UPSCALED DIFFUSION IN COAL PARTICLES

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(6 figures)

ABSTRACT. We use homogenisation to derive two types of upscaled diffusion adsorption model equations for carbon dioxide in small coal particles. The coal particles are considered to be composed of aromatic crystallites embedded in amorphous coal. The type of model equations depends on the ratio between the effective diffusion coefficients in the crystallites D_b and the amorphous background D_a with respect to the ratio of the square of their respective radii ε^2. In one model it is assumed that $D_b \sim D_a$ and in the other that $D_b \sim \varepsilon^2 D_a$. Effectively, both models lead to a single characteristic time for the adsorption rate. We assert, however, that two characteristic times would have been observed if $D_b \sim \varepsilon^3 D_a$. The model equations are used for the interpretation of CO_2 high-pressure adsorption experiments (<20 MPa) on a dry Pennsylvanian coal sample. The experiments determine the total excess sorption capacity for CO_2 and the rate at which the adsorption equilibrium is attained. Our preliminary experiment indicates that the adsorption rate is determined by a single characteristic time. Comparison to the modelling results leads to an estimated diffusion coefficient of the order of 10^{-11} m^2/s. Additional adsorption rate experiments are needed to confirm our preliminary results.

Keywords: upscaling, homogenisation, coal, diffusion, adsorption.

1. Introduction

One of the promising methods to reduce the discharge of the "greenhouse gas" carbon dioxide into the atmosphere is its sequestration in unminable coal seams, see however Lomborg (2001). A typical procedure is the injection of carbon dioxide via deviated wells drilled inside the coal seams. Carbon dioxide displaces the methane adsorbed on the internal surface of the coal. A production well gathers the methane as free gas. This process, known as carbon dioxide-enhanced coal bed methane production (CO_2-ECBM), is a producer of energy and at the same time reduces greenhouse concentrations as two carbon dioxide molecules displace one molecule of methane. After an extensive dewatering phase, carbon dioxide is injected and fills the cleat system of the coal and diffuses into the matrix blocks. In actual fact it is possible to discern a number of cleat systems at different scales. In the end the matrix blocks between the smallest cleat system have diameters typically of a few tens of microns (Gamson et al., 1993). Our interest is focused on the diffusion rate within the matrix blocks. This paper is about an attempt to find a procedure to determine the effective diffusion rate from the diffusion coefficients of the constituents comprising the coal particles. This attempt is based on a theoretical interpretation of coal adsorption experiments.

Much work has been carried out on the adsorption capacity of coal with respect to carbon dioxide. (Stevenson et al., 1991; Arri et al., 1992; Hall et al., 1994; Nodzenski, 1998; Clarkson & Bustin, 1999a; Clarkson & Bustin, 2000; Kross et al., 2002). The work found in the literature primarily focuses on the adsorption capacity of coal and not on the adsorption rate. The exceptions are the papers of Marecka & Mianowiski (1998) and Clarkson & Bustin (1999b). The interpretation of adsorption rate experiments requires a diffusion/adsorption model inside the coal particle. One of the well-known models that describe this is Ruckenstein's bidisperse model (see Ruckenstein, 1970). Other models are described in the paper of Bathia (1987). Ruckenstein's model describes relatively fast diffusion in a matrix, which forms the embedding of particulates with a much smaller diffusion coefficient. His derivation is, however, intuitive and he nowhere mentions any restrictive assumptions on the respective values of the diffusion coefficients. Indeed, nowhere in the literature there is a

systematic upscaling approach for the coal particles that consist of an amorphous embedding and clusters of stacked aromatic rings. A recently developed upscaling method, called homogenization (see Hornung, 1996), provides a systematic basis for upscaling. We show that the upscaled model equation depends on the order of magnitude of the ratio of the diffusion coefficients between the amorphous coal and the spherical aromatic crystallites. We distinguish two cases that lead to completely different model equations. One of the cases lead to equations, which are identical to the equations proposed by Ruckenstein. Our derivation shows that the model is only valid under restrictive assumptions.

2. Experimental set-up and procedure

We have measured CO_2 adsorption isotherms on ground moisture equilibrated and dry Pennsylvanian coal samples of different rank (0.72, 1.19 & 1.56% R_m) up to pressures of 20 MPa (200 bar). In this paper we only use the experiments with a coal sample with a reflectance of $0.72\%R_m$. The measurements were performed at 40, 60 & 80 °C. A volumetric method was used to determine the excess sorption of CO_2.
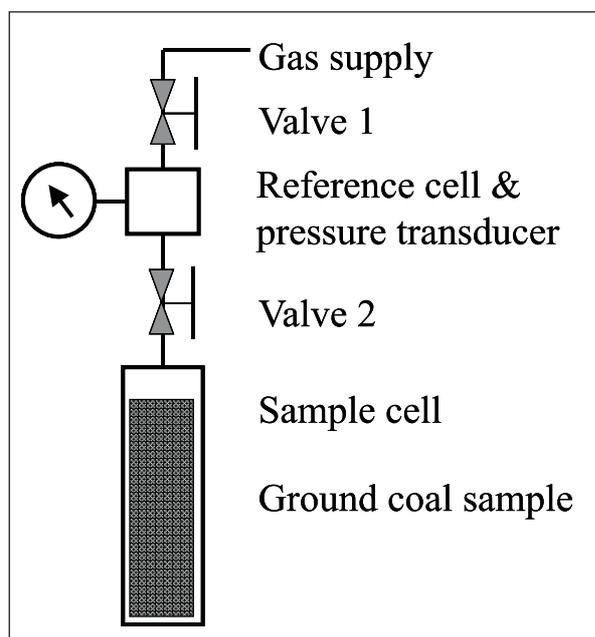

Figure 1. Schematic diagram of the adsorption set-up

The volume between valves V_1 and V_2 is the void volume of the pressure transducer and represents the known reference volume V_{ref}. Portions of 4 g of the ground coal are placed into the sample cell. Both cells are kept under constant temperature. After pressure equilibrium is reached in the reference cell the valve

V_1 is closed and valve V_2 is opened to expand gas into the sample cell. The amount of gas introduced to the system is computed from the amounts of gas transferred stepwise through the reference volume V_{ref} into the sample cell. During the process of adsorption sorbate gas molecules are removed from the free gas phase. This results in a free gas pressure drop within the experimental system. The pressure is monitored throughout the whole experiment (see Figure 2). From pressure data the amount of adsorbed gas can be determined by the use of the density of the gas phase calculated by an equation of state for CO_2 i.e. Setzmann & Wagner (1996). For detailed description of the experiments and results see Krooss et al. (2002). The raw data sets from sample Hengevelde-1 VI are a basis for the validation of the modelling work described below.
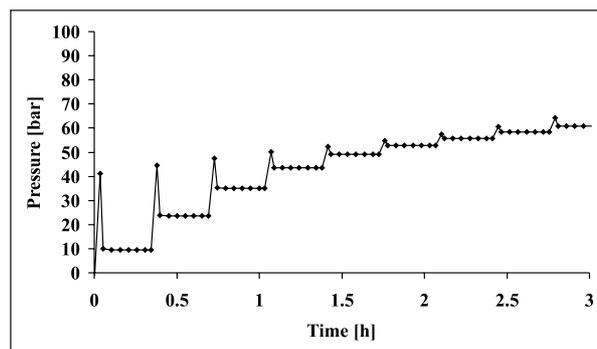

Figure 2. Monitoring the establishment of sorption equilibrium during individual pressure steps.

3. Experimental results

The experimental results show that the CO_2 sorption behaviour is very sensitive to variations in the experimental conditions and sample properties if the pressure reaches the critical pressure for CO_2 (73.8 bar). The variability of the observed CO_2 adsorption curves indicates that a quantitative prediction of the sorption capacity of coals for this gas is problematic. The Gibbs approach may be partly inadequate for a strong non-ideal gas at high pressures and comparatively low temperatures. Furthermore raw pressure data indicate, that an equilibrium time of 20 minutes for the first data point is not sufficient (see Figure 2).
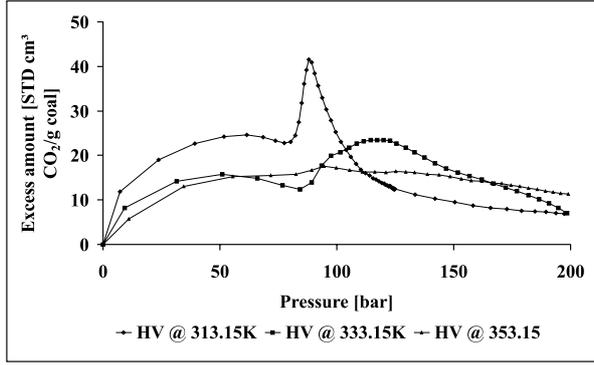
Figure 3. Adsorption Isotherms of CO_2 on dry Hengevelde-1 VI sample at 40, 60, & 80°C. Data points are calculated from each pressure drop curve (Figure 2).

4. Adsorption model of carbon dioxide in coal particles

We consider the coal as aggregates of coal matrix blocks with a diameter of 10-100 μm, which are surrounded by a system of fractures called the cleat system. Inside the cleat system transport by convection and diffusion occurs. The relatively large cleat spacing allows a free carbon dioxide gas phase to move around between the coal matrix blocks. Within the fracture system Darcy flow occurs as the main transport mechanism. The secondary transport mechanism is diffusion. The diffusion coefficient inside the fractures D_{frac} is of the order of $D \sim 10^{-5} \, P_0/P \, [m^2/s]$. Here P_0 denotes the atmospheric pressure and P the prevailing pressure. As the fractures become narrower Knudsen diffusion occurs i.e. the diffusion coefficient reduces due to collisions with the pore wall. Still the diffusion coefficients are much larger than 10^{-8} $[m^2/s]$. Therefore we assume that the coal matrix blocks are surrounded by a more or less constant carbon dioxide concentration. It is asserted that surface diffusion within the coal matrix blocks is the rate-limiting step for adsorption. In other words the pore diameters within the matrix blocks are of the order of a few molecular diameters (e.g. of carbon dioxide). In such a case the molecule hops from one adsorption site to the other and extremely low effective diffusion coefficients i.e. lower than 10^{-13} - 10^{-18} are expected. Therefore nowhere in the matrix blocks free movement of carbon dioxide molecules occurs i.e. there is always a strong interaction between the carbon dioxide and the solid phase.

The matrix blocks consist of two types of carbon structures viz. crystalline carbon and amorphous carbon (Lu et al., 2001). The crystalline carbon consists of stacks of aromatic rings, which may be connected to each other by aliphatic chains on the edges. The domain occupied by these particles is denoted by Ω_b. Here we assume that these crystallites are embedded in a highly disordered non-aromatic background, which occupies the domain denoted with Ω_a. For computational convenience we also assume that the matrix blocks have the shape of spheres with radius R_0 and that the crystallites are small spheres with a radius of $r_0 \ll R_0$. Both in the amorphous background and in the crystallites a surface diffusion process takes place. By surface diffusion we mean that the carbon dioxide molecules feel at all times the presence of the solid phase and hence hop from one site with a interaction potential minimum to the other. We consider two cases.

1. We assume that the effective surface diffusion coefficients in the amorphous part and in the crystalline parts are of the same order of magnitude $D_b \sim D_a$.

2. We assume that the effective surface diffusion coefficient in the amorphous part D_a is much bigger than in the crystalline parts D_b. More specifically we assume that $D_b \sim D_a \, (r_0/R_0)^2$.

The case where also particulates are present with $D_b \sim D_a \, (r_0/R_0)^3$ is left for future work. We denote the adsorbed concentration in the amorphous part as c_a. Its units are mass of carbon dioxide per unit volume of amorphous coal and its surrounding void space. We assume that at the boundary of the big spheres $R = R_0$ the adsorbed concentration is proportional to the concentration in the cleats.
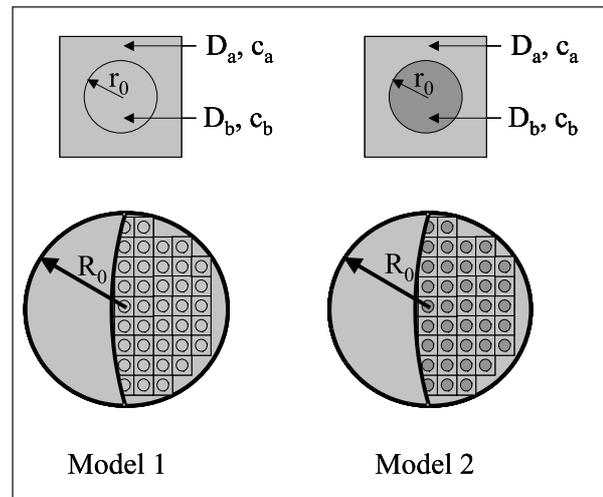

Figure 4. Heterogeneous diffusion model (Model 1) and distributed microstructure model (Model 2).

We denote the concentration in the crystalline part, as c_b. Its units are mass of carbon dioxide per unit volume of crystalline coal and the included void space. We assume that at the boundary of the small spheres the adsorbed concentration is proportional to the concentration in the amorphous coal $c_a(R,t)$ i.e. $c_b(r_0,t) = kc_a(R,t)$. Note that the concentration at the edge of the crystallites depends on its position in the big sphere.

The derivation of the two upscaled equations with homogenisation is tedious but straightforward. A full derivation requires a several pages and hence is outside the scope of the present paper. Here below we give the results, which have been derived following Hornung, 1996. This will be done in the next four sections.

4.1. Heterogeneous diffusion model

The heterogeneous diffusion model assumes that

$$\frac{\partial c}{\partial t} = \text{div}\left(D\,\text{grad}\,c\right) \text{ in } \Omega_a \quad \text{(Eq. 1)}$$

where c is the concentration inside the heterogeneous sphere and D is the space dependent diffusion coefficient. The concentration at the boundary of the amorphous coal particles can be expressed as

$$c_a(R_0,t) = c_0 = \overline{w}M_{CO_2}\,P/RT$$

where P is the pressure, R is the gas constant and T the temperature.

The average concentration $\overline{w}$ can be expressed in terms of w and k used in the distributed microstructure model as

$$\overline{w} = \left(\varphi_A + \left(1-\varphi_A\right)k\right)w$$

where φ_A is the fraction of amorphous coal in the coal particle and k is the ratio between the adsorption capacity of the particulates and the amorphous coal.

4.2. Distributed microstructure model

The distributed microstructure model assumes that $D_b \sim \varepsilon^2 D_a$ where ε is the ratio between the local scale and the global scale. We use the notation that c_a denotes the concentration of CO_2 outside the small particles i.e. in domain Ω_a and that c_b denotes the surface concentration inside the small particles in domain Ω_b. The boundary between of all the small aggregates is denoted as Γ. Hence the equations read

$$\frac{\partial c_a}{\partial t} = \text{div}\left(D_a\,\text{grad}\,c_a\right)k \qquad \text{in } \Omega_a \quad \text{(Eq. 2)}$$

for the amorphous coal and

$$\frac{\partial c_b}{\partial t} = \text{div}\left(D_b\,\text{grad}\,c_b\right) \qquad \text{in } \Omega_b \quad \text{(Eq. 3)}$$

for the spherical crystallites. c_a is the adsorbed concentration in the domain Ω_a. Furthermore c_b is the absorbed concentration inside the small spherical crystallites. Equation 2 states that the carbon dioxide is subjected to surface diffusion in the amorphous phase. In the way it is written c_a is the mass of carbon dioxide per unit volume amorphous phase inclusive the void space. We find this choice convenient because the pore space inside Ω_a does not provide a free space for the carbon dioxide molecules; it is too narrow. The effective "volume" diffusion coefficient is denoted as D_a. The diffusion coefficient D_a is related to a surface diffusion coefficient through a number of constant conversion factors. For our present purposes it is not useful to make this relation explicit. Equation 3 also considers only surface diffusion. The diffusion is driven by the gradient of the surface concentration of carbon dioxide within the domain Ω_b. We also express the units of the concentration of carbon dioxide c_b in the small spheres comprising the domain Ω_b as mass of carbon dioxide per unit volume of the sum of the pore space and the solid coal phase. For the equations derived in the paper it is not useful to relate the diffusion coefficient D_b in Ω_b to the surface diffusion coefficient in Ω_b. For us it is only relevant that $D_b\left(\text{grad}\,c_b\right)$ is the mass flux i.e. the mass transported through a unit surface inside Ω_b in the same way, as $D_a\left(\text{grad}\,c_a\right)$ is the mass flux in Ω_a.

Flux continuity at the boundary Γ between the crystallite and the amorphous non-aromatic part implies that $D_a\frac{\partial C_a}{\partial n} = D_b\frac{\partial C_b}{\partial n}$, where n denotes the coordinate perpendicular to the crystallite-amorphous interface.

4.3. Upscaled heterogeneous diffusion model

We apply the diffusion equation to model 1 shown in Figure 4. Homogenisation gives an effective diffusion equation.

$$\frac{\partial Rc}{\partial t} = D_{eff}\frac{\partial}{\partial R}\left(\frac{\partial Rc}{\partial R}\right) \quad \text{(Eq. 4)}$$

with the boundary condition $c\left(R_0,t\right) = \frac{\overline{w}P}{RT}$.

Here, D_{eff} is the effective diffusion coefficient and c the CO_2 concentration in terms of mass per unit volume of coal. The effective diffusion coefficient is obtained from a simulation of the models shown in Figure 4.

4.4. Upscaled equation for the distributed microstructure model

For the spheres within spheres we have that $\varepsilon = r_0/R_0$, where R_0 and r_0 are the radii of the amorphous coal particle and the spherical aromatic crystallites respectively. The equations read

$$\frac{\partial rc_a}{\partial t} = D_a \frac{\partial}{\partial r}\left(\frac{\partial rc_a}{\partial r}\right) \qquad \text{in } \Omega_a \quad (\text{Eq. 5a})$$

for the amorphous coal and

$$\frac{\partial rc_b}{\partial t} = D_b \frac{\partial}{\partial r}\left(\frac{\partial rc_b}{\partial r}\right) \qquad \text{in } \Omega_b \quad (\text{Eq. 5b})$$

for the spherical aromatic crystallites. c_a is the adsorbed concentration in the domain Ω_a. Furthermore c_b is the surface concentration inside the small spheres. At the boundary $r = r_0$ we obtain therefore

$$D_a \left(\frac{\partial c_a}{\partial r}\right)_{r=r_0+o} = D_b \left(\frac{\partial c_b}{\partial r}\right)_{r=r_0-o} \qquad (\text{Eq.6})$$

at $r = r_0$ and $kc_a = c_b$ at $r = r_0$.

Finally we have at the boundary $R = R_0$

$$c_a(R_0,t) = wc_0 = wM_{CO_2} \, P/RT$$

where w is the ratio between the adsorbed concentration in the amorphous coal and the free gas phase surrounding the coal particles. Both concentrations are expressed in terms of mass per unit bulk volume.

5. Modelling Results

We computed the cumulative amount $Q(t)$ of diffused/adsorbed CO_2 in the big coal particle using Stehfest's algorithm for inverse Laplace transformation (see 9. Annex). The coal particles have a diameter of 50 μm. For the second case the coal particle contains a volume fraction of 0.5 of crystallites with a radius one hundred times as small. Our simulations use diffusion coefficients for the large particles that range from $5x10^{-9}$ to $5x10^{-14}$ m^2/s. The diffusion coefficient in the small particle is 10000 times smaller than in the matrix. The adsorbed mass is 28 times the mass in the bulk. Using diffusion coefficients of $5x10^{-9}$ to $5x10^{-14}$ m^2/s in the first model gives a result that almost coincides with the second model. Hence it is impossible for experiments to discern between the two models.
A comparison to Figure 2 shows that the effective diffusion coefficient is of the 10^{-11} m^2/s.

6. Conclusions

The upscaled diffusion adsorption equation in coal particles can be obtained with the use of homogenisation as an upscaling method. We derive two upscaled diffusion/adsorption model equations. The type of model equation obtained depends on the ratio of the characteristic times i.e. R_0^2/D_a and r_0^2/D_b. One of the model equations is identical to the equations derived for Ruckenstein's bidisperse model. The bidisperse model is only valid for certain restrictive conditions for the ratio of the diffusion coefficients in the small and big spheres. The restrictive conditions imply that effectively there is only a single characteristic time that applies both to diffusion in the small spheres and in the big spheres. In this case the bidisperse model cannot be discerned from a model with a slightly heterogeneous diffusion coefficient distribution. It is asserted that in a model in which there are two distinct time scales completely different model equations apply. This we leave for future work.

7. Acknowledgements

8. References

ARRI, L.E., YEE, D., MORGAN, W.D., & JEANSONNE, M.W. 1992, Modelling Coal Bed Methane Production With Binary Gas Sorption. *SPE 24363*, Society of Petroleum Engineers Rocky Mountain Regional Meeting, Casper, Wyoming May 18-21.
BATHIA, S.K., 1987. Modelling the Pore Structure of Coal. *American Institute of Chemical Engineers Journal*, 33: 1707-1718.
CLARKSON, C.R. & BUSTIN, R.M., 1999a. The Effect of Pore Structure and Gas Pressure upon the Transport Properties of Coal: a Laboratory and Modelling Study. 1. Isotherms and Pore Volume Distributions. *Fuel*, 78: 1333-1344.
CLARKSON, C.R. & BUSTIN, R.M., 1999b. The Effect of Pore Structure and Gas Pressure upon the Transport Properties of Coal: a Laboratory and Modelling Study. 2. Adsorption Rate Modelling. *Fuel*, 78: 1345-1362.
CLARKSON, C.R. & BUSTIN, R.M. 2000. Binary Gas Adsorption/ Desorption isotherms: Effect of Moisture and Coal Composition upon Carbon Dioxide Selectivity over Methane. *International Journal of Coal Geology*, 42: 241-271.
GAMSON, P.D., BEAMISH, B.B. & JOHNSON, D.P., 1993. Coal Microstructure and their Effects on Natural Gas Recovery. *Fuel*, 72: 87-99.
HALL, F.E., CHUNHE, Z., GAZEM, K.A.M., ROBINSON, R.L. & YEE, D., 1994. Adsorption of Pure Methane, Nitrogen and Carbon Dioxide and Their Binary Mixtures on Wet Fruitland Coal. *SPE 29194*, Society of Petroleum Engineers Eastern Regional

Conference and Exhibition, Charleston, W.V., p. 329-344.

HORNUNG, U., 1996. Homogenisation and Porous Media. *Interdisciplinary Applied Mathematics* Volume 6, Springer Verlag, p. 129-146.

KROOSS, B.M., VAN BERGEN, F., GENSTERBLUM, Y., SIEMONS, N., PAGNIER, H.J.M. & DAVID, P., 2002. High Pressure Methane and Carbon Dioxide Adsorption Isotherms on Dry and Moisture-Equilibrated Pennsylvanian Coals. *International Journal of Coal Geology*, 51: 69-92.

LOMBORG, B, 2001. The Sceptical Environmentalist. Section 24, Global Warming, Cambridge University Press, p. 258-324.

LU, L., SAHAJWALLA, V., KONG, C. & HARRIS, D., 2001. Quantitative X-Ray Diffraction Analysis and Its Application to Various Coals. *Carbon*, 39: 1821-1833.

MARECKA, A. & MIANOWISKI, A., 1998. Kinetics of CO_2 and CH_4 Sorption on High Rank Coal at Ambient Temperatures. *Fuel*, 77: 1691-1696.

NODZENSKI, A., 1998. Sorption and Desorption of Gases (CH_4, CO_2) on Hard Coal and Activated Carbon at Elevated Pressures. *Fuel*, 77: 1243-1246.

RUCKENSTEIN, E., VAIDYANATHAN, A.S., & YOUNGQUIST, G.R., 1971. Sorption by Solids with Bidisperse Pore Structures. *Chemical Engineering Sciences*, 26: 1305-1318.

SPAN, R. & WAGNER, W., 1996. A New Equation of State for Carbon Dioxide Covering the Fluid Region From the Triple-Point Temperature to 1100 K at Pressures up to 800 Mpa. Journal of Physical and Chemical Reference *Data*, 25: 1509–1596.

STEVENSON, M.D., PINCZEWSKI, W.V., SOMERS, M.L. & BAGIO, S.E., 1991. Adsorption/Desorption of Multi-Component Gas Mixtures at In-Seam Conditions. *SPE 23026*, Society of Petroleum Engineers Asia Pacific Conference, Perth, Australia, November 4-7.

SMIT, M., 2001. Upscaling of Single Phase Flow of the Convection-Diffusion-Reactive Flow Equation, MSc. Thesis TU Delft 2001.

9. Annex. Solution of the upscaled equations in Laplace place

9.1. Heterogeneous diffusion model 1

We obtain after Laplace transformation of Eq. 4.

$$sRc = D_{eff} \frac{\partial^2 Rc}{\partial R^2} \quad \text{(Eq. 7)}$$

and we obtain

$$c = \frac{R_o}{R} \frac{\overline{w}}{s} \frac{M_{CO_2} P}{R_b T} \frac{\sinh\left(\sqrt{\frac{s}{D_{eff}}} R\right)}{\sinh\left(\sqrt{\frac{s}{D_{eff}}} R_o\right)} \quad \text{(Eq. 8)}$$

If we divide by s to get the integrated result, the cumulative flux is given as

$$Q = \frac{4\pi}{s^2} R_o^2 D_{eff} \left(\frac{\partial c}{\partial R}\right)_{R=R_o} = \frac{M_{CO_2} P \overline{w}}{R_b T} \frac{4\pi}{s^2} D_{eff} \left(-R_o + R_o^2 \sqrt{\frac{s}{D_{eff}}} \coth\left(\sqrt{\frac{s}{D_{eff}}} R_o\right)\right) \quad \text{(Eq. 9)}$$

In the long time limit i.e. when s is small we obtain after using that $L^{-1}\left[\frac{1}{s}\right] = 1$

$$Q(t \to \infty) = \overline{w} \frac{M_{CO_2} P}{R_b} \frac{4\pi R_o^3}{3} \quad \text{(Eq. 10)}$$

9.2. Distributed microstructure model 2 $D_b \sim \varepsilon^2 D_a$

We obtain

$$c_a = w \frac{R_o}{Rs} \frac{M_{CO_2} P}{R_b T} \frac{\sinh(\gamma R)}{\sinh(\gamma R_o)} \quad \text{(Eq. 11)}$$

If we divide by s to get the integrated result, the cumulative flux is given as

$$Q = \frac{4\pi}{s^2} R_o^2 D_{eff} \left(\frac{\partial c_a}{\partial R}\right)_{R=R_o} = \frac{4\pi}{s^2} D_{eff} w \frac{M_{CO_2} P}{R_b T} \left(-R_o + \gamma R_o^2 \coth(\gamma R_o)\right) \quad \text{(Eq. 12)}$$

where

$$\gamma^2 = \frac{s\varphi_A + \frac{3(1-\varphi_A)k D_b}{r_o}\left(-\frac{1}{r_o} + \sqrt{\frac{s}{D_b}}\coth\left(\sqrt{\frac{s}{D_b}}r_o\right)\right)}{D_{eff}} \quad \text{(Eq. 13)}$$

The effective diffusion coefficient is obtained the same way as mentioned in section 5.
In the long time limit, i.e. when s is small we obtain for γ^2

$$\gamma^2 := \left(\frac{\varphi_A + (1-\varphi_A)k}{D_{eff}}\right) s$$

and after using that $L^{-1}\left[\frac{1}{s}\right] = 1$

$$Q(t \to \infty) = \left(\varphi_A + (1-\varphi_A)k\right)\frac{w M_{CO_2} P}{R_b}\frac{4\pi R_o^3}{3} \quad \text{(Eq. 14)}$$
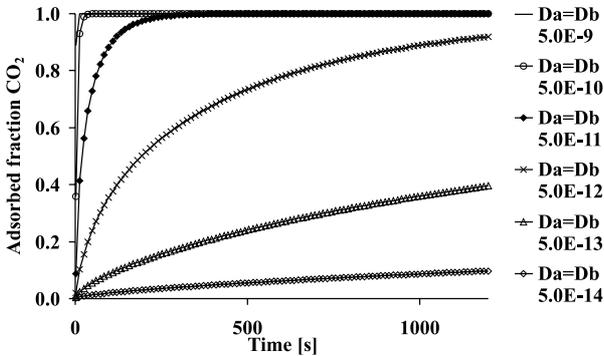

Figure 5. Results of the diffusion rate-modelling Model 1: $D_a = D_b$
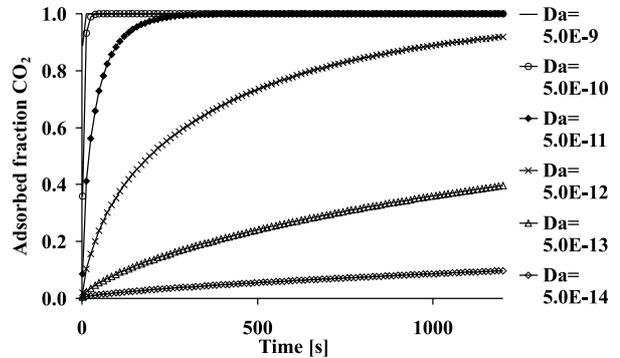

Figure 6. Results of the diffusion rate-modelling Model 2: $D_b \sim \varepsilon^2 D_a$.