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FLOW AND DIFFUSION OF A TWO-SPECIES GAS MIXTURE IN A POROUS SLAB

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ABSTRACT

The problem of mass transport of oxygen is considered in a soil whose upper surface is open to air at atmospheric pressure and in which the oxygen is preferentially removed at some reaction surface within the body of the soil. The soil is assumed to be a permeable slab filled with a two-species gas mixture, the first of which is removed at one face of the slab, while the other face is maintained at constant pressure ($\sim$ atmospheric).

It is shown that the maximum removal rate of the first gas is largely determined by the diffusion coefficient of the second gas, but enhanced to some extent by gas flow due to the pressure difference set up by gas removal. This pressure difference is very small ($\sim 10^{-4}$ atmospheres) even at the maximum removal rate. It is also shown that under some conditions, which are satisfied in the case of oxygen removal from air, the concentration of the first gas has the same functional dependence on distance, as expected in the case of diffusion with no gas flow, but with an enhanced diffusion coefficient. For the problem of interest, this enhancement is about 20 per cent.

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GASEOUS; DIFFUSION; GAS FLOW; SOILS

CONTENTS

1. INTRODUCTION

It is generally accepted [e.g. Linsley *et al.* 1949] that gas movement in soils is due predominantly to diffusion processes driven by concentration gradients set up in the soil by the preferential consumption of various constituents of the soil atmosphere. Experiments have been mounted to measure diffusion coefficients of gases in soil [Currie 1960, Papendick & Runkles 1965, Melhuish *et al.* 1974], based largely on the premise that the variation of gas concentration in soil can be described by a diffusion equation. Measurement of gas concentration in an experimental soil column as a function of time and distance, will then provide values of diffusion coefficients that can be used to estimate gas transport in field conditions.

Preferential consumption of one component in a two-gas mixture will produce a pressure gradient as well as a concentration gradient. In a one-component system the concentration gradient, $\partial c/\partial x$, would be directly proportional to the pressure gradient, $\partial p/\partial x$. If the pressure gradient in such a system were sufficiently small that gas flow could be assumed to occur at constant density, the mass transport due to the pressure difference would be

$$q = Kc \frac{\partial p}{\partial x} = Kp \frac{\partial c}{\partial x}$$

and that due to diffusion $q = D \dfrac{\partial c}{\partial x}$,

where K and D are the permeability and diffusion coefficients of the gas. Since $Kp \gg D$ when the pressure is about atmospheric, mass transport due to the pressure gradient would be expected to dominate over that due to diffusion. At first sight, the same might be expected to be true for a gas mixture, but it is for the very reason that gas flow due to the pressure gradient dominates, that it tends to remove the pressure gradient produced by preferential gas consumption, but still leaves the concentration gradient. We would therefore expect diffusion processes to dominate if gas flow maintains approximately uniform pressure throughout the system under the prevailing conditions of gas removal rate.

In this paper we examine the conditions under which diffusion processes dominate and the extent to which gas flow contributes to mass transport. The particular system of interest is air-filled soil in which oxygen is consumed preferentially at a reaction surface within the soil.

2. FORMULATION

Consider a permeable slab where a two-species gas mixture can enter at a face situated at the origin and where one of the gases is removed selectively at some other face, distance L to the right of the origin. Let the net gas velocity be $v(x)$ and the concentration of each gas species be $c_n(x)$. For each gas,

the rate of mass flow through unit area = $J_n + vc_n$, $n = 1,2$

where J_n is the mass flux due to diffusive processes.

The usual continuity arguments yield

$$\frac{\partial c_n}{\partial t} = - \frac{\partial}{\partial x} (J_n + vc_n) \quad . \tag{1}$$

If we apply Flick's law to diffusion and Darcy's law to gas flow,

$$J_1 = -D_1 \frac{\partial c_1}{\partial x} \quad , \tag{2}$$

$$J_2 = -D_2 \frac{\partial c_2}{\partial x} \quad , \tag{3}$$

$$v = -K \frac{\partial p}{\partial x} \quad , \tag{4}$$

where D_n, $n = 1,2$ = diffusion coefficients of species 1 and 2 respectively,

$p = p(x)$ is the total pressure of the gas at point x,

K = gas permeability.

The diffusion coefficients are assumed constant, which is tantamount to an assumption that no significant total pressure changes are expected in the system.

Using the gas law to relate pressure and gas concentration c_n

$$pV = \nu N_0 kT$$

$$= N_0 kT \sum_n \frac{m_n}{M_n}$$

where ν = the number of moles of gas in the volume V, and

m_n, M_n = mass and molecular weight of species n respectively in the volume V.

Hence we have

$$p = \sum_n \alpha_n c_n \quad , \tag{5}$$

with $\alpha_n = N_0 kT/M_n$.

3. <u>SOLUTION</u>

The steady state conditions

$$\frac{\partial c_n}{\partial t} = 0 \quad , \quad n = 1,2$$

yield $J_1 + vc_1 = \text{constant} = R$, say (6)

$J_2 + vc_2 = \text{constant} = Y$, say .

If only species 1 is consumed at $x = L$, then there is no mass transfer of species 2 at $x = L$ and

$$J_2 + vc_2 = 0 \text{ at } x = L$$

i.e.

$$Y = 0$$

and $J_2 + vc_2 = 0$ (7)

everywhere in the system. Similarly it follows that R is the removal rate of species 1.

Substituting equations 3 and 4 into equation 7 gives

$$c_2 = c_2^{o} \exp(K(P-p)/D) \tag{8}$$

where c_2^{o}, P = concentration of species 2, and the total pressure at $x = 0$. Combining equations 6 and 7, and using equation 4 yields

$$-D_1\alpha_1 \frac{\partial c_1}{\partial x} - D_2\alpha_2 \frac{\partial c_2}{\partial x} - Kp\frac{\partial p}{\partial x} = \alpha_1 R$$

from which it follows that

$$\frac{K}{2}(p^2-P^2) + D_1(p-P) + \alpha_2(D_2-D_1)(c_2-c_2^{o}) + \alpha_1 Rx = 0 \quad . \tag{9}$$

Substitution of equation 8 into equation 9 provides, in principle, the pressure p as a function of x. Again, in principle c_2 and c_1 can be found as functions of x by substituting for $p(x)$ in equations 8 and 5 in turn.

4. DISCUSSION

The evaluation of $p(x)$ involves solution of a transcendental equation. The situation is considerably simplified and the underlying physics clarified if it is assumed that the diffusion coefficients of the two gas species are equal, i.e.

$$D_1 = D_2 = D \quad .$$

In most practical problems, and certainly in the present problem, this assumption is a reasonable one [Jost 1960] and the solution to equation 9 reduces to

$$p = \left\{ (P+D/K)^2 - \frac{2\alpha_1 Rx}{K} \right\}^{\frac{1}{2}} - D/K \quad . \tag{10}$$

This expression for the pressure p would again be considerably simplified if we could assume

$$\beta = \frac{2\alpha_1 Rx}{(P+D/K)^2 K} << 1 \quad ,$$

and hence provide the solution as a power series of β. Let us for the moment expand the solution as a power series in β and find out later under what conditions the expansion is valid. The expressions for the pressure p and the concentrations c_1 and c_2 are then given by

$$p = P - \frac{\alpha_1 Rx}{(P+D/K)K} + \ldots \qquad (11)$$

$$c_2 = c_2^o \exp\left(\frac{\alpha_1 Rx}{(P+D/K)D}\right)$$

$$c_1 = \frac{p}{\alpha_1} - \frac{\alpha_2}{\alpha_1} c_2$$

$$= \frac{P}{\alpha_1}\left[1 - \frac{\alpha_1 Rx}{(P+D/K)PK}\right] - \frac{\alpha_2}{\alpha_1} c_2^o \exp\left(\frac{\alpha_1 Rx}{(P+D/K)D}\right) .$$

The maximum value of β will be determined by the maximum value, R_m of the removal rate R. We can evaluate R_m and find out under what conditions β_m the maximum value of β is less than unity. The maximum rate, R_m, that the species c_1 can be removed from the system at the face at x = L is the rate that makes c_1 zero at x = L, i.e.

$$c_1(L) = 0 = \frac{p(L)}{\alpha_1} - \frac{\alpha_2 c_2(L)}{\alpha_1}$$

i.e. $$\frac{P}{\alpha_2 c_2^o}\left[1 - \frac{\alpha_1 R_m L}{(P+D/K)PK}\right] = \exp\left(\frac{\alpha_1 R_m L}{(P+D/K)D}\right) . \qquad (12)$$

The diffusion coefficient for oxygen is about 0.2 $cm^2\ s^{-1}$ [Jost 1960] and $\sim$0.05 $cm^2\ s^{-1}$ in damp soil [Papendick & Runkles 1965]. The permeability, K, for gases in soil is typically of the order of 10^{-3} $cm^2\ Pa^{-1}\ s^{-1}$ [Carman 1956] leading to a value of D/K of the order of 5×10^1 Pa, which is very small compared to atmospheric pressure, P, of the order of 10^5 Pa. Hence if, as was assumed,

$$\frac{\alpha_1 R_m L}{(P+D/K)^2 K} \ll 1 ,$$

then $$\frac{\alpha_1 R_m L}{P(P+D/K)K} \ll 1 ,$$

and from equation 12

$$R_m \sim \frac{(P+D/K)D}{\alpha_1 L} \log (P/P_2) , \qquad (13)$$

where $P_2 = \alpha_2 c_2^o$ = partial pressure of species 2 at x = 0.

We can now evaluate β_m, the maximum value of β,

$$\beta_m = \frac{2\alpha_1 R_m L}{(P+D/K)^2 K}$$

$$= \frac{2D}{(P+D/K)K} \log (P/P_2) << 1 \quad ,$$

provided $P_2 >> P \exp - \left(\frac{K(P+D/K)}{2D}\right)$.

This means that the expansion which led to expression 11 for p(x) is valid even at the highest removal rate R_m, provided the partial pressure of species 2 at x = 0 is not a very small fraction of the initial total pressure; in other words, provided we are dealing with a gas mixture and not an almost pure gas.

Using equation 13 for R_m in equation 11, gives the pressure at x = L at the maximum removal rate as

$$p = P \left[1 - \frac{D}{PK} \log(P/P_2)\right] \quad .$$

Since, in most cases of practical interest, P/P_2 is the order of unity and $D/(PK) \sim 5 \times 10^{-4}$, the pressure drop across the slab is very small.

If the mass transport process of species 1 were purely a diffusion process, the maximum removal rate would be given by

$$R_m^D = Dc_1^o/L \quad ,$$

and $$R_m/R_m^D = \frac{(P+D/K)}{P_1} \log(P/P_2) \quad , \qquad (14)$$

where $P_1 = \alpha_1 c_1^o$ = partial pressure of species 1 at x = 0.

When $P_1 < P_2$, which is the case for the partial pressure of oxygen compared to that of nitrogen in air,

$$R_m/R_m^D \sim P/P_2 = 1 + P_1/P_2 \quad .$$

When $P_1 > P_2$

$$R_m/R_m^D = \frac{P}{P_1}\left[\frac{P/P_2-1}{P/P_2} + \frac{1}{2}\left(\frac{P/P_2-1}{P/P_2}\right)^2 \cdots\right]$$ [Abramowitz & Stegun 1964]

$$\sim 1 + \frac{1}{2} P_1/P \quad .$$

In both cases, the maximum removal rate, when gas flow as well as diffusion is taken into account, is only slightly enhanced compared to the maximum removal rate when diffusion processes alone are considered. We would therefore expect that the equations for the concentrations of species 1 and 2 could be expressed in forms similar to those that can be derived from solutions to the appropriate diffusion equations.

If $\frac{\alpha_1 Rx}{(P+D/K)D} < 1$, which is certainly true even at the highest removal rate, provided $P_1 < P_2 \left(\exp(\frac{KP}{D})-1\right)$, then

$$c_2 = c_2^o \exp\left(\frac{\alpha_1 Rx}{(P+D/K)D}\right) \sim c_2^o \left(1 + \frac{\alpha_1 Rx}{(P+D/K)D}\right) ,$$

and $$c_1 = c_1^o - \frac{Rx}{D} \frac{P_2}{(P+D/K)} . \qquad (15)$$

It can be seen that the concentration of species c_1 decreases linearly with x, as in simple diffusion, but with a 'diffusion coefficient'

$$D^1 = \frac{D(P+D/K)}{P_2} \sim \frac{DP}{P_2} .$$

When the diffusion coefficients of the two gases are not equal, we still have

$$p = P - \frac{\alpha_1 Rx}{PK} , \qquad (16)$$

but the maximum removal rate is given by

$$R_m = \frac{PD_2}{\alpha_1 L} \log (P/P_2) , \qquad (17)$$

and the ratio of the maximum removal rate to that due to diffusion alone is

$$\frac{R_m}{R_m^D} = \frac{PD_2}{P_1 D_1} \log (P/P_2) .$$

The expression analogous to equation 15 is

$$c_1 = c_1^o - \frac{Rx}{D_1} \frac{P_2}{(P_2+P_1 D_2/D_1)} .$$

5. INTERPRETATION

We can interpret the situation physically by appreciating that gas flow is a much faster process than gas diffusion. When one gas is preferentially removed at one face of the slab, the pressure drops and gas flows into the slab at the input face. The concentration of the second gas rises at x = L, since it cannot flow past this point. The ensuing increase in concentration will result in backward diffusion of this second gas. But since, under steady state conditions, there is no net mass flow of the second gas, backward diffusion must exactly balance the mass flow of this gas into the slab at $x = 0$. This is expressed mathematically by equation 7. Since diffusion processes are much slower than gas flow processes, only a small gas velocity, and hence a correspondingly low pressure drop, is required to ensure mass balance of the two processes. To first order, the pressure drop is zero; the pressure is everywhere the same in the system, and the physical process is one of diffusion of gas 1 in a gas mixture which can become pure gas 2 at $x = L$ if the removal rate of gas 1 is sufficiently high.

With this picture in mind, we should be able to deduce the maximum removal rate R_m. With a gas velocity $v = \alpha_1 R/P$ in the system (from equation 16), the input of gas 2 at $x = 0$ is $\alpha_1 R c_2^o/P$. The concentration gradient for gas 2 is $\left(\frac{P}{\alpha_2} - \frac{P_2}{\alpha_2}\right)/L$ so that the mass flowrate of this gas from $x = L$ to $x = 0$, due to diffusion, is $D_2 P_1/(\alpha_2 L)$. Balancing these two rates gives

$$R_m = \frac{D_2 P}{\alpha_1 L} \cdot \frac{P_1}{P_2}$$

which is the same as equation 16 if P_1/P_2 is assumed less than one.

6. CONCLUSIONS

It is clear from the above analysis that when, say gas 1, of a two-gas mixture is preferentially removed from one face of a permeable slab which has constant pressure maintained at the opposite face, the maximum rate of removal, under steady state conditions, is dictated by the rate at which gas 2 diffuses through the material of the slab. However, this removal rate is enhanced to some extent by gas flow due to the very small pressure difference set up by removal of gas at one face. The increase in the maximum rate compared to that expected from straight diffusion is

$$\frac{PD_2}{P_1 D_1} \log\ (P/P_2) \quad ,$$

where P is the total pressure, P_1 and P_2 are the partial pressures of the two species at the input face and D_1, D_2 are the respective diffusion coefficients.

In the case of interest, where oxygen is the gas removed and air the supply gas, the diffusion coefficients can be assumed equal. The ratio of the maximum removal rates then becomes

$$R_m/R_m^D = P/P_2 = 1.2 \quad ,$$

and the concentration of oxygen falls off with x approximately as

$$c_1 = c_1^o - \frac{Rx}{D} \cdot \frac{P_2}{P_1} \quad .$$

This is the same functional form as diffusion alone, but with a diffusion coefficient enhanced by 20 per cent. At the maximum removal rate the pressure at the face where oxygen is being removed is reduced with respect to that at the input face by the factor

$$\left[1 - \frac{D}{PK} \log (P/P_2)\right]$$

where $\frac{D}{PK} \log (P/P_2) \lesssim 10^{-4}$.

Hence, in this case, it is certainly reasonable to describe the process as a diffusion process at constant pressure, but with a diffusion coefficient increased by 20 per cent.

7. ACKNOWLEDGEMENT

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