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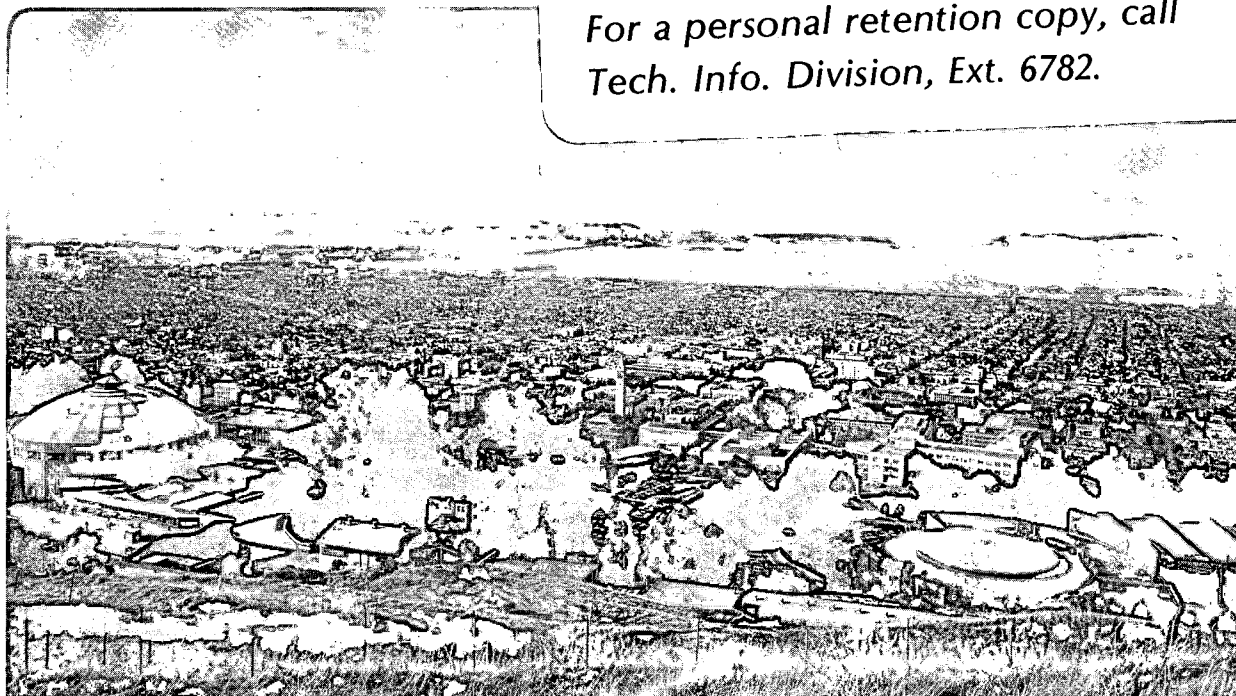
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THERMODYNAMIC COUPLING OF HEAT AND MATTER FLOWS
IN NEAR-FIELD REGIONS OF NUCLEAR WASTE REPOSITORIES

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ABSTRACT

In near-field regions of nuclear waste repositories, thermodynamically coupled flows of heat and matter can occur in addition to the independent flows in the presence of gradients of temperature, hydraulic potential, and composition. The following coupled effects can occur: thermal osmosis, thermal diffusion, chemical osmosis, thermal filtration, diffusion thermal effect, ultrafiltration, and coupled diffusion. Flows of heat and matter associated with these effects can modify the flows predictable from the direct effects, which are expressed by Fourier's law, Darcy's law, and Fick's law. The coupled effects can be treated quantitatively together with the direct effects by the methods of the thermodynamics of irreversible processes. The extent of departure of fully coupled flows from predictions based only on consideration of direct effects depends on the strengths of the gradients driving flows, and may be significant at early times in backfills and in near-field geologic environments of repositories. Approximate calculations using data from the literature and reasonable assumptions of repository conditions indicate that thermal-osmotic and chemical-osmotic flows of water in semipermeable backfills may exceed Darcian flows by two to three orders of magnitude, while flows of solutes may be reduced greatly by ultrafiltration and chemical osmosis, relative to the flows predicted by advection and diffusion alone. In permeable materials, thermal diffusion may contribute to solute flows to a smaller, but still significant, extent.

INTRODUCTION

Simultaneous processes of heat flow, fluid flow, and solute transport are expected to occur in the vicinity of nuclear waste repositories, and efforts to simulate these processes numerically are receiving increasing attention. (See, for example, [1].) In the near-field region, large gradients of temperature, hydraulic potential, and composition can give rise to additional, thermodynamically coupled processes in which flows of heat and matter are driven by seemingly unrelated forces. Such processes include thermal osmosis and thermal diffusion (Sorét effect), in which flows of volume and solutes are driven down a temperature gradient; thermal filtration and ultrafiltration, in which a flow of heat is driven down, and flows of solutes are driven against, a hydraulic potential gradient; and the diffusion thermal effect (Dufour effect) and chemical osmosis, in which flows of heat are driven down, and flows of volume are driven against, gradients of solute concentrations. These processes have been observed and quantified in laboratory experiments.

Thermodynamically coupled transport processes have been discussed in the literature of soil science and hydrogeology (e.g., [2-8]). They have been cited as causative factors of anomalous hydrologic phenomena associated with an underground nuclear explosion [9]. Chemical osmosis is believed to be the cause

of anomalously high differences of pore-water pressures across clay and shale aquitards which may act as semipermeable membranes [10,11].

Complete description of the evolution of a system supporting irreversible processes, including thermodynamically coupled processes, is a task beyond the scope of this paper. Instead, we will make some rough calculations showing the relative magnitudes of flows arising from various transport processes, using experimental data reported in the literature and reasonable assumptions about the magnitudes of gradients to be expected in near-field regions of nuclear waste repositories.

PHENOMENOLOGICAL EQUATIONS FOR HEAT AND MATTER FLOWS

Thermodynamically coupled transport processes can be described quantitatively by methods of the thermodynamics of irreversible processes [12,13,14]. In this formalism, each flow in an open system supporting irreversible processes is written as a linear function of all forces acting within the system. If the flows and forces have been defined correctly, the matrix of phenomenological coefficients relating them is symmetric [15]; the equalities between matrix elements are called Onsager's reciprocal relations.

Consider a $(n + 1)$ -component fluid of total mass density ρ_f consisting of water (index $i = 0$) and n solutes (index $i = 1, \dots, n$) in a saturated, porous or semipermeable medium acted on by gravity and gradients of temperature (T), pressure (P), and the composition-dependent part of the chemical potential (μ_i^c). The vector flows of heat (j_q) and volume (j_v), and the flows of solute relative to the flow of water (j_i^o), are given by the linear phenomenological equations

$$\begin{aligned} j_q &= -L_{qq} \frac{\nabla T}{T} - L_{qv} \nabla h - \sum_{k=1}^n L_{qk} F_{ck} \\ j_v &= -L_{vq} \frac{\nabla T}{T} - L_{vv} \nabla h - \sum_{k=1}^n L_{vk} F_{ck} \\ j_i^o &= -L_{iq} \frac{\nabla T}{T} - L_{iv} \nabla h - \sum_{k=1}^n L_{ik} F_{ck}, \quad i = 1, \dots, n, \end{aligned} \quad (1)$$

in which the vector forces ∇h and F_{ck} are given by

$$\nabla h = \nabla P + \rho_f g \nabla z, \quad F_{ck} = \nabla \mu_k^c + (1 - \rho_f \bar{V}_k) g \nabla z, \quad (2)$$

and ∇ is the vector gradient operator, g is the acceleration of gravity, z is the height above an arbitrary datum, and \bar{V}_k is the partial specific volume of solute k [14]. The flows are current densities, i.e., quantities of heat, volume, or mass per unit area per unit time. The reciprocal relations are

$$L_{qv} = L_{vq}, \quad L_{qi} = L_{iq}, \quad L_{vi} = L_{iv}, \quad L_{ik} = L_{ki}. \quad (3)$$

We identify various effects by reference to the phenomenological coefficients associated with them. The direct effects are Fourier's law (L_{qq}), Darcy's law (L_{vv}), and Fick's law (L_{ii}). The thermodynamically coupled effects and their corresponding inverse effects are thermal filtration (L_{qv}) and thermal osmosis (L_{vq}), the diffusion thermal effect (L_{qi}) and thermal diffusion (L_{iq}), chemical

osmosis (L_{vi}) and ultrafiltration (L_{iv}), and coupled diffusion (L_{ik} , $k \neq i$). The reciprocal relations have been verified in a large variety of experiments, implying the validity of the linear phenomenological equations in these cases [16].

The volume flow (j_v) and the solute flows (j_i^o , $i = 1, \dots, n$) are defined by

$$j_v = \sum_{i=0}^n \bar{V}_i j_i \quad (4)$$

and

$$j_i^o = j_i - \frac{\rho_i}{\rho_o} j_o, \quad i = 1, \dots, n, \quad (5)$$

where the j_i , $i = 0, \dots, n$, are the flows of water and solutes *relative to the center of mass of the system* and the ρ_i , $i = 0, \dots, n$, are the partial mass densities of water and solutes. We also note the relation

$$\sum_{i=0}^n \rho_i \bar{V}_i = 1. \quad (6)$$

For the purpose of the discussion to follow, we now simplify the phenomenological equations by neglecting the gravitational contribution to the force F_{ck} and assuming the presence of a single solute, denoted by index s , which forms an ideal solution with water. We focus attention on the matter flows, for which the phenomenological equations are now

$$j_v = -L_{vq} \frac{\nabla T}{T} - L_{vv} \nabla h - L_{vs} \nabla \mu_s^c \quad (7)$$

$$j_s^o = -L_{sq} \frac{\nabla T}{T} - L_{sv} \nabla h - L_{ss} \nabla \mu_s^c, \quad (8)$$

with the reciprocal relation

$$L_{sv} = L_{vs}. \quad (9)$$

Then (4), (5), and (6) become

$$j_v = \bar{V}_o j_o + \bar{V}_s j_s, \quad (10)$$

$$j_s^o = j_s - \frac{\rho_s}{\rho_o} j_o, \quad (11)$$

and

$$\rho_o \bar{V}_o + \rho_s \bar{V}_s = 1. \quad (12)$$

Solving (10) and (11) for j_o and j_s with the help of (12) gives

$$j_o = \rho_o \left[j_v - \frac{j_s^o}{\rho_s} (1 - \rho_o \bar{V}_o) \right] \quad (13)$$

and

$$j_s = \rho_s j_v + \rho_o \bar{V}_o j_s^o. \quad (14)$$

We assume that the solution is dilute enough that $\rho_o \bar{V}_o \approx 1$; then (13) and (14) become

$$j_o \approx \rho_o j_v \quad (15)$$

and

$$j_s \approx \rho_s j_v + j_s^o. \quad (16)$$

Finally, we note that in an ideal solution

$$\nabla \mu_s^c = \frac{RT}{M_s} \frac{\nabla \rho_s}{\rho_s}, \quad (17)$$

where R is the gas constant and M_s is the molecular weight of the solute. Substituting (7), (8), and (17) into (15) and (16) gives the phenomenological equations for water and solute flows relative to the center of mass:

$$j_o \approx -\rho_o \left(L_{vq} \frac{\nabla T}{T} + L_{vv} \nabla h + L_{vs} \frac{RT}{M_s} \frac{\nabla \rho_s}{\rho_s} \right), \quad (18)$$

$$j_s \approx -(\rho_s L_{vq} + L_{sq}) \frac{\nabla T}{T} - (\rho_s L_{vv} + L_{sv}) \nabla h - (\rho_s L_{vs} + L_{ss}) \frac{RT}{M_s} \frac{\nabla \rho_s}{\rho_s}. \quad (19)$$

We will use (7), (18), and (19) to compare flows of fluid and solute arising from thermodynamically coupled processes to the flows that would be predicted by the laws of Darcy and Fick.

APPLICATION TO A HYPOTHETICAL REPOSITORY ENVIRONMENT

In order to estimate possible magnitudes of thermodynamically coupled effects relative to direct effects, we assume conditions previously hypothesized for the near-field region of a repository sited in basalt. Values of phenomenological coefficients are taken from experimental data reported in the literature. Although a considerable literature exists on thermodynamically coupled processes in entirely fluid systems, data relevant to porous and semipermeable natural materials are relatively sparse. Thus, we will use data on thermal osmosis in kaolinite even though we recognize that kaolinite may not be a principal candidate for a backfill material. However, the results obtained should be approximately representative of clay backfills, in general. Also, no data have been reported on coupled diffusion in saturated, porous media or semipermeable media; therefore, this process is not considered in our calculations.

Repository Conditions

We assume that the repository is sited in basalt and that the near-field environment is saturated by ground water flowing down a regional hydraulic gradient equal to 10^{-3} ($\nabla h \approx 10 \text{ J/m}^4$). (This is the order of magnitude commonly assumed in calculations of solute transport [17]). To estimate the thermal effects, we adopt calculations reported [18] for a hypothetical basalt repository which indicate that at 50 years after closure the temperature a few tens of meters from the repository will be approximately 420 °K and the temperature

gradient will be approximately 2 °K/m. The ground water characteristic of this basalt has a dissolved solids content equal to a solute partial mass density (ρ_s) of 0.4 kg/m³. The molecular weight of the solute is assumed to be 0.1 kg/mole.

Thermal Osmosis in Kaolinite

Experiments on thermal osmosis of pure water through kaolinite [19] provide the following values of L_{vv} and L_{vq} corresponding to the experimental conditions:

$$L_{vv} \approx 5 \times 10^{-14} \text{ m}^5/(\text{J} \cdot \text{s})$$

$$L_{vq} \approx 8 \times 10^{-8} \text{ m}^2/\text{s}.$$

We assume that these values can be used to provide approximate results under our assumed repository conditions; then, using (7) with $\nabla \mu_s^c$ equal to zero, we calculate the following contributions to j_v from thermal osmosis and Darcy's law:

$$j_v(\text{thermal osmosis}) \approx 4 \times 10^{-10} \text{ m/s}$$

$$j_v(\text{Darcy}) \approx 5 \times 10^{-13} \text{ m/s}.$$

Thermal osmosis in this material, under the assumed temperature gradient, produces a volume flow (specific discharge) 800 times as large as the Darcian flow. It is clear that the kaolinite acts as a semipermeable membrane with an extremely small Darcian permeability.

A hydraulic gradient of about 0.8 ($\nabla h \approx 8000 \text{ J/m}^4$) would be required to produce a Darcian flow equal to the thermal osmotic flow estimated in this example.

Chemical Osmosis, Ultrafiltration, and Diffusion in Bentonite

Results of isothermal experiments with Wyoming bentonite [20] provide the following estimates of L_{sv} , L_{vv} , and L_{ss} :

$$L_{sv} \approx -0.8 \times 10^{-16} \text{ kg} \cdot \text{m}^2/(\text{J} \cdot \text{s})$$

$$L_{vv} \approx 2.4 \times 10^{-16} \text{ m}^5/(\text{J} \cdot \text{s})$$

$$L_{ss} \approx 6.8 \times 10^{-17} \text{ kg}^2/(\text{m} \cdot \text{J} \cdot \text{s}).$$

We assume that these values are valid under the assumed repository conditions and that the relative concentration gradient of the solute ($\nabla \rho_s / \rho_s$) is 0.1 m⁻¹. Then we use (18) and (19) with ∇T equal to zero to estimate contributions to flows of water and solute from processes driven by gradients of hydraulic potential and solute concentration.

From (18), the contributions to water flow from chemical osmosis and from Darcy's law are:

$$j_o(\text{chemical osmosis}) \approx -2.9 \times 10^{-10} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$j_o(\text{Darcy}) \approx 2.3 \times 10^{-12} \text{ kg}/(\text{m}^2 \cdot \text{s}).$$

Here the flow due to chemical osmosis is about 125 times larger than the Darcian flow and is directed *against* the gradient of solute concentration.

In (19), the flow of solute is composed of an advective part ($\rho_s L_{vv} \nabla h$), a part arising from ultrafiltration ($L_{sv} \nabla h$), a part arising from chemical osmosis ($\rho_s L_{vs} \nabla \mu_s^c$), and a part arising from Fickian diffusion ($L_{ss} \nabla \mu_s^c$). If each partial flow is regarded as a vector quantity, it is seen that the flow from ultrafiltration is directed *against* the advective flow and that the chemical osmotic flow is directed *against* the diffusive flow. The various contributions to the total flow of solute are:

$$j_s(\text{advection}) \approx 9.3 \times 10^{-16} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$j_s(\text{ultrafiltration}) \approx -8.2 \times 10^{-16} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$j_s(\text{total along } \nabla h) \approx 1.1 \times 10^{-16} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

and

$$j_s(\text{chemical osmosis}) \approx -1.2 \times 10^{-13} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$j_s(\text{diffusion}) \approx 2.4 \times 10^{-13} \text{ kg}/(\text{m}^2 \cdot \text{s})$$

$$j_s(\text{total along } \nabla \rho_s) \approx 1.2 \times 10^{-13} \text{ kg}/(\text{m}^2 \cdot \text{s}).$$

The bentonite used in this example is semipermeable and has characteristically low Darcian permeability and mass diffusivity; thus, the thermodynamically coupled processes, chemical osmosis and ultrafiltration, are significant contributors to flows of water and solute. In the case of solute transport, ultrafiltration reduces flow along the hydraulic potential gradient by about an order of magnitude relative to the value that would be calculated from Darcy's law alone, and chemical osmosis greatly reduces flow along the concentration gradient relative to the value that would be calculated from Fick's law alone.

Thermal and Fickian Diffusion in Permeable Material

In granular, noncohesive materials which are permeable to solutes, the coefficients L_{vq} and L_{vs} may be vanishingly small relative to other coefficients in the phenomenological equations, leaving thermal diffusion as the only (potentially) significant, thermodynamically coupled transport process. If a hydraulic potential gradient is absent in such a permeable material, (19) can be written:

$$j_s \approx -D_{ss}(\rho_s s_s \nabla T + \nabla \rho_s), \quad (20)$$

[14], where D_{ss} , the "diffusion coefficient", and s_s , the "Sorët coefficient", are defined by

$$D_{ss} = \frac{L_{ss} RT}{\rho_s M_s} \quad \text{and} \quad s_s = \frac{L_{sq} M_s}{L_{ss} RT^2}.$$

From (20), the ratio of the magnitude of solute flow produced by thermal diffusion to that produced by Fickian diffusion is:

$$\frac{j_s(\text{thermal diffusion})}{j_s(\text{Fickian diffusion})} = \frac{s_s |\nabla T|}{|\nabla \rho_s / \rho_s|}. \quad (21)$$

Recent measurements of thermal diffusion of solutes in a system containing saturated, 3- μm alumina have provided values of s_s of about $4 \times 10^{-3} \text{ }^\circ\text{K}^{-1}$ [21]. Using our assumed repository conditions and the reported value of s_s , the ratio given by (21) is 0.08; larger temperature gradients or smaller relative gradients of solute concentration would produce larger contributions by thermal diffusion to the total flow of solute.

CONCLUSIONS

Application of the thermodynamics of irreversible processes to transport processes near a nuclear waste repository results in phenomenological equations that encompass a broader range of physical phenomena than is accessible through consideration of simultaneous, direct processes (Fourier's law, Darcy's law, Fick's law) alone. Experimental evidence has verified the linear phenomenological equations and the reciprocal relations between the coefficients associated with the thermodynamically coupled processes in materials of interest in the nuclear waste disposal program.

The approximate calculations presented here indicate that thermodynamically coupled transport processes can contribute to mass flows in near-field regions of nuclear waste repositories. The magnitudes of the flows produced by these processes depend on the magnitudes of gradients of temperature, hydraulic potential, and composition, and on the properties of the solid phase supporting the flows. Backfills containing large proportions of clay can act as semipermeable membranes and produce mass flows by thermal osmosis, chemical osmosis, and ultrafiltration that are significant relative to Darcian and Fickian flows. Predictions of water and solute flows through semipermeable materials based only on Darcy's law and Fick's law could be seriously in error in magnitude and possibly also in direction, the latter depending on the relative alignments of driving forces. Thermal diffusion can be present also in such backfills, but would be the only significant coupled process expected in permeable backfills and in porous or fractured geological media.

These considerations imply needs for further experimental and computational research. Characterization of materials proposed for use as backfills should include measurement of phenomenological coefficients associated with thermodynamically coupled processes; this is especially important if the saturated materials can be expected to behave as semipermeable membranes. Also, numerical simulators of transport processes which are to be used to evaluate the performance of proposed nuclear waste repositories should be expanded in scope to include possible thermodynamically coupled processes in the near-field region. Sensitivity calculations should be done to evaluate the significance of thermodynamically coupled effects in relation to the direct effects.

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