NUMERICAL MODELLING ON SUPER-DIFFUSION OF CARBON-DIOXIDE IN COAL

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ABSTRACT

Case II (super)-diffusion is characterized by a diffusion like process that goes faster than the square root of time. Superdiffusion can occur in polymeric structures if a stress gradient enhances the diffusion process. In such a case the part of the polymer invaded by the penetrant, e.g. CO_2, undergoes a transition in structure from the glass state to a rubber like state. In ideal cases the transition zone can propagate proportional to time. The Thomas & Windle model, a model that describes anomalous diffusion behavior in polymers, was also proposed to describe diffusion of CO_2 in coal. The proposal was due to the similarities in structure between coal and glassy polymers. Coal has a molecular structure of carbon-carbon bonds with 'open holes' between the chains. If these holes are smaller in volume than the volume of a CO_2-molecule, the uptake of CO_2 leads to a geometric problem. The CO_2 molecules will squeeze themselves into the structure, resulting into a swollen rubbery coal. This phenomenon is happening due to the fact that a carbon-carbon dioxide bond is thermodynamically favored above the carbon-carbon bond and is more stable than the other. Analysis of the Thomas & Windle model shows there is a time where diffusion is much faster than conventional diffusion. The results also show that super-diffusion is only a transitional effect, i.e., there is an initial phase where relaxation dominates, a transitional phase that exhibits anomalous diffusion and a long time phase that shows the typical square root of time behavior of an ordinary diffusion process.

This study gives details of a numerical model used to solve the stress induced diffusion equation using the Finite Element Method implemented in Matlab. The numerical results show that for some favorable set of parameters diffusion can indeed be faster than Fickean diffusion during an intermediate stage. For other parameters the diffusion can be slower. A comparison to a laboratory result shows an example where diffusion appears to be slower.

INTRODUCTION

Concern about global warming has increased societal interest to reduce greenhouse gas emissions. Storage of CO_2 in geological formations in considered as one of the options to reduce carbon dioxide emissions. Storage into unminable coal layers can have the additional advantage that it displaces methane, leaving the CO_2 underground. At least one mole of CO_2 is stored for every mole methane produced.

There has been much research directed towards the economic feasibility for simultaneous CO_2 storage and enhancement of methane production (Enhanced Coal Bed Methane). Worldwide some field projects are taking place (Gorucu *et al.*, 2007) but in spite of elaborate laboratory research work there is still little or no fundamental understanding of the physics behind exchange reaction and swelling behavior.

Laboratory experiments show that coal undergoes a volume change. The changes are related to changes in the structure of the coal. Swelling of the coal can also be described by means of these structural changes.

Analogues features are also observed for organic sorbents penetrating into glassy polymers. The Thomas & Windle model appears to be the most successful for describing penetration of sorbents into the polymeric structure. In their approach, the diffusion of solvent is accompanied by a swelling of the polymer that is driven by the osmotic pressure.

The similarities in structure between coal and glassy polymers have led to the perception (Ritger *et al.*, 1987) that CO_2 penetration in coal has many analogous features that are observed for organic sorbents penetrating into glassy polymers. In other words, the application of the Thomas & Windle model on coal has been proposed. There is a claim by Thomas, Windle and others that the theories behind the observed features lead to super-diffusion, i.e., diffusion faster than Fick's Law describes. Fickean diffusion is proportional to the square root of time, whereas super-diffusion or Case-II diffusion is faster and can become proportional to time. The term "Case II" was coined by Alfrey *et al.* (1966) and is the name given to the anomalous diffusion behavior observed when a low molecular weight solvent (diluent) diffuses into a polymeric glass and causes it to undergo a glass to rubber state transition.

Recent work (Mazumder *et al.*, 2007) has given an analysis for the linearized (super)-diffusion equations. The main conclusions were that super-diffusion is only a transitional effect. For long times the behavior is Fickean. In this paper a numerical solution for the problem is given and the results are compared to previous work.

The organization of the paper is as follows: First we discuss "Previous Work" on the time dependence of the diffusion process. Then a sketch of the derivation of the model equations is given. A numerical model is presented in the next section. Finally the results are discussed and compared to experimental data.

PREVIOUS WORK

Anomalous diffusion behavior in polymeric materials has been studied for decades. There is a large amount of literature on the topic, which already dates back to the sixties. A conceptual picture of diffusion of a penetrant in a polymer is given in Fig. 1. An interface separates a modified rubbery region and the original glassy region. Thomas and Windle and later also Hui suggest that the interface motion is controlled by the coupling between osmotic-pressure-driven swelling and the nearly Fickean diffusion in the glassy region ahead of the front. Case II diffusion is characterized by linear kinetics and a sharp diffusion front and occurs in polymer-penetrant systems in which the penetrant causes substantial swelling of the polymer.

Coal behaves as a fractured medium, where the main fractures are vertical and are more or less continuous and are called face cleats. Perpendicular to these cleats another fracture system called butt-cleats is present. Almost all the permeability of a coal bed is due to these cleats. The permeability of the coal matrix is so small that the main transport mechanism is diffusion.

The mass uptake can be described by an empirical equation as follows:

$$\frac{M_t}{M_e} = k_1\sqrt{t} + k_2 t \approx kt^n , \qquad (1)$$

where M_t is the mass uptake at time t and M_e is the equilibrium mass uptake, k is a constant depending on the macromolecular network system and the penetrant and n is the diffusional exponent.

Diffusion according to Fick's Law for a thin slab is defined by $n = 0.5$ and Case II diffusion by $n = 1$. Anomalous transport behavior is intermediate between these two extremes. Fickean diffusion is controlled by the concentration gradient between the centre and the outside of the coal matrix. Additional transport is caused by a stress gradient induced by the penetration of molecules.

The Deborah number (D_e) is introduced as a means of characterizing penetrant uptake (Vrentas *et al.*, 1975). The Deborah number is defined as the ratio between two characteristic times, namely a structural relaxation time (λ) and a characteristic diffusion time (θ):

$$D_e = \frac{\lambda}{\theta} \qquad (2)$$

If the relaxation time is much larger than the diffusion time, there is effectively no time variation of the macromolecular structure during the diffusion process. The sorption process can then be described by Fickean diffusion ($D_e >> 1$). For $D_e << 1$ (relaxation time much smaller than diffusion time), changes in the structure occur instantaneously with respect to the time scale of diffusion. The transport process in this case can also be described by Fickean diffusion. In relation with the diffusional exponent n a system with $D_e << 1$ or $D_e >> 1$ can be characterized by $n = 0.5$. When the Deborah number is equal to the order of one (relaxation and diffusion time are of the same order) Case II diffusion becomes relevant.

Alfrey *et al.* (1966) have presented a second limiting case of transport, where the rate of transport is entirely controlled by molecular relaxation (Case II transport). Thomas *et al.* (1982) proposed that the rate controlling step at the front is the time dependent mechanical deformation of the glassy polymer in response to the thermodynamic swelling stress. The Thomas & Windle model stimulated experimental research on this special case of sorption. Lasky *et al.* (1988) and Gall *et al.* (1991) have done experiments on a number of polymer/sorbent systems using the Rutherford backscattering technique. Hui *et al.* (1987) dealt with both the initial transient penetration of the sorbent and the final steady state motion of the sorption front, all within the framework of the Thomas & Windle model. There are also other models of Case II transport. Govindjee *et al.* (1993) emphasize the representation of the thermodynamic driving forces arising from activity gradients and a glass to rubber transition. Durning (1985) extended the T&W model using irreversible thermodynamics. The viscous model has been replaced by the Maxwell visco-elastic model, so that the relaxation time can be defined. Using a force-balance, the relation between the osmotic pressure and the stresses on the coal were analyzed.

Argon *et al.* (1999) presented a mechanistic model by combining Case II diffusion with Fickean diffusion (Mazumder *et al.*, 2007).

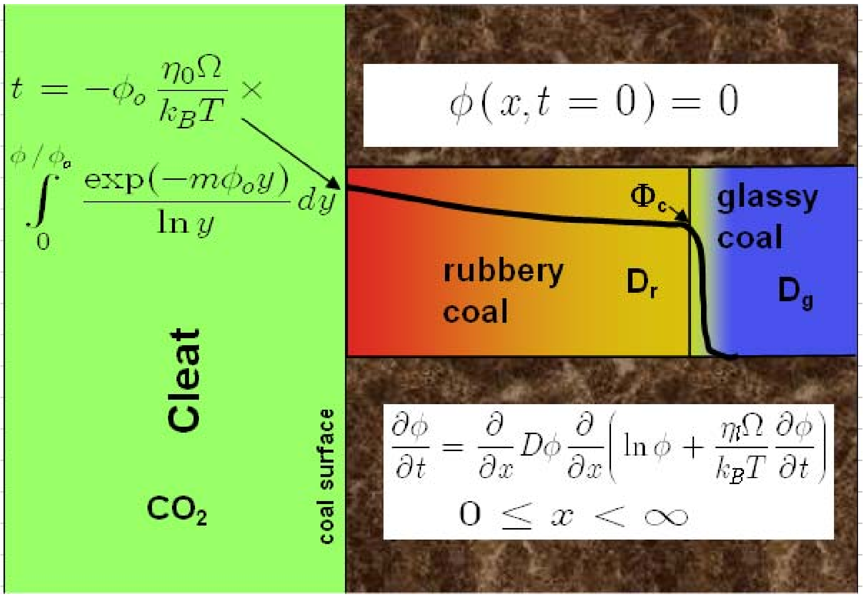

Fig. 1 Idealized concentration profile for Case II-transport into an infinite sheet. Fickean diffusion front ahead to the rubber-glass transition zone

The characteristics of Case II diffusion in coal (Fig. 1) can be summarized as follows:
The penetrant advances through the coal and converts the structure simultaneously, accompanied with a state change from glassy to rubber like coal. There exists a short rubber-glass transition zone. Downstream the concentration of the penetrant is zero; upstream the rubber state the penetrant is at equilibrium concentration. The rubbery part is substantially swollen with respect to the glassy part. After some initializing effects a semi steady state occurs, where a given concentration profile travels through the slab more or less proportional to time. The swollen matrix behind the advancing front is at uniform state. (Mazumder *et al.*, 2007)

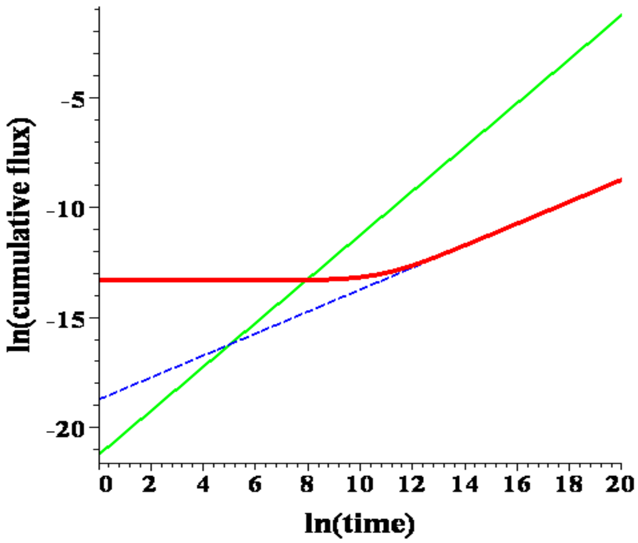

Fig. 2 Analysis for the linearized model equations (Mazumder et al., 2007)

Fig. 2 follows from an analysis of the prevailing transport processes. The green line indicates diffusion faster than Fickean diffusion, i.e. $n=1$. The blue dashed line is obtained when only considered Fickean diffusion ($n=0.5$). The red solid line indicates the time needed for the surface saturation effect. According to the Thomas and Windle model, the curve for the cumulative flux will follow the green curve until it hits the red curve and then follows the red line. After some initializing effects (saturation on the surface) an enhanced diffusion will start ($n=1$). At long times the diffusion will be according to Fick's Law ($n=0.5$).

DERIVATION OF THE EQUATIONS

The Thomas & Windle model describes the concentration of the penetrant (volume fraction), ϕ, as a function of the spatial dimension x and the time t. Thomas *et al.* (1982) treat the rate of change of volume fraction of penetrant as the rate of linear visous creep deformation driven by the osmotic stress P_{xx}. The amount of penetrant is expressed in terms of the volume fraction ϕ, which is related to the concentration by $\phi = \frac{c}{\Omega}$, where Ω is the partial molecular volume. The derived expression where the molar flux is driven by the volume fraction gradient and also by the stress gradient can be summarized by

$$J = -D\phi \frac{\partial}{\partial x}\left(\ln\phi + \frac{\Omega}{k_B T} P_{xx} \right). \tag{3}$$

Extended non-equilibrium thermodynamics (Jou *et al.*, 2001) suggests that vice-versa also the stress is related to molar flux gradient as

$$P_{xx} = -\eta_l \frac{\partial J}{\partial x} = \eta_l \frac{\partial \phi}{\partial t} \quad , \tag{4}$$

where η_l is the elongational viscosity.

The second equation follows from the mass balance equation, i.e.,

$$\frac{\partial \phi}{\partial t}+\frac{\partial J}{\partial x}=0 \ . \tag{5}$$

The diffusivity depends on the concentration of the penetrant. Below a critical volume fraction ϕ_c a diffusion coefficient characteristic of a glassy state is used (D_g), and above ϕ_c a diffusivity for the rubber (swollen) state is used (D_r). It can be expected that $D_r / D_g >> 1$. In the model an abrupt change of the diffusion coefficient at the critical volume fraction is used and D_r , D_g are assumed constant for $\phi > \phi_c$ and $\phi < \phi_c$ respectively.

By substitution of expression (4) in equation (3) we find

$$J=-D\frac{\partial}{\partial x}\left(\phi+\frac{\eta_l \Omega \phi}{k_B T}\frac{\partial \phi}{\partial t}\right). \tag{6}$$

Combining with the mass balance equation gives

$$\frac{\partial \phi}{\partial t}=\frac{\partial}{\partial x}\left[D\phi\frac{\partial}{\partial x}\left(\ln\phi+\frac{\eta_l \Omega \phi}{k_B T}\frac{\partial \phi}{\partial t}\right)\right]. \tag{7}$$

The elongational viscosity η_l is supposed to depend on the volume fraction of the penetrant as

$$\eta_l=\eta_o \exp(-m\phi), \tag{8}$$

where m is a material constant and η_o is the volumetric viscosity of the un-swollen coal sample. Final equilibrium concentration is reached when the coal has swollen and the concentration of CO_2 in the coal is in equilibrium with the CO_2 concentration in the fluid phase outside the coal. The concentration of the CO_2 in the stressed coal is also in equilibrium with the concentration in the fluid phase.

The change in chemical potential for stressed state of the coal is $d\mu=\Omega dP_{xx}+k_B T d\ln\phi$.

Balancing with the unstressed state ($P_{xx}^{(0)}$) leads to

$$\Omega dP_{xx}^{(0)}+k_B T\ln\phi_o=\Omega dP_{xx}+k_B T\ln\phi \ . \tag{9}$$

After substitution of equations (4) and (8) in equation (9) we obtain

$$\ln\phi/\phi_o=-\frac{\eta_0\Omega}{k_B T}\exp(-m\phi)\frac{d\phi}{dt}. \tag{10}$$

The solution of this equation is (with the initial condition ϕ=0 at t=0)

$$t_o=-\phi_o\frac{\eta_0\Omega}{k_B T}\int_0^{\phi/\phi_o}\frac{\exp(-m\phi_o y)}{\ln y}dy. \tag{11}$$

NUMERICAL CALCULATIONS

The general stress-induced diffusion equation (7) can be rewritten after elaboration to

$$\frac{\partial\phi}{\partial t} = \nabla\cdot\left\{D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right\}, \tag{12}$$

with $B = \frac{k_B T}{\eta_o\Omega}$.

This equation has to be solved numerically using the boundary conditions

$$t = -\frac{\phi_0\eta_0\Omega}{k_BT}\int_0^{\phi/\phi_o}\frac{e^{-my}\phi_0}{\ln y}dy \qquad \text{at } \underline{\mathrm{x}}\in\Gamma_1,$$

$$D(\phi)\frac{\partial\phi}{\partial x} + \frac{D(\phi)\phi}{B}\frac{\partial}{\partial x}\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right) = 0 \quad \text{at } \underline{\mathrm{x}}\in\Gamma_2 \ \ (\Gamma=\Gamma_1\cup\Gamma_2),$$

and initial value $\phi(\underline{\mathrm{x}},0) = 0$.

We solve the problem using the FEM. First we construct a Weak Formulation. In order to do so we multiply equation (12) by the test function $\psi(x,t)$

$$\int_\Omega\frac{\partial\phi}{\partial t}\psi d\Omega = \int_\Omega\left(\nabla\cdot\left\{D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right\}\psi\right)d\Omega.$$

Apply the product rule to rewrite the right-hand side

$$\int_\Omega\frac{\partial\phi}{\partial t}\psi d\Omega = \int_\Omega\nabla\cdot\left[D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right]\psi d\Omega +$$

$$\int_\Omega\left[D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right]\cdot\nabla\psi d\Omega.$$

The first term on the right-hand side becomes

$$\int_\Gamma\underline{n}\cdot\left(\left[D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right]\psi\right)d\Gamma = 0,$$

since $\psi|_{\Gamma_1} = 0.$

The Weak Formulation becomes

$$\int_\Omega\frac{\partial\phi}{\partial t}\psi d\Omega = \int_\Omega\left\{D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right\}\nabla\psi d\Omega.$$

The solution should satisfy the following conditions

Search for ϕ, for which $t = -\frac{\phi_0\eta_0\Omega}{k_BT}\int_0^{\phi/\phi_o}\frac{e^{-my}\phi_0}{\ln y}dy$ such that

$$\int_\Omega\frac{\partial\phi}{\partial t}\psi d\Omega = \int_\Omega\left\{D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right)\right\}\nabla\psi d\Omega,$$

for all $\psi(\underline{x},t)$ for which ψ =0 at $\underline{\mathrm{x}}\in\Gamma_1$.

Take piecewise linear basis functions (so-called HAT-functions) to construct solutions

$$\phi(\underline{x},t) = \sum_{j=1}^{n}c_j(t)\psi_j(\underline{x}).$$

First we rewrite the following term

$$\nabla\left(e^{-m\phi}\frac{\partial\phi}{\partial t}\right) = -me^{-m\phi}\nabla\phi\frac{\partial\phi}{\partial t} + e^{-m\phi}\nabla\left(\frac{\partial\phi}{\partial t}\right).$$

Substitution into the Weak Formulation gives

$$\int_{\Omega} \frac{\partial\phi}{\partial t}\psi d\Omega = \int_{\Omega} \left\{ D(\phi)\nabla\phi + \frac{D(\phi)\phi}{B}\left[e^{-m\phi}\nabla\left(\frac{\partial\phi}{\partial t}\right) - me^{-m\phi}\nabla\phi\frac{\partial\phi}{\partial t}\right]\right\}\cdot\nabla\psi d\Omega\,.$$

Now replace $\phi(\underline{x},t)$ and $\psi(\underline{x})$ with the linear basis functions

$$\int_{\Omega} \sum_{j=1}^{n} c_j\,'(t)\psi_j\psi_i d\Omega = \int_{\Omega} D(\phi)\nabla\cdot\left(\sum c_j(t)\psi_j\right)\cdot\nabla\psi_i d\Omega$$

$$+\int_{\Omega} \frac{D(\phi)\phi}{B}\left[e^{-m\phi}\nabla\left(\sum_{j=1}^{n} c_j\,'(t)\psi_j\right)\cdot\nabla\psi_i d\Omega - m\int_{\Omega} e^{-m\phi}\nabla\phi\cdot\left(\sum_{j=1}^{n} c_j\,'(t)\psi_j\right)\right]\cdot\nabla\psi_i d\Omega$$

Rewriting gives

$$\sum_{j=1}^{n} c_j\,'(t)\int_{\Omega}\psi_j\psi_i d\Omega = \sum_{j=1}^{n} c_j(t)\int_{\Omega} D(\phi)\nabla\psi_j\nabla\psi_i d\Omega + \sum_{j=1}^{n} c_j\,'(t)\int_{\Omega}\frac{D(\phi)\phi}{B}\left(e^{-m\phi}\nabla\psi_j\right)\cdot\nabla\psi_i d\Omega$$

$$-\sum_{j=1}^{n} c_j\,'(t)\int_{\Omega} me^{-m\phi}\nabla\phi\cdot\psi_j\nabla\psi_i d\Omega$$

This can be written again in matrix-vector form as

$$M(\phi)\underline{c}\,'(t) = S(\phi)\underline{c}(t), \text{ with } \underline{c} = \begin{pmatrix} c_1 \\ \cdot \\ \cdot \\ c_n \end{pmatrix}$$

where

$$M_{i,j}(\phi) = \int_{\Omega}\psi_j\psi_i d\Omega - \int_{\Omega}\frac{D(\phi)\phi}{B}e^{-m\phi}\nabla\psi_j\nabla\psi_i d\Omega + \int_{\Omega} me^{-m\phi}\nabla\phi\cdot\psi_j\nabla\psi_i d\Omega\,.$$

and

$$S_{i,j}(\phi) = \int_{\Omega} D(\phi)\nabla\psi_j\nabla\psi_i d\Omega\,.$$

The numerical scheme has been implemented in Matlab to obtain a solution for the stress-enhanced diffusion equation. Numerical evaluation of the integrals is done by using Newton-Cotes quadrature. Time integration was carried out by use of the IMEX (Implicit Explicit) method. The parameters that were used in the simulation are summarized in Table 1.

Table 1 Parameters used for the numerical calculations

Parameter	
D_g	10^{-11} m^2/s
D_r	10^{-10} m^2/s
M	10-30
Ω	1.68 x 10^{-29} m^3/molecule
η_0	10^{15} Ns/m^2
Φ_0	0.205
Φ_c	0.10 x Φ_0
Length	10^{-2} m
T	45°C

RESULTS & DISCUSSION

The results of the simulations are summarized in Fig. 3. In the figure we observe that first saturation of the surface exposed to the penetrant (CO_2) occurs. Subsequently the rate of penetration is faster that the square root of time. After saturation an intermediate relaxation process occurs, which is slower than the square root of time. After that the system starts to behave as a conventional diffusion process. Simulations have been done for several values of η_0.

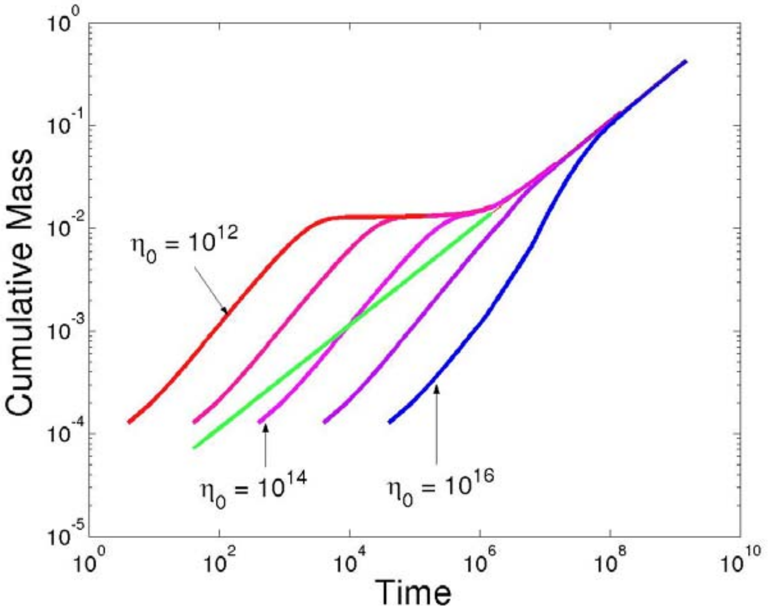

Fig. 3 Solution of the stress-induced diffusion equation for different parameters.

As shown in the figure, the start-up time for diffusion depends on the volumetric viscosity of CO_2 in the unswollen coal. High volumetric viscosity leads also to super-diffusion; only the starting time is later.

The results are in good agreement with the analysis of the linearized equations by Mazumder *et al*. (Fig. 2).

Solving the problem with “COMSOL Multyphysics” was unsuccessful. It is not yet clear why the model did not work.

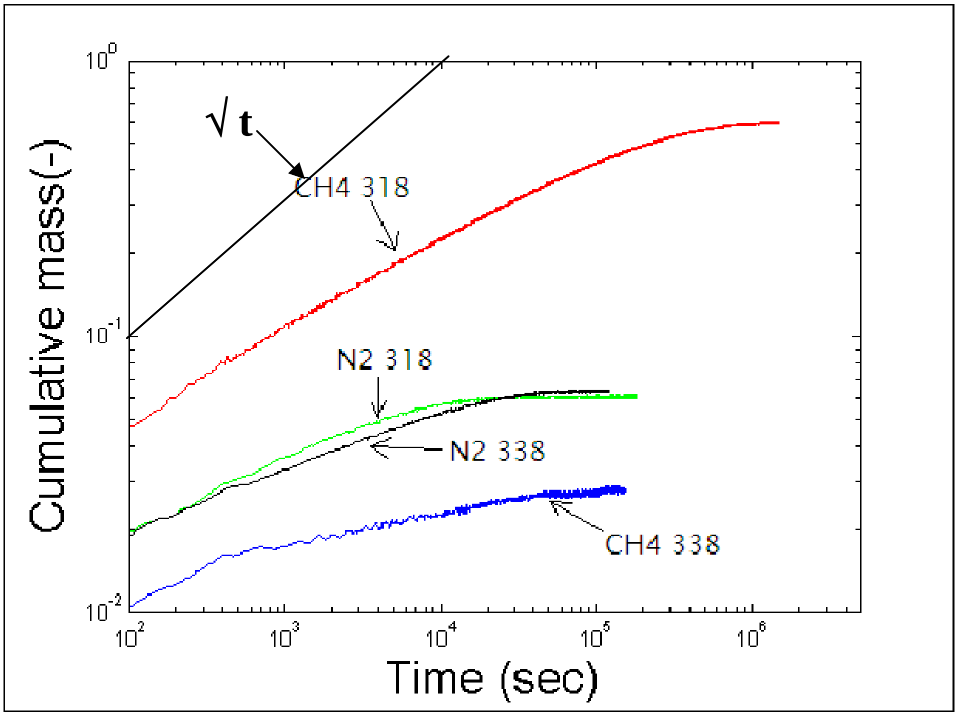

Fig. 4 Experimental result of diffusion behavior for various penetrants in coal (Elisa Battistutta)

Comparison to experiments in the laboratory show that for the coals used the observed sorption rate is slower than the square root of time (Fig. 4).

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