)$$

$$S_{ki}^{\beta\gamma} \approx S_{ki}^{\beta} \delta^{\beta\gamma} \quad (76b)$$

where, $\delta^{\beta\gamma} = 0$ if $\beta \neq \gamma$, and $\delta^{\beta\gamma} = 1$ for $\beta = \gamma$.

As a result of this assumption, because of equations (67),

and given the composition of $\pi_{km}^{\alpha\beta}$, we will find

$$L_{kl}^{f\beta} \approx 0 \tag{77a}$$

$$L_{kl}^{\alpha\beta} \approx n\rho^f C^\alpha (\pi_{km} \delta^{\alpha\beta}) (R_{lm}^\beta)^{-1} = L_{kl}^\beta \delta^{\alpha\beta} \tag{77b}$$

Upon substitution of equations (77) into (74) and (75), we obtain

$$v_k^{fr} = -K_{kl}^f (p_{,l}^f - \rho^f g_l) - M_{kl}^f T_{,l} \tag{78}$$

$$J_k^z = -L_{kl}^z \frac{\partial \mu_k^*}{\partial C^\alpha} C^\alpha - K_{kl}^z (p_{,l}^f - \rho^f g_l) - M_{kl}^z T_{,l} \tag{79}$$

It is apparent that if thermal and pressure diffusion effects are neglected, we recover classical forms of Darcy's and Fick's laws.

Case (c)

Saturated brine containing low concentration species

In this case the fluid consists of two major components (namely, water and salt) and $N-2$ other components existing at low concentrations. So that, we have

$$\rho^\gamma \ll \rho^f \text{ or } C^\gamma \ll 1 \text{ for } \gamma = 1 \text{ to } N-2 \tag{80}$$

Note that actually salt itself is composed of two components, i.e., sodium and chloride ions. However, in the absence of an electric field, we assume that no macroscopic separation of the two ions takes place and the two are always transported together. Then, modifying assumptions 12 and 13, one may say that ρ^f depends only on ρ^f and C^s (where the superscript 's' stands for the salt component), and μ_k^* depends on ρ^f , C^s and C^s . Also, the contribution of diffusive motions of all components to the (microscopic) mutual drag among themselves and to the solid-fluid interaction force is assumed negligible except for the salt component. Then, following an analysis analogous to what was done in the previous case, it can be shown that equations (69) reduce to the following forms

$$v_k^{fr} = -K_{kl}^f (p_{,l}^f - \rho^f g_l) - B_{kl}^f \rho_{,l}^f - D_{kl}^f C_{,l}^s - M_{kl}^f T_{,l} \tag{81}$$

$$J_k^s = -K_{kl}^s (p_{,l}^f - \rho^f g_l) - B_{kl}^s \rho_{,l}^f - D_{kl}^s C_{,l}^s - M_{kl}^s T_{,l} \tag{82}$$

$$J_k^\beta = -K_{kl}^\beta (p_{,l}^f - \rho^f g_l) - B_{kl}^\beta \rho_{,l}^f - (D_{kl}^\beta C_{,l}^\beta + D_{kl}^{\beta s} C_{,l}^s) - M_{kl}^\beta T_{,l} \quad \beta = 1 \text{ to } N-2 \tag{83}$$

An example of situations where these equations are applicable is the flow of groundwater passing a salt dome. In the vicinity of the dome, high salt concentrations, up to 300 g/l, may exist. So that the movement of salt due to its concentration gradient implies the movement of up to 25% of the fluid. This indicates that the pressure gradient is not the only force driving the fluid phase. Equation (81) establishes the relationship among the fluid flux and various driving forces in the flow of a saturated brine under nonisothermal conditions.

Case (d)

Fluid containing low-concentration components and at rest

In this case, the following assumption is valid.

Assumption 14:

The mean mass flux of fluid is zero, i.e., $v_k^{fr} = 0$.

Therefore, according to equation (69a), pressure gradient, gravity force, concentration gradients, and temperature gradient will have to attain an equilibrium relationship such that,

$$p_{,l}^f - \rho^f g_l = - (K_{kl}^f)^{-1} \left\{ B_{km}^f \rho_{,m}^f + \sum_\gamma D_{km}^{f\gamma} C_{,m}^\gamma + M_{km}^f T_{,m} \right\} \tag{84}$$

Substitution of this result into equation (69b) yields

$$J_k^z = -\mathcal{D}_{kl}^z \rho_{,l}^f - \sum_\beta \mathcal{B}_{kl}^{z\beta} C_{,l}^\beta - T_{kl}^z T_{,l} \tag{85}$$

where,

$$\mathcal{D}_{kl}^{z\gamma} = D_{kl}^{z\gamma} - K_{kn}^z (K_{mn}^f)^{-1} D_{ml}^{f\gamma} \tag{86a}$$

$$\mathcal{B}_{kl}^z = B_{kl}^z - K_{kn}^z (K_{mn}^f)^{-1} B_{ml}^f \tag{86b}$$

$$T_{kl}^z = M_{kl}^z - K_{kn}^z (K_{mn}^f)^{-1} M_{ml}^f \tag{86c}$$

Equation (85) may be regarded as an extended form of Fick's first law for multi-component solutions at high concentrations, at rest and under nonisothermal conditions.

Case (e)

A single-component fluid

This case is considered only to show that classical Darcy's law may be obtained as a special result of the present theory. This is readily achieved by examining of equations (63) to (66). For a single component fluid, we have $N=1$ and $\mu_k^* & u_k^z = 0$. Thus, in equation (63) only terms containing $(p_{,l}^f - \rho^f g_l)$ and $T_{,l}$ will survive and these will give the classical form of Darcy's law. From equation (64), it simply follows that K_{kl}^z and M_{kl}^z vanish for single-component fluids.

CONCLUSIONS

In this work, it is demonstrated that general conservation equations for multiphase systems, along with the Coleman and Noll method of exploitation of the entropy inequality, can be employed to develop a general thermodynamic basis for the study of species transport in porous media. By including density and concentration gradients among the list of independent variables, coupling effects in the motions of individual components and the mean motion of fluid phase are properly accounted for. By linearizations of resulting equations, general extensions of Darcy's law and Fick's law, applicable to the case of high-concentration solutions are obtained. It is found that in addition to the ordinary transport of fluid due to pressure gradients, concentration gradients also give rise to flow. Furthermore, effects of pressure, temperature, and external force fields on diffusion are properly modelled. Then, classical Darcy's law and Fick's law are shown to be valid, under isothermal conditions, only for the cases where all components of the fluid except one, exist at low concentrations, or where the fluid phase is at rest. As a case of practical interest, proper forms of Darcy's law and Fick's law for the motion of concentrated brine in porous media are given. In these equations, in addition to coefficients of permeability and dispersion, new

coefficients appear which are related to cross-coupling effects. They have to be determined experimentally and/or empirically. The development also provides a thermodynamic basis for chemico-osmosis theories.

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NOMENCLATURE

Symbols which are used only in Appendix B are not listed here.

a_k^a	acceleration vector equal to $D^a v_k^a / Dt$ (also a_k^a)
A^α	Helmholtz free energy function (also A^α in equation (34))
$\overset{*}{A}^\beta$	a relative Helmholtz free energy function (equation (45c))
B_{kl}^f	material coefficient (equation (65a), also B_{kl}^a in (66a))
\mathcal{B}_{kl}^α	material coefficient (equation (86b))
C^α	mass fraction of component α
d_{kl}^a	deformation rate tensor; $v_{(k,l}^a$)
det	determinant of a tensor
$D_{kl}^{f\gamma}$	material coefficient (equation (65b), also $D_{kl}^{\alpha\gamma}$ in (66b))
$\mathcal{D}_{kl}^{\alpha\gamma}$	material coefficient (equation (86a))
E^a	internal energy function (equation (25), also E^α in (29), and E^m in (41))
e_{kl}^r	infinitesimal strain tensor of the rock (equation (56a))
E_{KL}^r	strain tensor of the rock (equation (5))
F_k^r	motion of the rock phase (equation (4))
F_{kK}^r	displacement gradient tensor of the rock (equation (6))
g_k	gravity vector
g_k^a	external supply of momentum (also g_k^a in equations (24))
G^a	Gibb's free energy function (equations (50))
J^r	Jacobian of the rock motion (the paragraph following equation (8))
J_k^z	diffusive-dispersive flux vector (equation (22))
K_{kl}^f	material coefficient (equation (63), also K_{kl}^a in (64))
$L_{kl}^{f\beta}$	material coefficient (also $L_{kl}^{\alpha\beta}$ in equations (67))
M_{kl}^f	material coefficient (equation (63), also M_{kl}^a in (64))
n	porosity of the porous medium
N	number of components of the fluid phase
p^f	thermodynamic pressure of the fluid phase (equation (48a))
q_k^a	heat flux vector (equations (25), also q_k^z in (30) and q_k^m in (40b))

\hat{Q}^a	energy exchange term (equations (25), also \hat{Q}^α in (26c))
\hat{R}^a	mass exchange term (also \hat{R}^α in equations (21))
R_{kl}^f	material coefficient (equation (59), also R_{kl}^a in (60))
$\overset{*}{R}_{kl}^{\beta\gamma}$	defined in Assumption 10
S^r	internal entropy function (also S^α in equation (33), S^f in (31), and S^m in (40a))
$S_{kl}^{f\gamma}$	material coefficient (equation (59), also $S_{kl}^{\beta\gamma}$ in (60))
t	time
T	deviation of absolute temperature θ from a reference value (equation (56b))
T_o	reference value of the absolute temperature (equation (56b))
\hat{T}_k^a	momentum exchange term (also \hat{T}_k^α in equations (24))
T_{kl}^f	material coefficient (equation (59), also T_{kl}^a in (60))
u_k^α	diffusion-dispersion velocity of component α (equation (14))
v_k^r	velocity vector (equation (7), also v_k^α in (10) and v_k^f in (13))
v_k^{fr}	velocity of the fluid with respect to the rock (equation (17a))
$v_k^{r\alpha}$	velocity of component α with respect to the rock (equation (12))
x_k	position vector in the spatial frame of reference
X_K	position vector in the rock material frame of reference (equation (4))
Z_Λ	members of the set of thermodynamic quantities which vanish at equilibrium (equation (51))

Greek

Γ^r	rate of net production of entropy (also Γ^α and Γ^m in equation (32))
δ_{kl}	Kronecker delta (also δ_{KL})
$\delta_{kl}^{\alpha\beta}$	equal to δ_{kl} if $\alpha = \beta$ and zero otherwise (Assumption 10)
Δ^2	defined in equation (58)
θ	temperature function (equations (33) and (36))
μ^α	chemical potential (equation (48b), also μ^f in (48c))
$\overset{*}{\mu}^\beta$	relative chemical potential (equation (48b))
μ_{kl}^α	chemical potential tensor (equation (A17))
$\pi_{kl}^{\alpha\beta}$	inverse of the tensor $\overset{*}{R}_{kl}^{\beta\gamma}$ (Assumption 10)
ρ^a	mass density function (also ρ^α)
ρ_o^r	mass density of microscopically incompressible rock aggregates (equation (3))
σ_{kl}^a	stress tensor (also σ_{kl}^α in equations (24))
$e\sigma_{kl}^r$	effective stress tensor of the rock (equation (48d))
$\overset{*}{\sigma}_{kl}^\beta$	a relative stress tensor (equation (46c))
$\hat{\tau}_k^f$	dissipative part of \hat{T}_k^f (equation (47a))
$\overset{*}{\tau}_k^\beta$	dissipative part of $(\hat{T}_k^\beta - \hat{T}_k^N)$ (equation (47b))
T_{kl}^z	material coefficient (equation (86c))

ϕ_k^r	entropy flux vector (also ϕ_k^z in equations (35))
χ_Λ	members of the set of thermodynamic quantities which attain infinitesimal values in a linear theory
Ψ	a typical function
Ψ_Λ	members of the set of dependent constitutive variables (equation (44d))
Superscripts	
f	fluid phase
m	porous medium
N	component N of the fluid phase
r	rock (or solid) phase
s	salt component of brine
$\alpha, \beta, \gamma, \delta$	for fluid components; they may take upon values from 1 to N

Subscripts

k, l, m, n	Cartesian components of tensorial quantities in the spatial frame of reference; they range from 1 to 3
K, L, M, N	Cartesian components of tensorial quantities in the rock material frame of reference; they range from 1 to 3

Special Notation

$A_{(k,l)}$	symmetric part of a tensor equal to $\frac{1}{2}(A_{k,l} + A_{l,k})$
D^r/Dt	material derivative (equation (9b)), also D^z/Dt in (10)
$O(\Delta^2)$	of the order of magnitude of Δ^2
\sum_α	sum over all fluid components
$\Big _e$	evaluate at equilibrium
$\Big _o$	evaluate at $\chi_\Lambda = 0$

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APPENDIX A

Exploitation of the entropy inequality

According to the principle of admissibility, the second law shall not be violated by any set of constitutive relations. That is, substitution of equations (43) and (44) into relation (39) shall not violate the inequality. Restrictions following from this requirement are investigated here. The chain rule of differentiation should be used to evaluate any derivative that appears in the entropy inequality. In particular, from (44), we will have

$$\frac{D^f A^f}{Dt} = \frac{\partial A^f}{\partial \rho^f} \frac{D^f \rho^f}{Dt} + \sum_{\beta}^{N-1} \frac{\partial A^f}{\partial C^\beta} \frac{D^f C^\beta}{Dt} + \frac{\partial A^f}{\partial E_{KL}^f} \frac{D^f E_{KL}^f}{Dt} + \frac{\partial A^f}{\partial \theta} \frac{D^f \theta}{Dt} \quad (A1)$$

$$\frac{D^r A^r}{Dt} = \frac{\partial A^r}{\partial \rho^f} \frac{D^r \rho^f}{Dt} + \frac{\partial A^r}{\partial E_{KL}^r} \frac{D^r E_{KL}^r}{Dt} + \frac{\partial A^r}{\partial \theta} \frac{D^r \theta}{Dt} \quad (A2)$$

$$(A^\beta - A^N)_{,k} = \frac{\partial \hat{A}^\beta}{\partial \rho^f} \rho_{,k}^f + \sum_{\gamma}^{N-1} \frac{\partial \hat{A}^\beta}{\partial C^\gamma} C_{,k}^\gamma + \frac{\partial \hat{A}^\beta}{\partial E_{KL}^r} E_{KL,k}^r + \frac{\partial \hat{A}^\beta}{\partial \theta} \theta_{,k} \quad (A3)$$

where $\hat{A}^\beta = A^\beta - A^N$. In evaluating these terms, the following relations will prove useful.

$$\begin{aligned} \frac{D^f \rho^f}{Dt} &= -\frac{\rho^f}{n} \frac{D^f n}{Dt} - \rho^f d_{kk}^f + \rho^f \hat{R}^f \\ &= -\frac{1-n}{n} \rho^f d_{kk}^r - \rho^f d_{kk}^f - \frac{\rho^f}{n} v_k^f n_{,k} + \rho^f \left(1 - \frac{\rho^f}{\rho_o^r}\right) \hat{R}^f \end{aligned} \quad (A4)$$

$$\frac{D^r \rho^f}{Dt} = \frac{D^f \rho^f}{Dt} - v_k^f \rho_{,k}^f \quad (A5)$$

$$\frac{D^f E_{KL}^r}{Dt} = F_{(kK}^r F_{l)L}^r d_{kt}^r + v_k^f E_{KL,k}^r \quad (A6)$$

where equations (16b), (26a), (21a), and (43b) have been used. So, equations (A1) and (A2) may be expanded to obtain the following relations. Note that, use is also made of the equation of mass conservation of species, (21c).

$$\begin{aligned}
 n\rho^f \frac{D^f A^f}{Dt} = & d_{kl}^f \left[-n(\rho^f)^2 \frac{\partial A^f}{\partial \rho^f} \delta_{kl} \right] \\
 & + d_{kl}^r \left[-(1-n)(\rho^f)^2 \frac{\partial A^f}{\partial \rho^f} \delta_{kl} \right. \\
 & \quad \left. + n\rho^f \frac{\partial A^f}{\partial E_{KL}^r} F_{(kk}^r F_{l)L}^r \right] \\
 E_{KL,k}^r \left[n\rho^f \frac{\partial A^f}{\partial E_{KL}^r} v_k^{fr} \right] + & \frac{D^r \theta}{Dt} \left[n\rho^f \frac{\partial A^f}{\partial \theta} \right] \\
 + \theta_{,k} \left(n\rho^f \frac{\partial A^f}{\partial \theta} v_k^{fr} \right) + & v_k^{fr} \left(-(\rho^f)^2 \frac{\partial A^f}{\partial \rho^f} n_{,k} \right) \\
 + \sum_{\beta}^{N-1} u_{k,i}^{\beta} \left[-n\rho^f C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} \right] + & \sum_{\beta}^{N-1} u_k^{\beta} \\
 \times \left(-\frac{\partial A^f}{\partial C^{\beta}} (n\rho^f C^{\beta})_{,k} \right) & \\
 + n\rho^f \sum_{\beta}^{N-1} C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} \hat{R}^{\beta} - n\rho^f \sum_{\beta}^{N-1} & C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} \hat{R}^f \\
 + n\rho^f \left(1 - \frac{\rho^f}{\rho_o^r} \right) \frac{\partial A^f}{\partial \rho^f} \hat{R}^f & \quad (A7)
 \end{aligned}$$

$$\begin{aligned}
 (1-n)\rho_o^r \frac{D^r A^r}{Dt} = & d_{kl}^f \left[-(1-n)\rho_o^r \rho^f \frac{\partial A^r}{\partial \rho^f} \delta_{kl} \right] \\
 & + d_{kl}^r \left[-\frac{(1-n)^2}{n} \rho_o^r \rho^f \frac{\partial A^r}{\partial \rho^f} \delta_{kl} \right. \\
 & \quad \left. + (1-n)\rho_o^r \frac{\partial A^r}{\partial E_{KL}^r} F_{(kk}^r F_{l)L}^r \right] \\
 - v_k^{fr} \left(\frac{1-n}{n} \rho_o^r \rho^f \frac{\partial A^r}{\partial \rho^f} n_{,k} \right) & \\
 + (1-n)\rho_o^r \frac{\partial A^r}{\partial \rho^f} \rho_{,k}^f & \\
 + \frac{D^r \theta}{Dt} \left[(1-n)\rho_o^r \frac{\partial A^r}{\partial \theta} \right] & \\
 + (1-n)\rho^f \rho_o^r \left(1 - \frac{\rho^f}{\rho_o^r} \right) \frac{\partial A^r}{\partial \rho^f} \hat{R}^f & \quad (A8)
 \end{aligned}$$

Substitution of (A3), (A7) and (A8) into the entropy inequality (39), after rearrangement yields:

$$\begin{aligned}
 \theta \Gamma^m = & d_{kl}^f \left\{ n\rho^f \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \right) \delta_{kl} \right. \\
 & \quad \left. + n\rho^f \sum_{\alpha} C^{\alpha} u_k^{\alpha} u_l^{\alpha} + \sigma_{kl}^f \right\} \\
 & + d_{kl}^r \left\{ (1-n)\rho^f \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \right) \delta_{kl} \right. \\
 - (1-n) \left(\frac{n}{1-n} \rho^f \frac{\partial A^f}{\partial E_{KL}^r} + \rho_o^r \frac{\partial A^r}{\partial E_{KL}^r} \right) & F_{(kk}^r F_{l)L}^r + \sigma_{kl}^r \left\{ \right. \\
 + E_{KL,k}^r \left\{ -n\rho^f \left(\frac{\partial A^f}{\partial E_{KL}^r} v_k^{fr} + \sum_{\beta}^{N-1} C^{\beta} \frac{\partial \hat{A}^{\beta}}{\partial E_{KL}^r} u_k^{\beta} \right) \right\} & \\
 + \frac{D^r \theta}{Dt} \left\{ -\rho^m S^m - \left(n\rho^f \frac{\partial A^f}{\partial \theta} + (1-n)\rho_o^r \frac{\partial A^r}{\partial \theta} \right) \right\} &
 \end{aligned}$$

$$\begin{aligned}
 & + \sum_{\beta}^{N-1} u_{k,i}^{\beta} \left\{ n\rho^f C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} \delta_{kl} - n\rho^f C^{\beta} \hat{A}^{\beta} \delta_{kl} \right. \\
 & \quad \left. + \left(\sigma_{kl}^{\beta} - \frac{C^{\beta}}{C^N} \sigma_{kl}^N \right) \right\} \\
 & + v_k^{fr} \left[\rho^f \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \right) n_{,k} \right. \\
 & \quad \left. + (1-n)\rho_o^r \frac{\partial A^r}{\partial \rho^f} \rho_{,k}^f - n\rho^f \hat{T}_k^f \right] \\
 & + \sum_{\beta}^{N-1} u_k^{\beta} \left[\left(\frac{\partial A^f}{\partial C^{\beta}} - \hat{A}^{\beta} \right) (n\rho^f C^{\beta})_{,k} \right. \\
 & \quad \left. - n\rho^f C^{\beta} \left(\frac{\partial \hat{A}^{\beta}}{\partial \rho^f} \rho_{,k}^f + \sum_{\gamma}^{N-1} \frac{\partial \hat{A}^{\beta}}{\partial C^{\gamma}} C_{,k}^{\gamma} + \frac{\partial \hat{A}^{\beta}}{\partial \theta} \theta_{,k} \right) \right. \\
 & \quad \left. - \sigma_{kl}^N \left(\frac{C^{\beta}}{C^N} \right)_{,i} - n\rho^f C^{\beta} (\hat{T}_k^{\beta} - \hat{T}_k^N) \right] \\
 & - \sum_{\beta}^{N-1} n\rho^f C^{\beta} \left[\frac{\partial A^f}{\partial C^{\beta}} + \frac{1}{2} u_k^{\beta} u_k^{\beta} \right] \hat{R}^{\beta} \\
 & + \theta_{,k} \left[\frac{q_k^m}{\theta} - n\rho^f \left(\frac{\partial A^f}{\partial \theta} + S^f \right) v_k^{fr} - n\rho^f \sum_{\alpha} C^{\alpha} S^{\alpha} u_k^{\alpha} \right] \\
 & - n\rho^f \left[\left(1 - \frac{\rho^f}{\rho_o^r} \right) \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \right) \right. \\
 & \quad \left. - \sum_{\beta}^{N-1} C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} + \left(A^f - A^r + \frac{1}{2} v_k^{fr} v_k^{fr} \right) \right] \hat{R}^f \geq 0 \quad (A9)
 \end{aligned}$$

Now, as implied by Assumption 6, none of constitutive functions depend on d_{kl}^f , d_{kl}^r , $u_{k,i}^{\beta}$, $E_{KL,k}^r$ and $D^r \theta / Dt$. Therefore, according to equation (A9), $\theta \Gamma^m$ is a linear function of these variables. Then, the necessary and sufficient condition for Γ to be nonnegative for all independent thermodynamic states is that coefficients of above-mentioned variables in equation (A9) must vanish independently. Hence, all terms inside curly brackets in that equation are set equal to zero. Results are as follows:

$$\sigma_{kl}^f = -n\rho^f \delta_{kl} - n\rho^f \sum_{\alpha} C^{\alpha} u_k^{\alpha} u_l^{\alpha} \quad (A10)$$

$$\begin{aligned}
 \sigma_{kl}^r = & -(1-n)\rho^f \delta_{kl} + (1-n) \left(\frac{n}{1-n} \rho^f \frac{\partial A^f}{\partial E_{KL}^r} \right. \\
 & \quad \left. + \rho_o^r \frac{\partial A^r}{\partial E_{KL}^r} \right) F_{(kk}^r F_{l)L}^r \quad (A11)
 \end{aligned}$$

$$\begin{aligned}
 \hat{\sigma}_{kl}^{\beta} = \sigma_{kl}^{\beta} - \frac{C^{\beta}}{C^N} \sigma_{kl}^N = & -n\rho^f C^{\beta} \frac{\partial A^f}{\partial C^{\beta}} \delta_{kl} + n\rho^f C^{\beta} \hat{A}^{\beta} \delta_{kl} \quad (A12)
 \end{aligned}$$

$$\rho^m S^m = - \left(n\rho^f \frac{\partial A^f}{\partial \theta} + (1-n)\rho_o^r \frac{\partial A^r}{\partial \theta} \right) \quad (A13)$$

$$\frac{\partial A^f}{\partial E_{KL}^r} v_k^{fr} + \sum_{\beta}^{N-1} \frac{\partial \hat{A}^{\beta}}{\partial E_{KL}^r} u_k^{\beta} = 0 \quad (A14)$$

where,

$$\rho^f = \rho^f(\rho^f, C^{\gamma}, E_{KL}^r, \theta) = \rho^f \left(\rho^f \frac{\partial A^f}{\partial \rho^f} + \frac{1-n}{n} \rho_o^r \frac{\partial A^r}{\partial \rho^f} \right) \quad (A15)$$

Further conclusions can be drawn out of above relations. In particular, in equation (A14), because $v_k^{f,r}$ and u_k^β ($\beta = 1$ to $N - 1$) may vary independently, coefficients of $v_k^{f,r}$ and u_k^β must vanish separately, i.e.,

$$\frac{\partial A^f}{\partial E_{KL}^f} = \frac{\partial \hat{A}^\beta}{\partial E_{KL}^\beta} = 0 \quad (\text{A16})$$

Therefore, in equation (A11), the term involving $\partial A^f / \partial E_{KL}^f$ should drop out. In above equations, p^f may be identified as the thermodynamic pressure of fluid phase. Following Bowen and Wiese¹⁷ and Bowen⁷, one may define a generalized chemical potential tensor μ_{kl}^α , so that,

$$\sigma_{kl}^\alpha = -n\rho^f C^\alpha (\mu_{kl}^\alpha - A^\alpha \delta_{kl}) \quad \alpha = 1 \text{ to } N \quad (\text{A17})$$

Introducing this definition into equation (A12) results in the following relation for μ_{kl}^β ,

$$\mu_{kl}^\beta - \mu_{kl}^N = \frac{\partial A^f}{\partial C^\beta} \delta_{kl} \quad (\text{A18})$$

which is a reminiscence of the classical result in thermodynamics for chemical potentials of components of a mixture of fluids.

On the other hand, substitution of (A10) and (A17) into (28), after some manipulation, yields:

$$n\rho^f \mu_{kl}^N = n\rho^f \delta_{kl} - n\rho^f \sum_{\beta}^{N-1} C^\beta (\mu_{kl}^\beta - \mu_{kl}^N) + n\rho^f A^f \delta_{kl} \quad (\text{A19})$$

where relations (2b) and (38) have been used. From (A18) and (A19), it is readily established that μ_{kl}^β is an isotropic tensor, i.e., within the context of the present theory, chemical potentials are scalars. Therefore, equation (A18) may be written as follows,

$$\hat{\mu}^\beta = \mu^\beta - \mu^N = \frac{\partial A^f}{\partial C^\beta} = \hat{\mu}^\beta(\rho^f, C^\gamma, \theta) \quad (\text{A20})$$

Furthermore, multiplication of (A20) by C^β , summation over $\beta = 1$ to $N - 1$, and usage of equation (A19) will yield another familiar relationship:

$$\mu^f = \sum_{\alpha} C^\alpha \mu^\alpha = \frac{p^f}{\rho^f} + A^f \quad (\text{A21})$$

Now, the remaining portion of entropy inequality (A9), called the residual entropy inequality, becomes

$$\begin{aligned} \theta \Gamma^m = & \left(\frac{q_k^m}{\theta} - n\rho^f \left(\frac{\partial A^f}{\partial \theta} + S^f \right) v_k^{f,r} - n\rho^f \sum_{\alpha} C^\alpha S^\alpha u_k^\alpha \right) \theta_{,k} \\ & - n\rho^f \hat{v}_k^f v_k^{f,r} - n\rho^f \sum_{\beta} \hat{v}_k^\beta u_k^\beta - n\rho^f \sum_{\beta} C^\beta \left(\hat{\mu}^\beta + \frac{1}{2} u_k^{\beta 2} \right) \hat{R}^\beta \\ & - n\rho^f \left[(G^f - G^r) + \frac{1}{2} v_k^{f,r} v_k^{f,r} - \sum_{\beta} C^\beta \hat{\mu}^\beta \right] \hat{R}^f \geq 0 \end{aligned} \quad (\text{A22})$$

where \hat{v}_k^f and \hat{v}_k^β are the extraneous parts of \hat{T}_k^f and $(\hat{T}_k^\beta - \hat{T}_k^N)$, respectively, such that,

$$n\rho^f \hat{T}_k^f = n\rho^f \hat{v}_k^f + p^f n_{,k} + (1-n)\rho_a^f \frac{\partial A^r}{\partial \rho^f} \rho_{,k}^f \quad (\text{A23})$$

$$\begin{aligned} n\rho^f C^\beta (\hat{T}_k^\beta - \hat{T}_k^N) = & n\rho^f C^\beta \hat{v}_k^\beta + (\hat{\mu}^\beta - \hat{A}^\beta) (n\rho^f C^\beta)_{,k} \\ & - n\rho^f C^\beta \hat{A}_{,k}^\beta - \sigma_{kl}^N \left(\frac{C^\beta}{C^N} \right)_{,l} \end{aligned} \quad (\text{A24})$$

and G^f and G^r are Gibb's free energy functions for fluid and solid phases defined by

$$G^f = \frac{p^f}{\rho^f} + A^f \quad (\text{A25})$$

$$G^r = \frac{p^r}{\rho^r} + A^r \quad (\text{A26})$$

APPENDIX B

Possible mechanisms of mass exchange

The term $n\rho^f \hat{R}^\alpha$ accounts for the net supply of mass to the species α by internal and external sources or sinks. We recall from Part 1 that it is defined by:

$$\hat{R}^\alpha = \bar{\rho}^\alpha + \tilde{r}^\alpha \quad (\text{B1})$$

where \tilde{r}^α is the rate of exchange of mass due to homogenous interactions and $\bar{\rho}^\alpha$ may be considered as the rate of all other mechanisms of mass exchange. To be more specific, we consider the following list of possible mechanisms.

Homogeneous chemical reactions between component α and other components, $\tilde{r}^\alpha = + \sum_{i=1}^I v^{i\alpha} \psi^i$.

Heterogeneous chemical reactions between the component α and the solid phase, $+n\rho^f R_{het}^\alpha$.

Addition of component α due to dissolution of solid phase into the fluid phase, $+(1-n)C^{r\alpha} R_{dst}^r$.

Depletion of mass of component α due to the precipitation onto the solid phase, $-nC\alpha R_{prc}^f$.

Depletion of mass of component α due to adsorption onto the solid phase, $-a^s R_{ads}^\alpha$.

Addition of mass of component α due to desorption from the solid phase, $+a^s R_{dsp}^\alpha$.

Addition of component α due to the injection of fluid into the porous medium via a network of wells and/or tubes, $+C^{f\alpha} I_{inj}^f$.

Depletion of component α due to the withdrawal of fluid from the porous medium via a network of wells and/or tubes, $-C^{f\alpha} I_{wth}^f$.

Note that I_{inj}^f and I_{wth}^f can be specified by means of the δ -function.

where,

$v^{i\alpha}$ is the stoichiometric coefficient of the i th reaction,

I is the total number of possible reactions,

ψ^i is the (macroscopic) rate of progress of reaction i , per unit mass of the fluid phase,

R_{het}^α is the (macroscopic) rate of production of component α per unit mass of fluid phase, due to chemical reaction with the solid phase,

$C^{r\alpha}$ is the mass fraction of component α extant to the solid phase.

R_{dst}^r is the rate of dissolution of the solid per its unit volume,

R_{prc}^f is the rate of precipitation of fluid phase per its unit volume,
 α^s is the specific internal surface area of the porous medium,
 R_{ads}^α is the rate of adsorption of component α per unit area of internal surfaces of the porous medium,
 R_{dsp}^α is the rate of desorption of component α per unit area of internal surfaces of the porous medium,
 I_{inj}^f is the rate of injection of fluid per unit volume of the porous medium,
 C'^α is the mass fraction of component α in the injected fluid, and
 I_{wth}^f is the rate of withdrawal of fluid per unit volume of porous medium.

So, the mass exchange term $n\rho^f C^\alpha \hat{R}^\alpha$ may be written as,

$$n\rho^f C^\alpha \hat{R}^\alpha = n\rho^f \sum_{i=1}^I v^{i\alpha} \psi^i + n\rho^f R_{het}^\alpha + (1-n)C^{r\alpha} R_{dst}^\alpha - nC^\alpha R_{prc}^f - \alpha^s R_{ads}^\alpha + \alpha^s R_{dsp}^\alpha + C'^\alpha I_{inj}^f - C^\alpha I_{wth}^f \quad (B2)$$

The following restrictions apply to above quantities.

$$\sum_{\alpha} v^{i\alpha} = 0 \quad (B2)$$

$$\sum_{\alpha} C'^\alpha = 1 \quad (B3)$$

$$\sum_{\alpha}^{N-1} C^{r\alpha} = C^r \quad (B4)$$

$$n\rho^f e^f(\rho) = n\rho^f \sum_{\alpha}^{N-1} R_{het}^\alpha + (1-n)C^r R_{dst}^\alpha - n \sum_{\alpha}^{N-1} C^\alpha R_{prc}^f - \alpha^s \sum_{\alpha}^{N-1} R_{ads}^\alpha + \alpha^s \sum_{\alpha}^{N-1} R_{dsp}^\alpha \quad (B5)$$

where,

C^r is the total mass of solid-phase pollutants per unit mass of the solid, and

$e^f(\rho)$ is the net rate of exchange of mass between the fluid and the solid per unit mass of the fluid.

Then, from equation (26a), one has,

$$n\rho^f \hat{R}^f = n\rho^f \sum_{\alpha} C^\alpha \hat{R}^\alpha = n\rho^f e^f(\rho) + (I_{inj}^f - I_{wth}^f) \quad (B6)$$

Should one be interested to make such a partitioning, then, it will be necessary to employ balance of mass of species extant in the solid phase as well. In some cases, it may be also necessary to consider the mass accumulated on the solid-fluid interfaces and write a balance of mass equation for the species residing on these interfaces. In any event, appropriate constitutive relations will have to be given for the rate terms appearing in equation (B2). An example of such constitutive relations is found in the work of Nguyen *et al.*¹⁸. This area demands further research.