Dependence of adsorption/diffusion processes in porous media on bulk and surface permeabilities

B. ALBERS

Weierstrass Institute,
for Applied Analysis and Stochastics,
Mohrenstrasse 39,D-10117 Berlin,
e-mail : albers@wias-berlin.de

THE PAPER CONTAINS a macroscopic continuum model for adsorption in porous materials (B. ALBERS [1, 2]) which is an extension of the model for porous bodies by K. WILMAŃSKI [7] on mass exchange processes. We consider the flow of a fluid/adsorbate mixture through channels of a solid component. The fluid serves as carrier for an adsorbate whose mass balance equation contains a source term. Due to low adsorbate concentration we deal with a physical adsorption process which means that particles of the adsorbate stick to the skeleton due to weak van der Waals forces. The model contains two different permeability parameters whose nature is completely different: The first one, the usual bulk permeability coefficient, describes the resistance of the skeleton to the flow of the fluid/adsorbate mixture. The second one describes the surface resistance to the outflow of the mixture from the solid. This work shows within a simple example the range of these parameters and the dependence of adsorption/diffusion on them.

1. Introduction

IN THIS PAPER we present a parameter analysis within a continuum mechanical approach on adsorption/diffusion processes in three component porous media. The considered model and possible practical applications have extensively been shown in ALBERS [2, 1]. We consider the flow of a fluid through channels of the skeleton. The latter serves as a carrier for an adsorbate whose mass balance contains a source term. This term consists of two parts: one of them extends Langmuirs theory about possible places for the adsorbate to settle down on the internal surface to non-equilibrium processes. The other one takes into account changes of the internal surface and couples them with the source of porosity which is a part of a balance equation for the scalar field of porosity (see: WILMAŃSKI [8]).

1.1. Type of adsorption process considered

We consider physical adsorption processes. This means that particles of the adsorbate stick to the skeleton due to weak van der Waals forces. The type of mass exchange between fluid and skeleton (adsorption, chemisorption, capillary effects) mainly depends on two factors namely the particle size of the solid and the concentration of the adsorbate in the fluid.

For our model we consider very low adsorbate concentration. This entitles us to use the LANGMUIR theory of adsorption (see: [7]). It is based on the concept of the number of bare and occupied sites on the surface of a solid. Langmuir assumed that the adsorbate particles settle down on the solid in one single layer, and that there is – depending on the energy landscape of the surface – a certain number of places where they are able to settle down.[1]

Obviously this is only possible if the adsorbate concentration is small. Otherwise the Langmuir isotherm of occupied sites reaches saturation. In the past many modifications of this theory appeared. One of them is the BET-model (see: [4]) which is based on the Langmuir theory but allows multilayer adsorption. This means that particles are also able to stick to already adsorbed particles and therefore there can appear several layers of adsorbate particles. For our purpose there is no need to use this more complicated version of the Langmuir model because we assume low concentrations. In addition it should be mentioned that there are some doubts concerning the description of multilayer adsorption (e.g. interaction of adsorbate particles of different layers).

One of the important factors for the shape of the adsorption isotherm is the size of solid particles in relation to the pore size between them. According to GREGG/SING [5] there occur six types of adsorption isotherms. The three most important of them are shown in the figure below.

The first one a) is the graph of the common monolayer Langmuir isotherm. In principle it describes the adsorption of particles on plane surfaces. But it also holds in our case considering the porous material to be a soil. The pore size of

---

[1]The assumption of a monolayer adsorption is related to the way in which particles of the adsorbate interact with the internal surface. In the case of crystalline solids the energy landscape of the internal surface is periodic, i.e. energetic isolines form a 2D family of closed lines which define spots of the highest interactions. This yields the concept of occupied and bare sites introduced by Langmuir. As a consequence we obtain a formula for the mass source which is used in this work. The assumption on the monolayer structure of adsorption yields the necessity of the assumption on small concentration of the adsorbate. In contrast to the above described mechanism a multilayer adsorption occurs when particles of the adsorbate in the fluid phase interact with particles of the adsorbate which have already settled down on the internal surface. Such an interaction is isotropic, i.e. one cannot introduce the notion of bare sides and, even if applicable, the formula for mass sources used in this paper would have to admit a discontinuous change of material parameters which is not the case. A detailed description of such adsorption processes can be found in GREGG/SING [5].
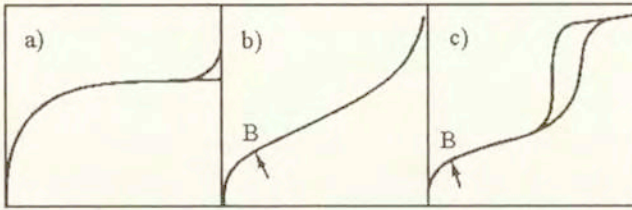
Fig. 1. Three most important types of adsorption isotherms (adsorbed amount vs. relative partial pressure)

this soil is big enough for the curvature of the pores not to play any important role. This is different in the case of isotherm c). This form of isotherm arises in case of the so-called mesopores (20-500 Å in diameter). Both b) and c) describe multilayer adsorption processes which is indicated by the existence of the inflection point B. Before reaching this point the monolayer process runs according the Langmuir isotherm i.e. adsorption is restricted to a thin layer on the walls. After that b) and c) show different behaviour. Although in both cases the slope increases, in b) the rise first is approximately linear and then rather rapid for higher relative pressures while in c) the amount adsorbed possesses another inflection point before the saturation vapour pressure is reached. A characteristic feature of c) is its hysteresis loop. This is due to the capillary condensation in the finest pores.

Summing up the investigated model is intended to describe physical adsorption with low concentrated adsorbate on a porous medium with relatively large pores. Then the Langmuir isotherm looks as shown in a) which is restricted to monolayer adsorption.

1.2. Intention of the work

The intention of this work is to show the dependence of the fields and the adsorption rate on model parameters. The two most important of them are the permeability coefficient π and the surface permeability α. These two permeability parameters possess a completely different nature. The first one is an element of the field equations and reflects properties of the material. It has been shown in [1] that the two component continuum model can be simplified to the so-called reaction-diffusion models widespread among mathematicians (for example KNABNER [6]) if one entirely neglects the motion of the skeleton, and the acceleration of the fluid. From two momentum balance equations there remains solely the Darcy law. If we do so we see that the permeability parameter π of the two component model is related to a coefficient of the Darcy law which contains

the true viscosity of the fluid. This implies the importance of the permeability parameter: it describes the resistance of the skeleton to the flow of the fluid as well as the true viscosity of the fluid.

In this work we study the parameters within a one-dimensional example. In this case the permeability parameter is a constant scalar. But for multidimensional investigations it is conceivable that it could be tensorial.

The other permeability coefficient, the surface resistance α, enters the model due to the boundary conditions of third type and, consequently, accounts for properties of the surface. Boundary conditions for porous media are strongly related to flow conditions in the vicinity of the boundary. Generally there arises a boundary layer: a thin layer where friction forces play an important role because the fluid sticks to the body. But especially for dull bodies this boundary layer can come off the body if the pressure in flow direction increases rapidly which means that there arise whirls if the fluid arives at the end of the body. That is what happens if the body enters the surface of the porous media and flows through and against the channels of the skeleton. The parameter α is the leading quantity for the fluid velocity. Therefore we show at the end a very important feature, namely a maximum in the dependence of the adsorption rate on diffusion.

2. Adsorption/diffusion model

We consider a process in a three component porous medium. A fluid-adsorbate mixture flows through channels of a porous medium. Particles of adsorbate settle down on the internal surface of the skeleton.

2.1. Mass balances (in terms of mass densities)

Then the mass balance equations have the form

$$(2.1) \quad \begin{aligned} \frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) &= -\hat{\rho}^A, \\ \frac{\partial \rho^F}{\partial t} + \operatorname{div}\left(\rho^F \mathbf{v}^F\right) &= 0, \\ \frac{\partial \rho^A}{\partial t} + \operatorname{div}\left(\rho^A \mathbf{v}^F\right) &= \hat{\rho}^A, \end{aligned}$$

where ρ^S, ρ^F and ρ^A are the mass densities of the components, $\mathbf{v}^F$ is the common velocity of fluid and adsorbate before the adsorbate settles down and its velocity changes to that of the skeleton $\mathbf{v}^S$. $\hat{\rho}^A$ denotes the intensity of the mass source. Of course, it appears with opposite signs in the balances for skeleton and adsorbate, as the total conservation of mass must be fulfilled.

2.2. Mass source

This mass transfer rate from the liquid to the solid phase per unit time is given by the relation

$$(2.2) \qquad \hat{\rho}^A = -\frac{m^A}{V}\frac{d\left(\xi\,f_{\text{int}}\right)}{dt} = -\frac{m^A}{V}\left(f_{\text{int}}\frac{d\xi}{dt} + \xi\frac{d\,f_{\text{int}}}{dt}\right),$$

whose derivation is based on the classical LANGMUIR adsorption theory about *occupied* (ξ) and *bare* $(1 - \xi)$ *sites* (see [7]) where the existence of possible places for adsorption on a surface is mainly explained by the landscape of the interaction energy with their quasiperiodic distribution of maxima for crystalline skeletons). Another important factor for the extent of adsorption is the *internal surface area* of the solid f_{int}. V is the representative elementary volume *REV* which is small in comparison with the volume of the whole flow regime but big against volumes of single pores of the skeleton. The mass of adsorbate per unit of the internal surface area is denoted by m_A.

The first contribution on the right-hand side of (2.2) describes the change of the fraction of occupied sites. It is specified by the Langmuir evolution equation

$$(2.3) \qquad \frac{d\xi}{dt} = a\left(1 - \xi\right)p^A - b\xi e^{-\frac{E_b}{kT}},$$

where p^A is the partial pressure of the adsorbate in the fluid phase and a and b are material parameters. The energy barrier E_b for particles adsorbed on the skeleton is assumed to be constant. Furthermore k denotes the Boltzmann constant and T is the absolute temperature. The right hand side of (2.3) again consists of two terms: the adsorption rate (first term) and the desorption rate (second term). In full phase equilibrium they are equal so that the time change of occupied sites is equal to zero. In this case we get from (2.3) the well-known *Langmuir isotherm* of occupied sites

$$(2.4) \qquad \xi_L = \frac{\frac{p^A}{p_0}}{1 + \frac{p^A}{p_0}}, \quad \text{with} \quad p_0 := \frac{b}{a}e^{-\frac{E_b}{kT}}.$$

The other part of (2.2) describes the change of the internal surface. We assume that this change is coupled with relaxation of the porosity n, which is described by the balance equation of porosity. Motivated by elementary considerations about changes of the internal surface and of the porosity in a porous medium yielding film adsorption we assume [2]

---

[2] As an example let us consider a porous body with spherical holes connected with each other by negligibly small channels (one of the holes is shown in the picture). A film adsorption process

(2.5)
$$\frac{1}{f_{\text{int}}}\frac{d f_{\text{int}}}{dt} \propto \frac{\hat{n}}{n}.$$

Finally we arrive at

(2.6)
$$\hat{\rho}^A = -\rho_{ad}^A \left\{ \left[(1-\xi)\frac{cp^L}{p_0} - \xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau}\Delta \right\},$$

where τ_{ad} denotes the characteristic time of adsorption, p_0 is a reference pressure of adsorption defined in (2.4), ν is a proportionality factor and $\rho_{ad}^A := \frac{m^A f_{\text{int}}}{V}$.

2.3. Mass balances (in terms of concentration)

It is common to use a form of mass balances containing quantities related to the concentration c:

(2.7)
$$\frac{\partial \rho^S}{\partial t} + \operatorname{div}\left(\rho^S \mathbf{v}^S\right) = -\rho^L \hat{c},$$
$$\frac{\partial \rho^L}{\partial t} + \operatorname{div}\left(\rho^L \mathbf{v}^F\right) = \rho^L \hat{c},$$
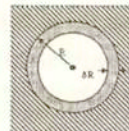$$\frac{\partial c}{\partial t} + \mathbf{v}^F \cdot \operatorname{grad} c = (1-c)\,\hat{c}.$$

For the transformation we have used the following definitions

(2.8)
$$\rho^L := \rho^F + \rho^A, \qquad c := \frac{\rho^A}{\rho^L}, \qquad \hat{c} := \frac{\hat{\rho}^A}{\rho^L},$$

where ρ^L denotes the mass density of liquid phases, c is the concentration and $\hat{c}$ is the concentration source.

---

takes place if the adsorbate settles down on the internal surface in an almost homogeneous manner. This yields small changes of the radius R of the pores, say δR. If N is the number of holes in REV then the total volume of holes V^F and the internal surface f_{int} in REV are satisfying the relations

$$V^F = N \cdot \frac{4}{3}\pi R^3, \quad \delta V^F = N \cdot 4\pi R^2 \delta R \;\Rightarrow\; \frac{\delta n}{n} = 3\frac{\delta R}{R}$$
$$f_{\text{int}} = N \cdot 4\pi R^2, \quad \delta f_{\text{int}} = N \cdot 8\pi R \delta R \;\Rightarrow\; \frac{\delta f_{\text{int}}}{f_{\text{int}}} = 2\frac{\delta R}{R}$$
$$\Rightarrow \frac{\delta n}{n} \propto \frac{\delta f_{\text{int}}}{f_{\text{int}}}.$$

2.4. Momentum balances

We want to account for the deformations of the skeleton which means that we also need momentum balance equations to describe the problem. Due to the common velocity of fluid and adsorbate we are left with two of them

$$(2.9) \qquad \frac{\partial \rho^S \mathbf{v}^S}{\partial t} + \mathrm{div}\left(\rho^S \mathbf{v}^S \otimes \mathbf{v}^S - \mathbf{T}^S\right) = \hat{\mathbf{p}}^S,$$

$$\frac{\partial \rho^L \mathbf{v}^F}{\partial t} + \mathrm{div}\left(\rho^L \mathbf{v}^F \otimes \mathbf{v}^F + \mathrm{p}^L \mathbf{1}\right) = \hat{\mathbf{p}}^F,$$

where the partial pressure in the liquid phase p^L (i.e. in the fluid and adsorbate phases together) is the sum of the partial pressures in the fluid p^F, and in the adsorbate p^A. For small adsorbate concentration as assumed in our case we expect according to Dalton's law that $p^A \cong cp^L$. Furthermore $\mathbf{T}^S$ denotes the partial Cauchy stress tensor in the skeleton, and $\hat{\mathbf{p}}^F = -\pi\left(\mathbf{v}^F - \mathbf{v}^S\right) + \rho^L \hat{c}\mathbf{v}^F$ is the momentum source in the liquid and $\hat{\mathbf{p}}^S = \pi\left(\mathbf{v}^F - \mathbf{v}^S\right) - \rho^L \hat{c}\mathbf{v}^S$ is the momentum source in the skeleton where π denotes the permeability coefficient of the whole system. [3]

2.5. Porosity balance

According to the works of K. WILMAŃSKI (see e.g. [7]) we have an additional balance equation for the scalar field of porosity

$$(2.10) \qquad \frac{\partial n}{\partial t} + \mathbf{v}^S \cdot \mathrm{grad}\, n + n_E \, \mathrm{div}\left(\mathbf{v}^F - \mathbf{v}^S\right) = \hat{n} = -\frac{\Delta}{\tau}.$$

Here $\Delta = n - n_E$ is the deviation of the porosity n from its equilibrium value n_E and τ is the *relaxation time of porosity*. The above shape of the source of porosity $\hat{n}$ is based on assumptions on small deviations from thermodynamic equilibrium. In this work we consider a linear model in which $n_E = \mathrm{const}$.

3. One-dimensional example

We are interested in the influence of the two permeability coefficients π and α on the flow of a fluid-adsorbate mixture through soils. Therefore we solve the following one-dimensional example:

---

[3] This form of the momentum sources follows in a thermodynamically linear approach from the principle of material objectivity together with the bulk conservation laws which yield

$$\hat{\mathbf{p}}^S + \hat{\mathbf{p}}^L = 0 \text{ and } \hat{\rho}^L + \hat{\rho}^S = 0.$$

In the typical situation which we consider in this paper the form of the momentum sources can be simplified if we compare the order of magnitude of terms: $\pi \approx 10^9 \frac{\mathrm{kg}}{\mathrm{m}^3 \mathrm{s}}$ and $\hat{\rho}^L = \rho^L \hat{c} \approx 230 \frac{\mathrm{kg}}{\mathrm{m}^3} \cdot 10^{-5} \frac{1}{\mathrm{s}} = 2.3 \cdot 10^{-3} \frac{\mathrm{kg}}{\mathrm{m}^3 \mathrm{s}}$, i.e. we can neglect the influence of mass sources.
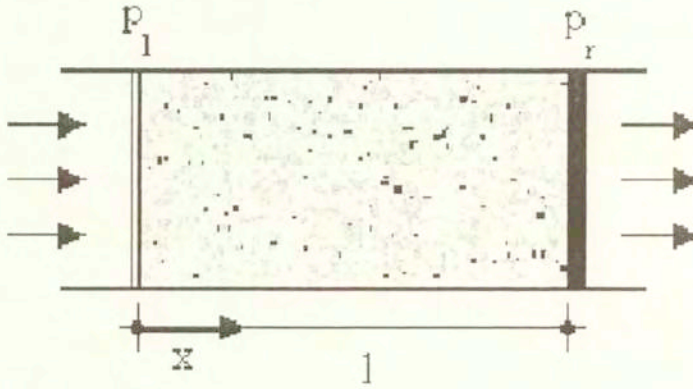
FIG. 2. Flow through porous body

Due to a difference of the external pressure, with p_l at $x = 0$ being larger than p_r at $x = l$ (see: Fig. 2), the mixture flows along the direction x through the porous body. The low concentrated adsorbate is carried by the fluid and has therefore the same velocity v^F. Then the isothermal process is described by the fields

$$(3.1) \qquad \left\{ \rho^S, \rho^L, c, v^F, v^S, e^S, \Delta, \xi, f_{\text{int}} \right\},$$

where the last three unknowns are the above introduced additional microstructural fields describing changes of porosity and mass exchange processes.

For simplification we make the following assumptions:

- the skeleton does not move, i.e. $v^S \equiv 0$,
- the inertia forces are small i.e. the acceleration terms in the momentum balances can be neglected,
- small changes in time of the velocity gradient, i.e. the porosity balance reduces to the algebraic relation $\Delta \simeq -n_E \tau \frac{\partial v^F}{\partial x}$.

The third assumption follows from the fact that the relaxation time of porosity τ is very small. In the formal solution of the balance equation of porosity

$$\frac{\partial \Delta}{\partial t} + \frac{\Delta}{\tau} = -n_E \frac{\partial v^F}{\partial x} \Rightarrow \Delta$$

$$(3.2)$$
$$= -n_E \int_0^t \frac{\partial v^F}{\partial x}(\eta) \, e^{-\frac{t-\eta}{\tau}} \, d\eta \simeq -n_E \frac{\partial v^F}{\partial x}(t) \int_0^t e^{-\frac{t-\eta}{\tau}} \, d\eta = -n_E \tau \frac{\partial v^F}{\partial x},$$

we have assumed that the characteristic macroscopic time t is much larger than τ.

3.1. Governing set of equations and constitutive relations

Under these assumptions the balance equations for the example have the following form

$$\frac{\partial \rho^L}{\partial t} + \frac{\partial \rho^L v^F}{\partial x} = -\rho_{ad}^A \left\{ \left[\frac{cp^L}{p_0} - \left(1 + \frac{cp^L}{p_0}\right)\xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau} \Delta \right\},$$

$$(3.3) \quad \frac{\partial c}{\partial t} + v^F \frac{\partial c}{\partial x} = -(1 - c) \frac{\rho_{ad}^A}{\rho^L} \left\{ \left[\frac{cp^L}{p_0} - \left(1 + \frac{cp^L}{p_0}\right)\xi \right] \frac{1}{\tau_{ad}} - \xi \frac{\nu}{\tau} \Delta \right\},$$

$$\frac{\partial p^L}{\partial x} + \pi v^F = 0, \qquad n_E \frac{\partial v^F}{\partial x} = -\frac{\Delta}{\tau}, \qquad \frac{\partial \xi}{\partial t} = \left[(1 - \xi) \frac{cp^L}{p_0} - \xi \right] \frac{1}{\tau_{ad}}.$$

The constitutive relation for the pressure in the liquid phase p^L is assumed to be linear

$$(3.4) \qquad p^L = p_0^L + \kappa \left(\rho^L - \rho_0^L \right) + \beta \Delta,$$

where p_0^L and ρ_0^L are initial values of the pressure and the mass density for the liquid phase. κ denotes the constant compressibility coefficient and β is a constant material coupling parameter.

3.2. Boundary conditions

The boundary conditions are assumed to be of third type. They express the flow through the boundary of the body in dependence on the difference of the partial pressure in the liquid and the part of the external pressure which acts on the fluid, as well as on the permeability α of the surface. The latter is one of the permeability coefficients whose influence we want to determine furtheron. Hence

$$(3.5) \qquad \begin{aligned} x &= 0: & -\rho^L v^F &= \alpha \left(p^L - np_l \right), \\ x &= l: & \rho^L v^F &= \alpha \left(p^L - np_r \right). \end{aligned}$$

3.3. Solution method

We use a regular perturbation method to find an approximate solution of the problem. We make the following linear ansatz

$$(3.6) \qquad \begin{aligned} \rho^L &= \rho_0^L + \varepsilon \rho_1^L, & v^F &= \varepsilon v_1^F, & \Delta &= \varepsilon \Delta_1, \\ c &= c_0 + \varepsilon c_1, & \xi &= \xi_L + \varepsilon \xi_1, & \varepsilon &= \frac{p_l - p_r}{p_r}, \end{aligned}$$

where ρ_0^L, c_0 and ξ_L are the initial values of the corresponding fields. Initial values of fluid/adsorbate velocity and the change of porosity are zero. The expansions which depend on a small parameter ε are truncated after first order contributions. The definition of ε is based on the assumption that the pressure difference between the left and the right boundary is small.

We use Laplace transforms to find an analytical solution of the linear problem and to get numerical solutions for the inverse Laplace transform we use a FORTRAN-solver. For a detailed illustration of the solution and a discussion of the results for the fields see [1], [2].

3.4. Parameters

To illustrate the above presented example and to study the permeability parameters we choose the following values

Length of the body l	1m	Coupling constant β	1GPa
Initial mass density ρ_0^L	$2.3 \cdot 10^2 \; \frac{\text{kg}}{\text{m}^3}$	Equilibrium porosity n_E	0.23
Initial concentration c_0	10^{-3}	Initial pressure p_0^L	23 kPa
Langmuir pressure p_0	10 kPa	Pressure on right h.s. p_r	100 kPa
Proportionality factor ν	10	Compressibility κ	$2.25 \cdot 10^6 \; \frac{\text{m}^2}{\text{s}^2}$
Permeability of solid π	$10^9 \; \frac{\text{kg}}{\text{m}^3\text{s}}$	Permeability of surface α	$4 \cdot 10^{-8} \; \frac{\text{s}}{\text{m}}$
Relaxation time τ	10^{-3} s	Charact. time of adsorp. τ_{ad}	1 s
Fraction of occupied		mass density of adsorbate	
sites in equilibrium ξ_L	$2.3 \cdot 10^{-2}$	on internal surface ρ_{ad}^A	$40 \; \frac{\text{kg}}{\text{m}^3}$

Mass density and porosity have been chosen to have typical values for rocks and soils. The values for material parameters β and τ have been chosen on the basis of estimates of the attenuation of acoustic waves. The influence of permeability is expressed by two constants π and α. The first one describes the resistance of the skeleton to the flow of the fluid/adsorbate mixture. The second one describes the surface resistance to the outflow of the mixture from the solid. Its appearance is connected with a boundary layer between the porous body and the external world.

4. Parameter analysis

In this section we investigate the influence of several model parameters on the behavior of the fields and the adsorption rate (negative value of the source of concentration).

Special attention is paid to permeability coefficients π and α. Physically they describe the resistance of the skeleton to the flow of fluid but they arise from different microstructural properties of the system. While π represents the resis-

tance of the skeleton against theflow of the liquid in the inner part of the porous body, α describes the surface resistance against in- and outflow of the liquid into and out of the body. The latter parameter is coupled with the appearance of a boundary layer in the transition zone between the porous body and the external world (see [2]).

First we consider the influence of the bulk permeability parameter π. Some results connected to variations of this parameter are already shown in earlier works without mass exchange [3], [2]. There we have studied the radial flow through a cylinder under small and large deformations.

The role played by this coefficient in the present case is illustrated in the figures bellow (Fig. 3) where the fields (11) of our example are shown in dependence on π for three different times (at the beginning, $\frac{t}{\tau_{ad}} = 1$, curve 1 in the Figures, at an intermediate instance, $\frac{t}{\tau_{ad}} = 5$, curve 2, and for the large time lapse of the process, $\frac{t}{\tau_{ad}} = 10$, curve 3). For π we have chosen values between 10^8 and 10^{10} $\frac{kg}{m^3 s}$. The value $\pi = 10^9$ $\frac{kg}{m^3 s}$ used in former works lies in the middle of this region. A further reduction of π beneath $10^8 \frac{kg}{m^3 s}$, i.e. for a more permeable material, the relative velocity becomes so big that the mass exchange cannot appear, and, consequently, all fields become independent of the bulk permeability. On the other hand, for values bigger than 10^{10} $\frac{kg}{m^3 s}$ the numerical inverse Laplace transformation cannot be performed by the code used in this work (huge exponents). In this part of the analysis we use, as in the earlier works, the value of the surface permeabiltity parameter $\alpha = 4 \cdot 10^{-8}$ $\frac{s}{m}$.

As we see in Fig. 3 (the upper left diagram) the change of the mass density of the liquid increases with decreasing permeability parameter π (i.e. with increasing permeability of the material) at any instant of time. However for advanced times this change is much better pronounced. The velocity of the liquid increases with decreasing permeability coefficient (the upper right diagram). Essential changes of the velocity appear solely in the middle region of the permeability coefficient. These changes are nonmonotonous in time (there exists a local minimum!). This is different in the case of changes of porosity (the middle left diagram). Changes of porosity have a similar time dependence for different permeabilities with a rapid growth in an initial time interval, and a subsequent decay for large times. The value of the maximum change of porosity appearing between these two regions is decaying with growing permeability coefficient with a simultaneous shift to larger times. In the Figure we can see solely a projection of this behavior for a chosen interval of time. Obviously for small permeabilities we observe already a large time behavior (a monotonous decay from curve 1 to curve 3) while for large permeabilities we see still the behavior in the initial interval of time (a monotonous growth from curve 1 to curve 3). The absolute values of changes of the adsorbate concentration in the fluid (the middle right
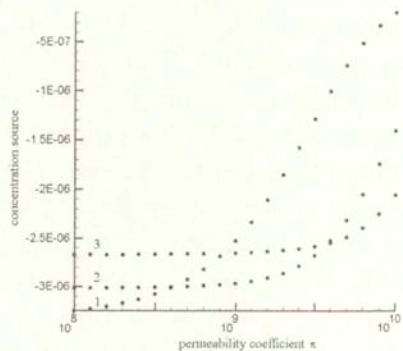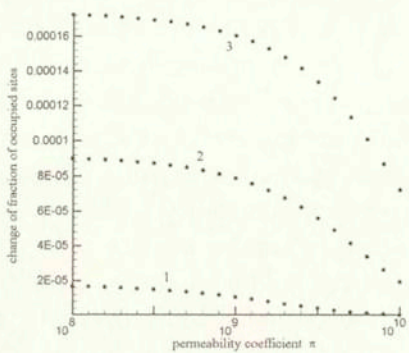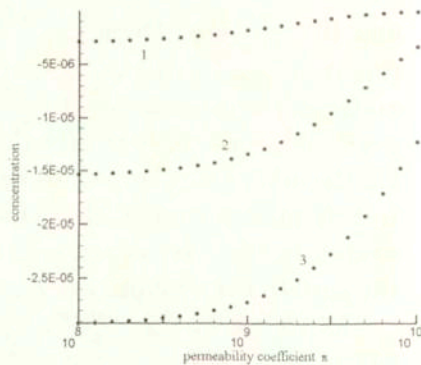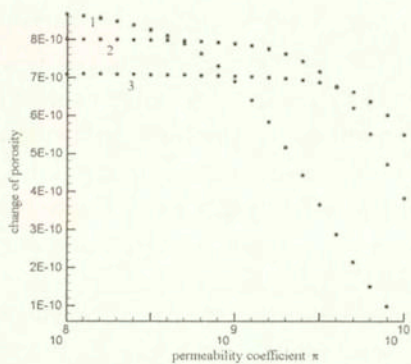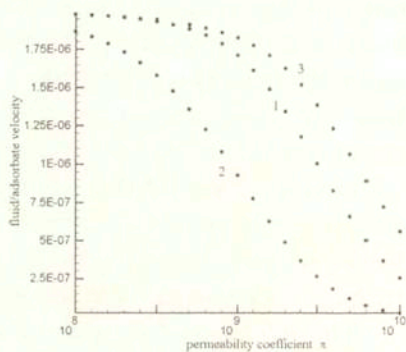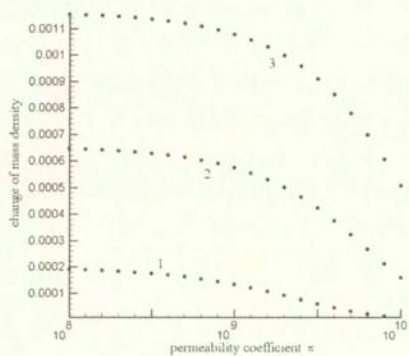
FIG. 3. Influence of the permeability parameter π on several fields and the concentration source.
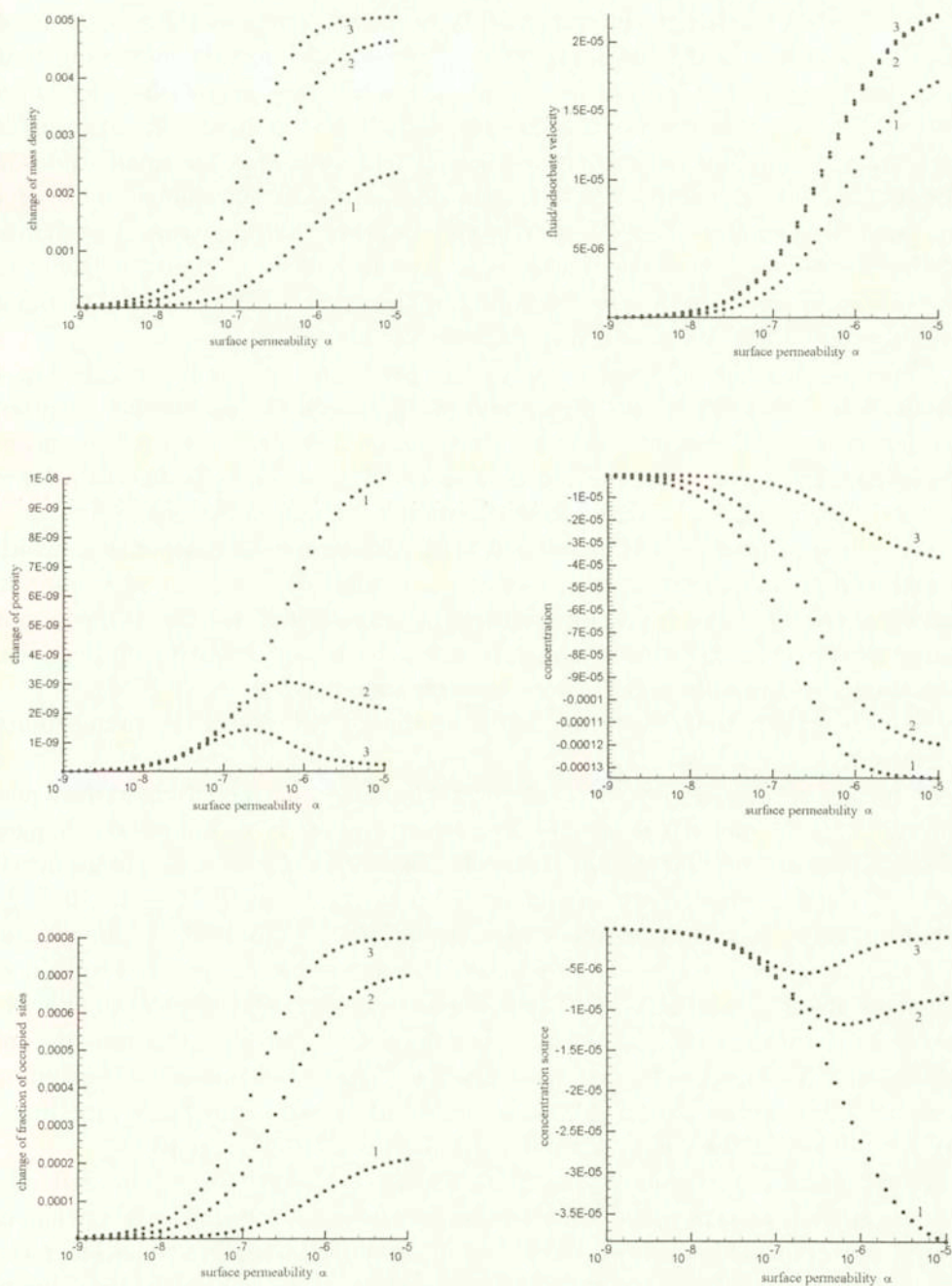
FIG. 4. Influence of the permeability parameter α on several fields and the concentration source.

http://rcin.org.pl

diagram) react on changes in permeability in the same way as these of the mass density of liquid: at the beginning changes are small but with increasing time they become larger. Changes for larger values of π are higher than for small ones. The change of the fraction of occupied sites (the lower left diagram) is coupled with the change of concentration. This means that for small values of the permeability the fraction of occupied sites also does not change much. But in time it decreases in the same way as the concentration increases. The change of the rate of adsorption (the lower right diagram) shows a similar behavior to the change of porosity. At the beginning of the process the permeability has a big influence. Later the rate changes mainly for big values of π.

Now we show the influence of the surface permeability parameter α. In Fig. 4 again changes of fields $\rho^L, v^F, \Delta, c, \xi$ and of the concentration source $\hat{c}$ are given for the same three instants of time which we used before, this time, however, depending on α with values in the interval $10^{-9}\ \frac{s}{m}$ to $10^{-5}\ \frac{s}{m}$. The value $\alpha = 4 \cdot 10^{-8}\ \frac{s}{m}$ which has been used in earlier works lies within this interval.

It follows from Fig. 4 that outside of the above mentioned region – which means towards the limiting values of α – the fields do not react any more on changes of α. The limit $\alpha = 0$ means that the boundary of the porous medium is impermeable. $\alpha \to \infty$ yields a behavior similar to composites with a proportional (constant) load distribution between the components.

For the calculations we have used the value of $10^9\ \frac{kg}{m^3s}$ of the permeability coefficient π.

Changes of the mass density of the liquid increase with increasing surface permeability (the upper left diagram). The sensitivity of these changes on changes of α is different in different time intervals. Namely, in our example, in an initial interval these changes react on changes of α in the range $10^{-8}\ \frac{s}{m}$ to $10^{-5}\ \frac{s}{m}$, while in later intervals it reduces to a region $10^{-8}\ \frac{s}{m}$ to $10^{-6}\ \frac{s}{m}$. Simultaneously changes become considerably bigger in these reduced regions of influence. Changes of velocity of the liquid (the upper right diagram) show a similar behavior to changes of the mass density but differences for different times are not so strongly developed as for the mass density. They are smaller at the beginning than for later times, and they become nearly identical in this large time limit. Also for this field the region of influence is between $10^{-8}\frac{s}{m}$ and $10^{-5}\frac{s}{m}$.

Changes of porosity have a very interesting behavior (the middle left diagram). For any instant of time there exists a value of α for which the change of porosity as a function of α reaches a maximum. With increasing time this maximum shifts to smaller values of α, and its value decreases. The absolute value of changes of concentration (the middle right diagram) behaves in similar manner to changes of the mass density. At the beginning of the process the surface permeability has much bigger influence on changes of concentration than for larger times. Simultaneously for each time the change of concentration as a function

of α decreases. The change of fraction of occupied sites (the lower left diagram) also changes similar to the mass density. It increases with increasing surface permeability. In a small region of influence changes are very rapid. The behavior of the source of concentration (the lower right diagram) is similar to changes of porosity. Also for this quantity there arises an extremum. At the beginning of the process changes are much bigger than for larger times.

Another important parameter of the model is the equilibrium value of porosity n_E. Its role in the model is still not fully understood. For instance, in [3] we had mentioned that for the nonlinear example without mass exchange arose problems with values of $n_E \gtrsim 0.6$. For higher values of porosity the deformations exceeded 100%, and most likely the mechanical behavior of the model should be unstable. We know as well that in many processes of practical bearing the equilibrium porosity cannot be assumed to be constant but it should rather fulfil a constitutive relation of its own. It is easy to check that such models must be nonlinear.

These questions do not arise in the present model with adsorption. The reason is that we consider linear deviations from an initial state, and, consequently, small deformations, and a linear dependence on n_E in constitutive quantities. The initial porosity itself is a constant material parameter rather than a constitutive quantity. Therefore we can admit a bigger range of n_E ($0.1 \leq n_E \leq 0.9$). Certainly solutions for fields may depend parametrically on the initial porosity in a nonlinear manner. In our model all fields but one are linear with respect to n_E. This is the field of velocity v^F. Also the source of concentration depends in a nonlinear way on n_E. We have:
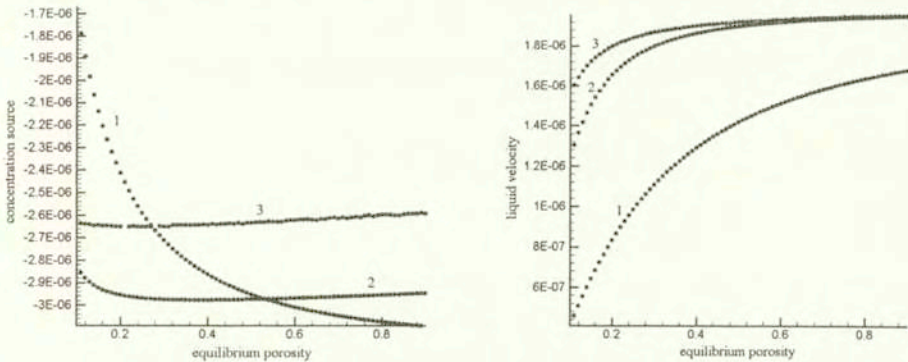

FIG. 5. Influence of the equilibrium porosity n_E on several fields and the concentration source.

The liquid velocity is, of course, zero for $n_E = 0$. For porosities in the range $0 \lesssim n_E \lesssim 0.5$ it increases rapidly with increasing porosity. The source of concen-

tration as a function of time jumps at the initial interval of time to high values
for small initial porosities, and subsequently relaxes towards a constant value. A
similar behavior with a smaller initial jump is visible also for bigger equilibrium
porosities, but the behavior is not monotonous. For high porosities the jump
does not appear at all.

The model contains another new parameter, namely the coupling parameter
β. In problems of wave propagation it has high influence (see e.g. K. WILMAŃSKI
[9]). Therefore it was very interesting to see that this coefficient did not have
any influence in these adsorption problems.

5. Coupling of adsorption and diffusion

The most important result of the adsorption model is the form of coupling of
adsorption and diffusion. It is shown how the amount adsorbed (absolute value of
the concentration source) depends on the relative velocity of the components. In
Fig. 6 the source of concentration over the fluid/adsorbate velocity is shown. Due
to the assumption that the skeleton does not move the fluid/adsorbat velocity in
our case stands for the relative velocity of the components. As follows from the
boundary conditions this quantity is mainly driven by the surface permeability
parameter α. According to (3.5) holds at the boundary

$$(5.1) \qquad\qquad v^F = \mp \frac{\alpha \left(p^L - n p_{l/r} \right)}{\rho^L}.$$

This yields solutions for the fluid/adsorbate velocity dependent parametri-
cally on α [1]. Therefore for calculation of the source of concentration in de-
pendence on the velocity we choose the permeability coefficient α as a control
parameter. This is done for $x = 0.5$ m, i.e. in the middle of the region.

According to the initial conditions the source starts with thevalue zero for
both $(v^F - v^S, t = 0)$, and $(v^F - v^S = 0, t)$. Of course, the source of concen-
tration is a negative value because the adsorbate sticks to the skeleton and the
concentration in the liquid becomes lower than the initial value. The results
shown in Fig. 6 are twofold: firstly one can see the characteristic time behavior
of the intensity of adsorption. The concentration source decreases after a jump at
the beginning of the process until it reaches a value of approximately $-3.5 \cdot 10^{-5}$.
The duration of the initial jump is not clearly visible in this Figure but probably
it is of the order of the relaxation time of porosity τ of 10^{-3} s (see: Sec. 3, Table
with material parameters). We recall that the source of concentration consists
of two contributions: the Langmuir part, and the change of the internal surface
due to changes of porosity. After the initial jump (the influence of the second
contribution) values increase – first rapidly and then more and more slowly (the
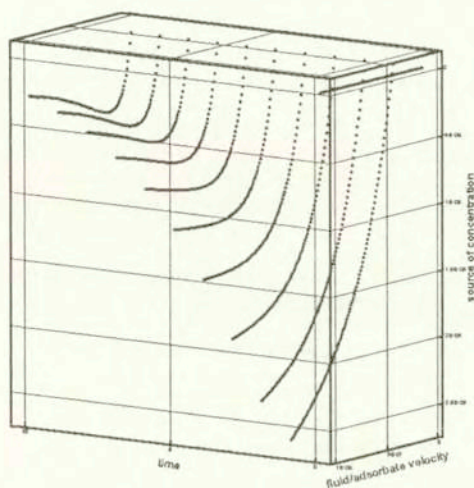first contribution) – until they reach an asymptotic value of nearly $-1.5 \cdot 10^{-6}$.

FIG. 6. Influence of diffusion

The other important feature is the dependence on the relative velocity. This also depends on the progress of the process. At the beginning the source of concentration decreases for every velocity and approaches an asymptotic value. However after a certain time lapse the curves possess a minimum with respect to the velocity dependence, and it lies in the range of relatively small velocities. With increasing time this minimum becomes stronger pronounced.

This behavior though expected can be used in practical applications to control rates of adsorption processes by changing diffusion velocities. For instance processes running along maxima would be most effective in procedures of settling the pollutants on solid filters.

6. Final Remarks

The present work on adsorption/diffusion is restricted to isothermal processes. However, it is obvious that, at least in some practically relevant mass exchange processes, it is necessary to extend the model by accounting also for chemical reactions. This requires the presence of thermal effects, and it shall be the subject of the forthcoming work. Another restriction is, that only small adsorbate concentration is allowed because we use the Langmuir theory which accounts for monolayer adsorption. If we want to describe transport processes with any concentration we have to consider multilayer adsorption which should be a further possible extension of the model.

References

1. B. ALBERS, *Coupling of adsorption and diffusion in porous and granular materials. A 1-D example of the boundary value problem*, Arch. Appl. Mech. **70**, 7, 519-531, 2000.

2. B. ALBERS, *Makroskopische Beschreibung von Adsorptions-Diffusions-Vorgängen in porösen Körpern*, PhD-Thesis, Logos-Verlag, Berlin 2000.

3. B. ALBERS, K. WILMAŃSKI, *An axisymmetric steady-state flow through a poroelastic medium under large deformations*, Arch. Appl. Mech. **69**, 2, 121 - 132, 1999.

4. S. BRUNAUER, P.H. EMMETT, E. TELLER, *Adsorption of gases in multimolecular layers*, J. Amer. Chem. Soc., **60**, 309-319, 1938.

5. S. J. GREGG, K. S. W. SING, *Adsorption, surface area and porosity*, Academic Press, London 1982.

6. P. KNABNER, *Mathematische Modelle für Transport und Sorption gelöster Stoffe in porösen Medien*, Peter Lang Verlag, Frankfurt 1991.

7. I. LANGMUIR, *The constitution and fundamental properties of solids and liquids*, Part 1, J. Am. Chem. Soc., **38**, 2221-2295, 1916. I. LANGMUIR, *The constitution and fundamental properties of solids and liquids*, Part 2, J. Am. Chem. Soc., **39**, 1848, 1917. I. LANGMUIR, *The adsorption of gases on plane surfaces of glass, mica and platinum*, J. Am. Chem. Soc., **40**, 1361-1403, 1918.

8. K. WILMAŃSKI, *A thermodynamic model of compressible porous materials with the balance equation of porosity*, Transport in Porous Media, **32**, 21-47, 1998.

9. K. WILMAŃSKI, *On weak discontinuity waves in porous materials*, [in:] M. MARQUES, J. RODRIGUES (Hrsg.), Trends in Applications of Mathematics to Mechanics, 71-83, Longman, Harlow, Essex 1995.