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ABSTRACT

Analysis of observed distributions of water adsorbed by compacted MX-80 bentonite in the presence of temperature gradients according to methods of the thermodynamics of irreversible processes indicates the possibility of coupling among fluxes of heat and mass. Additional experiments are suggested to confirm the existence of coupling.

INTRODUCTION

Highly compacted bentonite is under consideration for use as a buffer material in geological repositories for high-level radioactive wastes. In order to assess the suitability of bentonite for this use, it is necessary to be able to predict the rate and spatial extent of water uptake and water distribution in highly compacted bentonite in the presence of thermal gradients.

The "Buffer Mass Test" (BMT) was conducted by workers in Sweden as part of the Stripa Project [1,2]. The BMT measured uptake and spatial distributions of water infiltrating annuli of compacted MX-80 sodium bentonite heated from within and surrounded by granitic rock; the measurements provided a body of data very valuable for comparison to results of theoretical calculations.

Results of experiments on adsorption of water by highly compacted MX-80 bentonite have been reported by workers in Switzerland [3]. The experiments included measurements of heats of immersion and adsorption-desorption isotherms. These measurements provide the basis for prediction of water vapor pressures in equilibrium with bentonite having specified adsorbed water contents at various temperatures.

The present work offers a phenomenological description of the processes influencing movement of water in compacted bentonite in the presence of a variable thermal field. The theory is applied to the bentonite buffer-water system in an assumed steady state of heat and mass transport, using critical data derived from the experimental work done in Switzerland [3]. Results of the theory are compared to distributions of adsorbed water in buffers observed in the Swedish BMT experiments [2].

PHENOMENOLOGICAL EQUATIONS FOR HEAT AND MASS FLUXES

The development of the theory relating fluxes of heat and mass to the thermodynamic forces driving the fluxes is based on the thermodynamics of irreversible processes. The present development begins with the time-dependent form of the Gibbs equation for the system under consideration. The basis for this equation and detailed discussions of the application of the thermodynamics of irreversible processes to porous and semipermeable media have been given previously in the literature (e.g., [4],[5]).

For a system of bentonite with an adsorbed water phase and a gas phase containing water vapor and air, we write the time-dependent Gibbs equation:

$$T \frac{\partial C_s}{\partial t} = \frac{\partial C_e}{\partial t} - \mu_v \frac{\partial}{\partial t}(\epsilon \rho_v) - \mu_c \frac{\partial}{\partial t}[\rho_s(1 - \epsilon)w] - \mu_a \frac{\partial}{\partial t}(\epsilon \rho_a), \quad (1)$$

where T is absolute temperature, t is time, C_s and C_e are concentrations of entropy and static energy, μ_i is the chemical potential (partial specific Gibbs free energy) of mobile

component i , ρ_i is the density of component i , ϵ is the void fraction, ρ_s is the density of bentonite. w is the water content of the bentonite (mass of water/mass of bentonite), and the components are water vapor ($i = v$), adsorbed water ($i = c$), and air ($i = a$). Here we have ignored any contributions from external potentials (e.g., gravity). We must replace the time derivatives on the right side of (1). To do this, we use the balance equation for static energy [4],

$$\frac{\partial C_\epsilon}{\partial t} = -\bar{\nabla} \cdot (\bar{J}_q + \bar{J}_v \bar{H}_v + \bar{J}_c \bar{H}_c + \bar{J}_a \bar{H}_a), \quad (2)$$

where \bar{J}_q , \bar{J}_v , \bar{J}_c , and \bar{J}_a are the fluxes of heat and the mobile components, and the \bar{H}_i are the partial specific enthalpies of the components. The balance equations for mass of the mobile components are

$$\frac{\partial}{\partial t}(\epsilon \rho_v) = -\bar{\nabla} \cdot \bar{J}_v - J_r, \quad (3)$$

$$\frac{\partial}{\partial t}[\rho_s(1 - \epsilon)w] = -\bar{\nabla} \cdot \bar{J}_c + J_r, \quad (4)$$

$$\frac{\partial}{\partial t}(\epsilon \rho_a) = -\bar{\nabla} \cdot \bar{J}_a, \quad (5)$$

where J_r is the rate of transfer of water from the gas phase to the adsorbed phase. Substituting (2)–(5) into (1) and using $\mu_i = \bar{H}_i - T\bar{S}_i$ where \bar{S}_i is the partial specific entropy of component i gives

$$\frac{\partial C_s}{\partial t} = -\bar{\nabla} \cdot \bar{J}_s - \bar{J}_s \cdot \frac{\bar{\nabla} T}{T} - \frac{1}{T} (\bar{J}_v \cdot \bar{\nabla} \mu_v + \bar{J}_c \cdot \bar{\nabla} \mu_c + \bar{J}_a \cdot \bar{\nabla} \mu_a) - \frac{1}{T}(\mu_c - \mu_v)J_r, \quad (6)$$

where the flux of entropy, \bar{J}_s , is defined by

$$\bar{J}_s = \frac{\bar{J}_q}{T} + \bar{J}_v \bar{S}_v + \bar{J}_c \bar{S}_c + \bar{J}_a \bar{S}_a. \quad (7)$$

The general balance equation for entropy is

$$\frac{\partial C_s}{\partial t} = -\bar{\nabla} \cdot \bar{J}_s + \sigma, \quad (8)$$

where σ is the rate of production of entropy by irreversible processes. Comparing (6) and (8), we identify σ explicitly and use the result to define the dissipation function, Φ , by

$$\Phi = T\sigma = \bar{J}_s \cdot \bar{\nabla} T - \bar{J}_v \cdot \bar{\nabla} \mu_v - \bar{J}_c \cdot \bar{\nabla} \mu_c - \bar{J}_a \cdot \bar{\nabla} \mu_a - (\mu_c - \mu_v)J_r. \quad (9)$$

The chemical potential gradients are given by [7]:

$$\bar{\nabla} \mu_v = -\bar{S}_v \bar{\nabla} T + \frac{RT}{M_w} \bar{\nabla} \ln P_v, \quad (10)$$

$$\bar{\nabla} \mu_c = -\bar{S}_c \bar{\nabla} T + \bar{\nabla} \psi_m + \left(\frac{1}{\rho_c} - \bar{V}_c \right) \bar{\nabla} P_a, \quad (11)$$

$$\bar{\nabla} \mu_a = -\bar{S}_a \bar{\nabla} T + \frac{RT}{M_a} \bar{\nabla} \ln P_a, \quad (12)$$

where P_v and P_a are partial pressures of water vapor and air (assumed to be perfect gases), M_w and M_a are the respective molecular weights, R is the gas constant, ψ_m is the matrix potential, and \bar{V}_c is the partial specific volume of adsorbed water. In order to use

Above the frequency for which $\omega RC \gg 1$ the capacitance effectively integrates the current to make the device a broadband monitor with response

$$Z_P \Rightarrow \frac{Iq}{AcC} \quad (3.5)$$

(b) Stripline. The image current is useful in explaining the basic features of the response of a stripline pickup (Fig. 2). In this geometry the stripline receives a fraction $g \sim w/2\pi a$ of the image current. As a short pulse of the, assumed positive, beam current $i_B(t)$ reaches the upstream end, it repels positive charges into the output line and along the stripline. If the characteristic impedances of both these are Z_L , a prompt signal of $1/2 Z_L g i_B(t)$ is seen at the output and an equal pulse propagates downstream with velocity c . At time l/c later the beam, assumed to have velocity βc , and the pulse arrive at the downstream end where the departing beam releases into the stripline a negative pulse $-g i$. One half of this cancels the positive current traveling downstream and one half survives to propagate upstream. It enters the output line at time $2l/c$ and is seen as a negative pulse of voltage $-1/2 Z_L g i$ (upper Fig. 3). It is now easy to see what signals are produced if the beam velocity βc were low. The output then will depend upon how the downstream end is terminated. In Fig. 3 are shown the signals for three cases of downstream termination. Lack of fidelity in the response results if reflections arise from imperfect impedance matching especially where the stripline joins the outgoing lines. The seemingly superfluous downstream matching resistor may be desired to absorb some of these reflections. If one Fourier analyzes the response for $\beta = 1$, the result is:

$$Z_P = Z_L g e^{j(\pi/2 - k_o l)} \sin k_o l \quad (3.6)$$

with $k_o = \omega/c$ and at output Z_L . This response is all real and a maximum at $k_o l = \pi/2$, i.e., at $l = \lambda/4$. For this reason the device is often called a "quarter-wave loop." Zeroes in the response occur when the line length is a multiple of one-half wavelength. (These zeroes may be removed if the signals from the downstream end can be suppressed; this has been done with ferrite absorbers

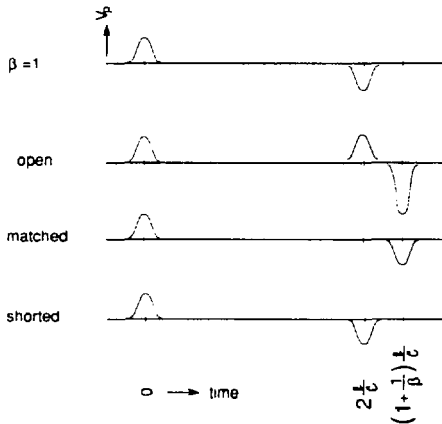


Fig. 3. Stripline signals for various back terminations.

where \bar{V}_c is assumed in [3] to be $1.00 \times 10^{-3} \text{ m}^3/\text{kg}$ and P_0 equals $2.313 \times 10^3 \text{ N/m}^2$ at 20°C . Then the adsorption isotherm at 20°C (293 K) is

$$\ln P_v(293 \text{ K}) = 7.7463 - \exp(1.0933 - 17.8w), \quad (20)$$

with P_v in units N/m^2 .

Dependence of Adsorption Isotherms on Temperature

The variation of the adsorption isotherm with temperature at constant water content is given by

$$\left[\frac{\partial \ln P_v}{\partial (1/T)} \right]_w = -\frac{M_w}{R} q^{st}, \quad (21)$$

where q^{st} is the specific isosteric heat of adsorption [6]. q^{st} is related to the specific residual heat of immersion, h_f , by

$$q^{st} = \Delta H^{vap} - \left[\frac{\partial h_f}{\partial w} \right]_T, \quad (22)$$

where ΔH^{vap} is the specific heat of vaporization of $\text{H}_2\text{O}(l)$, equal to $2.419 \times 10^6 \text{ J/kg}$ at 34°C .

The Swiss workers measured h_f as a function of initial water content, w , at 34°C in the compacted MX-80 bentonite used for the isotherm measurement at 20°C . The results fitted the function

$$h_f = 47.18 \times 10^3 \exp(-8.53w - 29.28w^2) \text{ J/kg}. \quad (23)$$

Integration of (21), assuming q^{st} constant and using (22) and (23), gives

$$\ln P_v(T) = \ln P_v(293 \text{ K}) + \frac{M_w}{R} q^{st} \left(\frac{1}{293} - \frac{1}{T} \right), \quad (24)$$

where $\ln P_v(293 \text{ K})$ is given by (20) and

$$\frac{M_w}{R} q^{st} = 5.242 \times 10^3 + 1.023 \times 10^2 (8.53 + 58.56w) \exp(-8.53w - 29.28w^2). \quad (25)$$

ANALYSIS OF RESULTS OF BUFFER MASS TEST

The Swedish workers have published [2] graphs of adsorbed water contents, w , and temperatures, T , versus radial distance, r , from the centerline of the heaters measured within two annular bentonite buffers in the BMT: hole 3 after 15 months of heating at 600 W, and hole 4 after 10 months of heating at 600 W. For the present analysis, values of w and T were read from the graphs at discrete values of r and the corresponding values of $\ln P_v(T)$ were calculated using (24). Fig. 1 shows graphs of $\ln P_v$ against $M_w/R T$ for each experiment. According to (17), the slope of such a graph should equal the value of the coefficient C_c , defined by

$$C_c = \frac{L_{aa}L_{ww} - L_{aw}L_{aw}}{L_{aa}L_{ww} - L_{aw}^2}. \quad (26)$$

The graphs in Fig. 1 have non-zero slopes (significant at the 95% confidence level [9]) equal to $(-1.45 \pm 0.12) \times 10^6 \text{ kg/J}$ for the experiment in hole 3 and $(-1.78 \pm 0.10) \times 10^6 \text{ kg/J}$ for the

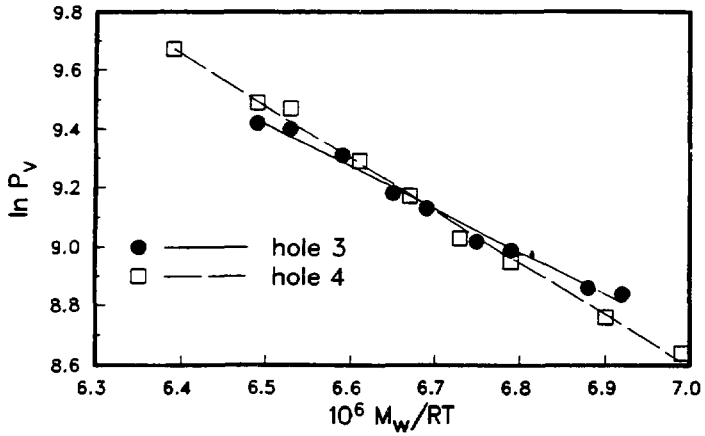


Figure 1. $\ln P_v$ (calculated) vs. M_w/RT for BMT experiments [2] in holes 3 and 4. Points were read from graphs in [2]; lines are linear fits to points by least squares method.

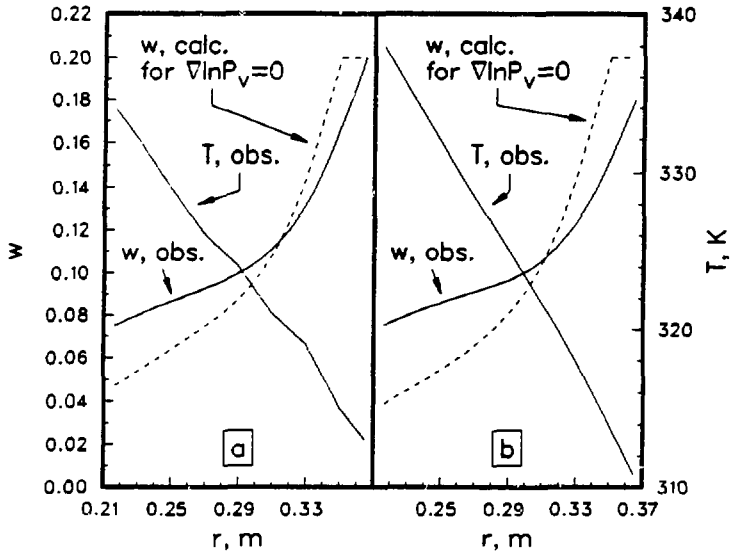


Figure 2. T and w vs. radial distance, r . Solid lines: T , w observed in BMT experiments [2]. Dashed lines: w calculated for condition $\nabla \ln P_v = 0$. (a) hole 3, (b) hole 4.

experiment in hole 4. These results indicate the possibility of coupling among the processes transporting heat, water, and air in these tests. It is expected that the phenomenological coefficients are not constant, but are functions of temperature and compositions of the gas and adsorbed phases.

The profiles of T and w observed in the two experiments are shown in Figs. 2(a) and 2(b). Also shown are calculated profiles of w for the same T -profiles under the assumption that $\bar{\nabla} \ln P_v = 0$, i.e., that $C_c = 0$. The calculated profiles correspond to the same mass of water per unit length of bentonite annulus as the observed profiles. The calculated, constant value of $\ln P_v$ was 9.02 for both cases. We note that in both cases the calculated adsorbed water content reaches the saturation value ($w = 0.20$) near the outer edges of the bentonite annuli. From these results, it appears that coupling among transport processes may have produced a less pronounced variation of w , and hence of swelling pressures, than would be predicted without consideration of coupling.

CONCLUSIONS

The calculations presented here indicate the possibility of coupling among transport processes in the tested bentonite buffers. However, this conclusion must be regarded as highly tentative, given that the critical experiments were performed by different workers in different laboratories using different samples of the buffer materials. Further experimental work is needed to confirm the existence of coupling in these materials, and to determine the dependence on temperature and composition of the phenomenological coefficients for both coupled and direct processes. Measurements of residual heats of immersion at several different temperatures would provide data on the temperature variation of the isosteric heat of adsorption and would improve the accuracy of calculated adsorption curves as functions of temperature. Measurement of desorption scanning curves along the adsorption isotherms would allow desorption hysteresis to be accounted for in the analysis.

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