

# MODELLING CARBON CAPTURE BY ADSORPTION

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## Abstract

The following report concerns the development of mathematical models to describe carbon capture by adsorption in a packed column. In the first part we follow the work of Dantas *et al* (Chem. Engng J., 2011) and examine their coupled system of differential equations describing the concentration of the gas, the temperature and the amount of adsorbed material. A preliminary numerical solution is also presented, however, this does not reproduce the experimental data. In the second section we start from the standard equations for gas and temperature flow in a pipe, which are then averaged over a porous cross-section. This process leads to a system slightly different to that presented in the literature which often follows from the equations of Dantas *et al*. We go on to explain the differences (and errors) with the earlier model and how these can affect the interpretation of experimental data. The model developed in the present report has since been developed further and shown to agree very well with data.

## Problem posed for the study group

Despite international agreements to limit carbon emissions, measurements have shown an annual increase almost every year since 1959. Current increases appear

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ready to continue, driven by a projected 3% increase in coal consumption, 12% increase in natural gas consumption and 5% increase in oil consumption. Given the already high levels of greenhouse gases in the atmosphere the IPCC, the international body that issues comprehensive reports on climate change, has estimated that the world will need to remove an average of 10 gigatons of CO<sub>2</sub> (10 billion tons) a year from the atmosphere by midcentury.

With this in mind the following questions were posed to the study group:

1. Can we improve current/develop new models?
2. Are there useful models other than adsorption?
3. What are the best methods? What is the state of the art?
4. Where to place devices?
5. What about removal of other greenhouse gases?

## 1 Introduction

Articles regarding carbon capture often begin by citing the fact that the carbon dioxide levels in the atmosphere have risen significantly in recent years. Since 1959 the concentration of carbon dioxide levels went from 280 parts per million (ppm) to over 400ppm [3]. The dramatic increase is much larger than the natural fluctuations in CO<sub>2</sub>. This is owing to the effect of humans in their utilisation of fossil fuels, mostly in electricity generation and transportation. These increased levels of CO<sub>2</sub> have (along with additional greenhouse gases) led to significant climate change. If this pattern continues there may be catastrophic consequences.

Owing to the fact that our existence somewhat relies on the consumption of fossil fuels, the solution of no longer using them is not yet viable. Instead, it is easier to look at ways to remove the greenhouse gases from the atmosphere once they have been emitted.

There are many solutions that have been presented for the removal of carbon dioxide from the atmosphere and the storage thereof.

The most researched options are:

- The planting of trees. This option is the most environmentally, economically and politically viable, but seems impossible. In order to counter the effects of the CO<sub>2</sub> in the atmosphere, enough trees would need to be planted to cover a land mass equal to thrice the landmass of India. [9].
- Storage of carbon dioxide underground. One option would be to emit the CO<sub>2</sub> directly underground, at depths of around 800m [3]. This CO<sub>2</sub> could be emitted into abandoned oil wells, or in porous sedimentary rock levels between caprock levels. Thereafter the CO<sub>2</sub> will be dissolved into brine.

- The production of bio-char. Burning agricultural waste into biochar (a type of charcoal), and then using that as fertiliser, boosts crop yields and locks carbon away for centuries under the soil [9].
- Spreading metallic dust over the ocean to sink phyto-plankton taking the carbon with them down to the bottom of the ocean [9].
- Injection of the CO<sub>2</sub> into the ocean at a depth of 3500m. This solution is costly [10].
- **Capturing using adsorption**, which is the focus of our report. The CO<sub>2</sub> is pumped through a porous material that is able to adsorb the gas, and so carbon does not reach the atmosphere after production.

The following report is split into two sections: the first covers work carried out during the MISG, the second subsequent work on the correct problem formulation. Although this is a rather unusual approach it has been done since it appears that accepted equations in the literature contain a number of errors. Since these were the subject of the MISG study the results are likely to be inaccurate, consequently it is important to at least formulate the correct governing equations which may then be studied further. The typical experimental set-up modelled in the following involves a circular cross-section column containing an adsorbing material, this is then placed inside an oven or furnace to regulate the temperature. Gas is passed through the column and the concentration measured at the outlet.

## 2 Research carried out during MISG

### 2.1 Fixed bed adsorption model (Dantas et al 2011)

In [4], they used CO<sub>2</sub> capture by adsorption, as is regarded as attractive as a post-combustion treatment of the flue gas. The carbon capture experiment is mainly based on preferential adsorption of this gas on a porous adsorbent. In this experiment, the adsorption of the carbon dioxide-nitrogen mixture on activated carbon, packed in a fixed-bed, was studied. Their 'Linear Driving Force' (LDF) model, considered the energy and momentum balances to describe the kinetics of the CO<sub>2</sub> and the carbon-dioxide-nitrogen mixture adsorption on the activated carbon. The model for gas phase concentration is given by

$$\frac{\partial C_j}{\partial t} + \nabla \cdot (C_j \mathbf{u}) = D \nabla^2 C_j - \frac{(1 - \epsilon)}{\epsilon} \rho_p \frac{\partial q_j}{\partial t} \quad (1)$$

where  $\epsilon$  is the bed void fraction and the gas phase concentration of component  $j$  is  $C_j$ . The amount adsorbed by the sorbent (converted from a gas to solid) is defined as  $q_j$  and we have the diffusion coefficient,  $D$ . In this section the velocity  $\mathbf{u}$  is the

superficial velocity, i.e. that which would be observed if there was no porous media in the column and the particle density is  $\rho_p$ .

The following equation defines the adsorption rate of component  $j$  onto the sorbent:

$$\frac{\partial q_j}{\partial t} = K_{L,j}(q_j^* - q_j),$$

where  $q_j^*$  is the maximum adsorption amount for the system and defined as

$$q_j^* = \frac{q_j^m K_j^{eq} P_j}{[1 + (K_j^{eq} P_j)^n]^{1/n}}.$$

The coefficient  $K_{L,j}$  is the overall adsorption coefficient of the component also known as the LDF overall mass transfer coefficient. We define the pressure with regards to the  $j$ -th component as

$$P_j = C_j R T_g \quad (2)$$

by making use of the *Ideal Gas Law*, and the equilibrium adsorption coefficient is

$$K_j^{eq} = K_j^0 e^{-\Delta H / R T_g}.$$

Equation (2) is defined by the total pressure  $P_j$  with regards to component  $j$ , the gas temperature  $T_g$  and the universal gas constant  $R$ .

The pressure-velocity relation is described by the Ergun equation

$$-\frac{\partial P}{\partial x} = 150 \frac{\mu_g (1 - \epsilon)^2}{\epsilon^2 \delta_p^2} u + 1.75 \frac{(1 - \epsilon)}{\epsilon^2 \delta_p} \rho_g u^2, \quad (3)$$

where  $\mu_g$  is the gas viscosity,  $\rho_g$  the density and  $d_p$  the particle diameter.

The energy balance for the system can be seen as follows:

$$\begin{aligned} \epsilon \rho_g C_{v,g} \frac{\partial T_g}{\partial t} + \rho_g C_{p,g} \frac{\partial (u T_g)}{\partial x} &= \epsilon \lambda_L \frac{\partial^2 T_g}{\partial x^2} - (1 - \epsilon) \rho_p C_s \frac{\partial T_s}{\partial t} \\ &+ (1 - \epsilon) \rho_p \sum_j (-\Delta H_j) \frac{\partial q_j}{\partial t} - \frac{4h_w}{\epsilon \delta_{int}} (T_g - T_w), \end{aligned} \quad (4)$$

where  $C_{v,g}$  is the molar heat at constant volume for the gas phase of the system and the molar heat at constant pressure for the gas phase is  $C_{p,g}$ . The effective thermal conductivity is  $\lambda_L$  and  $C_s$  is the solid specific heat. The quantity  $-\Delta H_i$  is the adsorption heat for the  $j$  component at zero coverage and  $h_w$  is the internal convective heat coefficient between the gas and the column wall. Finally we have  $d_{int}$  as the bed diameter and  $T_w$  as the wall temperature.

We can now define the solid phase energy balance as

$$\rho_p C_s \frac{\partial T_s}{\partial t} = \frac{6h_f}{d_p} (T_g - T_s) + \rho_p (-\Delta H_i) \frac{\partial q_j}{\partial t}, \quad (5)$$

where  $h_f$  is the film heat transfer coefficient between the gas and the adsorbent.

For the column wall the energy and temperature can be expressed as

$$\rho_w C_{p,w} \frac{\partial T_w}{\partial t} = \alpha_w h_w (T_g - T_w) - \alpha_{wi} U (T_w - T_\infty) , \quad (6)$$

where  $\rho_w$  is the column wall density and the column wall specific heat is  $C_{p,w}$ . Also  $\alpha_w$  is the ratio of the internal surface area to the volume of the column wall,  $\alpha_{wi}$  is the ratio of the logarithmic mean surface area of the column shell to the volume of the column,  $U$  is the external overall heat transfer coefficient and  $T_\infty$  is the external air temperature.

The boundary conditions are as follows:

$$x = 0 : \quad \epsilon D_L \cdot \frac{\partial C_i}{\partial x} \Big|_{x^+} = -u (C_j \Big|_{x^-} - C_j \Big|_{x^+}) , \quad (7)$$

$$\epsilon \lambda_L \cdot \frac{\partial T_g}{\partial x} \Big|_{x^+} = -u C C_{p,g} (T_g \Big|_{x^-} - T_g \Big|_{x^+}) , \quad (8)$$

$$x = L : \quad \frac{\partial C_i}{\partial x} \Big|_{x^-} = 0 , \quad (9)$$

$$\frac{\partial T_g}{\partial x} \Big|_{x^-} = 0 , \quad (10)$$

$$x = 0 : \quad u C \Big|_{x^-} = u C \Big|_{x^+} . \quad (11)$$

The initial conditions for the system are as follows:

$$P = P_0 , \quad T_w = T_g = T_s = T_i . \quad (12)$$

In one of the experiments reported in [4] the porous media is pre-treated with  $N_2$  until saturated, subsequently only  $CO_2$  is adsorbed, in which case

$$\begin{cases} C_i = q_i(x, 0) = 0 & \text{for } CO_2 , \\ C_i(x, 0) = \frac{P}{RT_i} q_i(x, 0) = q_{sat} & \text{for } N_2 . \end{cases} \quad (13)$$

Note, these are the conditions as stated in [4] but they are somewhat confusing. The temperature condition at  $x = 0$  involves an undefined parameter  $C$ , indeed in Dantas' paper it also appears in the gas temperature equation. If we assume  $C$  represents some concentration then it is dimensionally incorrect. Comparison with the corresponding term in the heat equation (4) shows that it should be replaced by  $\rho_g$ , which has the correct dimensions. The boundary condition (11) makes little sense whether  $C = \rho_g$  or  $C_i$ . The mysterious product  $u C C_{p,g}$  could simply be written as a heat transfer coefficient. In the following section this issue is resolved.

## 2.2 One-dimensional model

For the solving method of the equation we simplified (1) in order to obtain the following equations:

$$\frac{\partial c}{\partial t} + U \frac{\partial c}{\partial x} = D \frac{\partial^2 c}{\partial x^2} - \rho \frac{(1 - \epsilon) \partial q}{\epsilon \partial t}, \quad (14)$$

$$\frac{\partial q}{\partial t} = K_L (q^* - q), \quad (15)$$

where, if we substitute in the values from the top of the section we find:

$$q^* = \frac{q_m K_0 \epsilon^{-\Delta H/(RT_g)} RT_g c_0 c}{[1 + (K_0 \epsilon^{-\Delta H/(RT_g)} RT_g c_0 c)^n]^{1/n}}.$$

So in non-dimensionalised form we find equation (14) to be

$$\frac{c_0}{\tau} \frac{\partial c}{\partial t} + \frac{U c_0}{L} \frac{\partial c}{\partial x} = \frac{D c_0}{L^2} \frac{\partial^2 c}{\partial x^2} - \frac{\rho(1 - \epsilon) Q}{\epsilon \tau} \frac{\partial q}{\partial t} \quad (16)$$

and

$$\frac{\partial q}{\partial t} = K_L \tau (q^* - q).$$

Table 1: Parameter Values

Parameter	Value
$q_m$	10.05
$K_0$	$7.62e - 10$
$\Delta H$	$-21.84e3$
$K_L$	0.7
$R$	8.314
$T_g$	373
$c_0$	3.67
$\rho$	1140
$\epsilon$	0.52
$D_L$	$1e - 3$
$L$	0.83

For the modelling of the experiments we used the values provided in Table 1. We then looked at the relative size of terms. The following value:

$$K_0 e^{-\Delta H/(RT_g)} RT_g c_0 \approx 10^{-2} \ll 1$$

and so

$$q^* \approx q_m K_0 e^{-\Delta H/(RT_g)} RT_g c_0 .$$

This indicates the scale

$$Q = q_m K_0 \epsilon^{-\Delta H/(RT_g)} RT_g c_0 \approx 0.1 .$$

Assuming the gas is supplied primarily through advection we look to balance terms in the following equation:

$$\frac{\epsilon L}{U\tau} \frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} = \frac{\epsilon D}{UL} \frac{\partial^2 c}{\partial x^2} - \frac{\rho(1-\epsilon)QK_L L}{c_0 U} \frac{\partial q}{\partial t} \quad (17)$$

and

$$\frac{\partial q}{\partial t} = K_L \tau (q^* - q) = K_L \tau (c - q) .$$

The relative size of these terms are:

$$\frac{\epsilon L}{U\tau} \approx 3 ; \quad \frac{\epsilon D}{UL} \approx 0.006 ; \quad \frac{\rho(1-\epsilon)QK_L L}{c_0 U} \approx 1.2 .$$

So the diffusion may be neglected and the equations will be as follows:

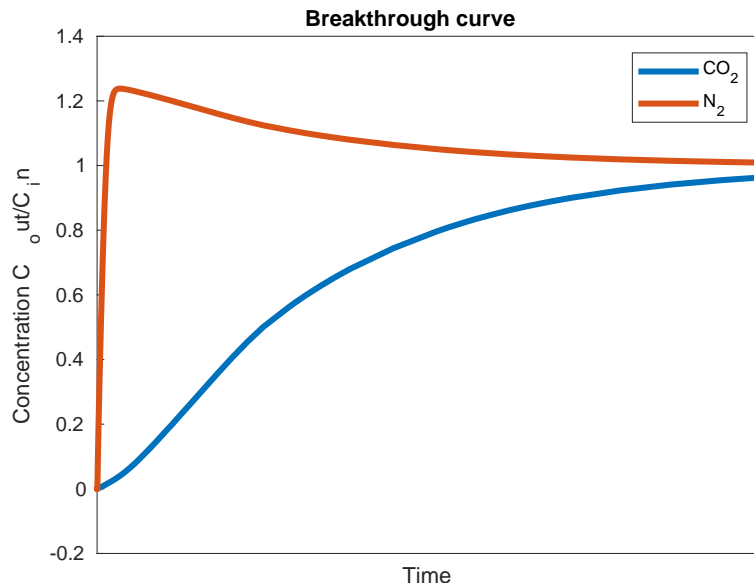
$$\alpha \frac{\partial c}{\partial t} + \frac{\partial c}{\partial x} = -\beta (c - q) ,$$

$$\frac{\partial q}{\partial t} = c - q ,$$

subject to  $c(x, 0) = 0$ ,  $q(x, 0) = 0$ ,  $c(0, t) = 1$ . This provides a simple mathematical model that could be compared against the numerical solution of the full system.

In [4, Fig. 5] it takes between one and six minutes for any CO<sub>2</sub> to escape from the filter. The adsorption equation indicates a grouping,  $K_L \tau \approx \tau$ . This suggests a time-scale on the order of seconds, that is. adsorption is fast. Working on a longer time-scale indicates  $q \approx c$  which then reduces the size of the final term in the concentration equation, permitting a more sensible balance.

## 2.3 Results and discussion



To validate the system we now present a result for the adsorption of a  $CO_2$ ,  $N_2$  system. Parameter values are taken from Dantas [4]. The numerical scheme used MATLAB routines involving the method of lines with a Chebyshev spectral method in space and ODE15s in time. In Figure 1 we present the concentration at the outlet for the experiment where the bed has previously been saturated with  $N_2$ . The curves resemble those in the literature, with  $CO_2$  initially being adsorbed rapidly. The removal of  $CO_2$  leads to a faster flow of nitrogen, hence a higher proportion of nitrogen exits the pipe than enters. The most striking difference between the results presented here and experiments is the fact that breakthrough, when the  $CO_2$  first exits the pipe, occurs almost immediately. In the experiments this can take of the order minutes and so indicates an issue with the sink term in the present case although as will be seen in the following section, there are many possible sources of error.



### 3 Correct problem formulation?

We begin by stating the standard heat equations for a flowing compressible gas and stationary solid:

$$(\rho c)_g \left( \frac{\partial T}{\partial t} + \frac{\partial(uT)}{\partial x} + \frac{1}{r} \frac{\partial(rwT)}{\partial r} \right) = k_g \left( \frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) - p \left( \frac{\partial u}{\partial x} + \frac{1}{r} \frac{\partial(rw)}{\partial r} \right), \quad (18)$$

$$(\rho c)_s \frac{\partial \theta}{\partial t} = k_s \left( \frac{\partial^2 \theta}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \theta}{\partial r} \right) \right) + \rho_q \Sigma_i \Delta H \frac{\partial q_i}{\partial t}. \quad (19)$$

In writing down these equations we allow for radial flow, however since the gas must flow around the solid particles the true velocity is rather complex. Further, the dominant flow will be along the column. For these reasons it is standard to assume plug flow, that is

$$\mathbf{u} = (u(x, r), w(x, r)) \approx (u(x), 0).$$

In fact the assumption on  $w$  is unnecessary since during the averaging process discussed below the integrals involving  $w$  end up using the values

$$w(x, 0) = w(x, R) = 0$$

and hence the average is automatically zero. In contrast to the previous section our velocity is here the interstitial velocity, that is, the actual (average) velocity of the gas in the porous media. We have also made a few (hopefully sensible) notational changes from the previous sections,  $T, \theta$  now represent gas and solid temperatures. Thermal conductivity is  $k$ . The adsorption heat is taken to be a positive constant. Finally the density  $\rho_q$  in the final term of the solid heat equation is that of the adsorbate on the solid which is not necessarily the same as that of the solid. In all previous studies  $\rho_q$  is set to the solid density, here we leave it unspecified. The first equation represents heat flow in the gas, the second equation heat flow in the solid. The solid equation incorporates the energy released during the adsorption. This energy enters the solid since the adsorbate bonds to the solid, thus allowing conductive heat transport. This is in fact an approximation, the correct heat equations should neglect this source term and instead incorporate it in a separate equation describing the growth rate of the solid (the Stefan condition). This may be seen in studies of ablation, see [8] for example. Here, to avoid solving the full moving boundary problem and further complicating the solution, the heat generated is added to the solid since this is a much better conductor than the gas. Heat exchange with the gas is then accounted for by the convective boundary condition between the two components. We write a partial derivative, rather than a full one since  $q_i$  must also be  $x$  dependent (at the inlet gas interacts with the adsorbate immediately, whereas it takes a finite time to interact with material further

down thus indicating a clear  $x$  dependence). We define  $c$  as the *specific heat capacity, measured at constant pressure*.

It is important to realise that these equations only hold within the domain occupied by each material. Since the domain consists of a packed porous media this domain is complex and varies along the column. To treat the equations in any sensible way we must average the equations over a cross-section. Not all cross-sections will have the same fraction of solid to gas so strictly we are thinking in terms of an ensemble average, which would be a typical average over a number of cross-sections.

We now define average quantities

$$\begin{aligned} \epsilon\pi R^2 \tilde{T} &= \int_{r=0}^R \int_{\theta=0}^{2\pi} T r \, dr \, d\theta, \quad \Rightarrow \quad \tilde{T} = \frac{2}{\epsilon R^2} \int_0^R T r \, dr \\ \tilde{\theta} &= \frac{2}{(1-\epsilon)R^2} \int_0^R \theta r \, dr, \quad \tilde{q} = \frac{2}{(1-\epsilon)R^2} \int_0^R q r \, dr, \end{aligned} \quad (20)$$

where  $\epsilon$  is the void fraction. In the  $T$  integral the integrand is only non-zero over an area  $\epsilon\pi R^2$  of the cross-section. The solid (and hence material adsorbed onto the solid) occupies an area  $(1-\epsilon)\pi R^2$ . A formal way to deal with the switch between materials would be to introduce an indicator function  $\chi$ , where  $\chi = 1$  corresponds to the gas phase and  $\chi = 0$  the solid. We could then integrate  $\chi T$ ,  $(1-\chi)\theta$ ,  $(1-\chi)q$  to determine the average values. However, in order to actually incorporate  $\chi$  requires detailed information about the cross-section, such as the shape and roughness of the material. This is obviously a complex function, which varies along the channel. In the absence of such detailed information we simply define the averages as above, where it is understood that the integrals apply over the appropriate region and must then be divided by the appropriate area. We must also take care to account for interchange at the boundaries.

Averaging the gas heat equation leads to

$$\begin{aligned} \frac{2(\rho c)_g}{\epsilon R^2} \int_0^R \left( \frac{\partial T}{\partial t} + \frac{\partial(uT)}{\partial x} \right) r \, dr = & \quad (21) \\ \frac{2k_g}{\epsilon R^2} \int_0^R \left( \frac{\partial^2 T}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) r \, dr - \frac{2}{\epsilon R^2} \int_0^R p \frac{\partial u}{\partial x} r \, dr. \end{aligned}$$

Since  $R$  is a constant the  $t$  and  $x$  derivatives may be taken outside the integral while the diffusion term may be directly integrated

$$(\rho c)_g \left( \frac{\partial \tilde{T}}{\partial t} + \frac{\partial(u\tilde{T})}{\partial x} \right) = k_g \frac{\partial^2 \tilde{T}}{\partial x^2} + \frac{2k_g}{\epsilon R^2} \sum_j r_j \left. \frac{\partial T}{\partial r} \right|_{r_j} - \frac{p}{\epsilon} \frac{\partial u}{\partial x}. \quad (22)$$

The final term accounts for the fact that the gas occupies distinct zones. In a cross-section completely occupied by gas the integral would result in  $rT_r|_0^R$ , that is, the summation requires information at two points  $r_j = 0, R$ . Here we must account for

all other interfaces over the cross-section. If we define the gas phase as occupying  $(r_1, r_2), (r_3, r_4), \dots, (r_{n-1}, r_n)$  (where  $n$  is even) then

$$\begin{aligned} k_g \int_0^R \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) r \, dr &= k_g \sum_{j=1}^n (-1)^j r_j \left. \frac{\partial T}{\partial r} \right|_{r_j} \\ &= \sum_{j=1}^n (-1)^{j+1} h_j r_j (T - \theta)|_{r_j}, \end{aligned} \quad (23)$$

where we have assumed convective heat exchange at each boundary,

$$-k_g \frac{\partial T}{\partial r} = h(T - \theta). \quad (24)$$

If the outer boundary  $r_n = R$  then  $\theta$  is replaced by  $T_w$  in the boundary condition there and  $h = h_{wg}$ . Assuming  $T$  and  $\theta$  may be approximated by their average values we now write

$$\begin{aligned} k_g \int_0^R \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) r \, dr &= (\tilde{T} - \tilde{\theta}) \sum_{j=1}^{n-1} (-1)^{j+1} h_j r_j - h_{wg} R (\tilde{T} - T_w), \\ &= R \bar{h}_{gs} (\tilde{\theta} - \tilde{T}) + R h_{wg} (T_w - \tilde{T}), \end{aligned} \quad (25)$$

where the composite heat transfer coefficient is defined as

$$R \bar{h}_{gs} = \sum_{j=1}^{n-1} (-1)^j h_j r_j.$$

The heat equation may now be written

$$(\rho c)_g \left( \frac{\partial \tilde{T}}{\partial t} + \frac{\partial(u\tilde{T})}{\partial x} \right) = k_g \frac{\partial^2 \tilde{T}}{\partial x^2} + \frac{2\bar{h}_{gs}}{\epsilon R} (\tilde{\theta} - \tilde{T}) + \frac{2h_{wg}}{\epsilon R} (T_w - \tilde{T}) - \frac{p}{\epsilon} \frac{\partial u}{\partial x}. \quad (26)$$

Applying the same approach to the solid heat equation leads to

$$\begin{aligned} (\rho c)_s \frac{\partial \tilde{\theta}}{\partial t} &= k_s \frac{\partial^2 \tilde{\theta}}{\partial x^2} + \frac{2\bar{h}_{gs}}{(1-\epsilon)R} (\tilde{T} - \tilde{\theta}) + \frac{2h_{ws}}{(1-\epsilon)R} (T_w - \tilde{\theta}) \\ &\quad + \rho_q \Sigma_i \Delta H \frac{\partial \tilde{q}_i}{\partial t}. \end{aligned} \quad (27)$$

When the gas and solid are taken to have different temperatures this is termed the ‘non-equilibrium thermal model’ in [7]. If we set  $\tilde{T} = \tilde{\theta} = \tilde{\phi}$  then the ‘equilibrium thermal model’ is found. A single equation for  $\tilde{\phi}$  is obtained by adding  $\epsilon$  times equation (26) to  $(1 - \epsilon)$  times equation (27):

$$\begin{aligned} (\rho c)_p \frac{\partial \tilde{\phi}}{\partial t} + \epsilon (\rho c)_g \frac{\partial(u\tilde{\phi})}{\partial x} &= k_p \frac{\partial^2 \tilde{\phi}}{\partial x^2} + \frac{2(h_{wg} + h_{ws})}{R} (T_w - \tilde{\phi}) \\ &\quad + (1 - \epsilon) \rho_q \Sigma_i \Delta H \frac{\partial \tilde{q}_i}{\partial t} - p \frac{\partial u}{\partial x}, \end{aligned} \quad (28)$$

where the subscript  $p$  denotes the porous medium,

$$z_p = \epsilon z_g + (1 - \epsilon) z_s .$$

Certain studies also model the wall temperature. If we define the average

$$\tilde{T}_W = \frac{2}{\epsilon[(R + t_W)^2 - R^2]} \int_R^{R+t_w} T_W r \, dr , \quad (29)$$

where  $t_W$  is the wall thickness, then the averaged heat equation in the wall gives

$$(\rho c)_W \frac{\partial \tilde{T}_W}{\partial t} = k_W \frac{\partial^2 \tilde{T}_W}{\partial x^2} + h_{Wa} \frac{2(R + t_w)}{[(R + t_w)^2 - R^2]} (T_a - \tilde{T}_W) \quad (30)$$

$$- h_W \frac{2R}{[(R + t_w)^2 - R^2]} (\tilde{T}_W - \tilde{\phi}) , \quad (31)$$

where subscript  $a$  denotes the ambient value. The value  $\tilde{T}_W$  then replaces  $T_W$  in previous equations.

The concentration equation follows in a completely analogous manner. Within the gas phase the concentration of any given component is described by the standard diffusion equation

$$\frac{\partial C_i}{\partial t} + \frac{\partial(uC_i)}{\partial x} + \frac{1}{r} \frac{\partial}{\partial r} (r w C_i) = D \left( \frac{\partial^2 C_i}{\partial x^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial C_i}{\partial r} \right) \right) . \quad (32)$$

We average this over the cross-section, noting that the gas occupies an area  $\epsilon \pi R^2$ ,

$$\frac{\partial \tilde{C}_i}{\partial t} + \frac{\partial(u\tilde{C}_i)}{\partial x} = D \frac{\partial^2 \tilde{C}_i}{\partial x^2} + \frac{2}{\epsilon R^2} \sum_j r_j D \frac{\partial C_i}{\partial r} \Big|_{r_j} . \quad (33)$$

Now there is no exchange at the wall since the flux is proportional to  $C_r(R, z, t) = 0$ .

Due to the complex nature of the adsorbing surfaces the exchange must also be treated in an average manner. The rate at which a component is adsorbed must balance the flux to the surface. Summing all surfaces located at  $r_j$  this may be expressed as

$$(1 - \epsilon) \pi R^2 \rho_q \frac{\partial \tilde{q}_i}{\partial t} = \sum_{j=1}^{n-1} (2\pi r_j) D \frac{\partial C_i}{\partial r} \Big|_{r_j} . \quad (34)$$

The average concentration,  $\tilde{C}_i(x, t)$ , is therefore described by

$$\frac{\partial \tilde{C}_i}{\partial t} + u \frac{\partial \tilde{C}_i}{\partial x} = D \frac{\partial^2 \tilde{C}_i}{\partial x^2} + \frac{1 - \epsilon}{\epsilon} \rho_q \frac{\partial \tilde{q}_i}{\partial t} . \quad (35)$$

The coefficient  $D$  is an 'effective axial dispersion coefficient' which lumps all mechanisms which contribute to axial mixing (for example, molecular diffusion or turbulent mixing as flow passes round particles and recombines) [11, pp 208, 209]. It may be assumed to have the same value for each component.

Finally, consider the boundary conditions on concentration and temperature. At the inlet the gas has concentration  $C_{i0}$  of component  $i$ , just inside the column it moves with velocity  $u$  and is adsorbed by the porous media. The velocity just outside the column will be the same as that just inside, and occupying the same area since any gas above a solid section will have zero velocity and so not contribute to the gas flux. Balancing the flux of concentrate across the boundary  $x = 0$  gives

$$u(0^-)C_i(0^-, t) = u(0^-)C_{i0} = u(0^+)\tilde{C}_i(0^+, t) - D\frac{\partial\tilde{C}_i(0^+, t)}{\partial x}. \quad (36)$$

At the outlet  $x = L$  a similar balance occurs

$$u(L^-)\tilde{C}_i(L^-, t) - D\frac{\partial\tilde{C}_i(L^-, t)}{\partial x} = u(L^+)C_i(L^+, t). \quad (37)$$

At this boundary it seems reasonable to assume that instantaneous mixing with the ambient gas does not occur at  $x = L^+$  and so  $\tilde{C}_i(L^-, t) \approx C_i(L^+, t)$ . The outlet condition then becomes

$$\frac{\partial\tilde{C}_i(L^-, t)}{\partial x} = 0. \quad (38)$$

For the temperature we may carry out a similar balance, in this case for the energy flux

$$u(0^-)(\rho c)_g T(0^-, t) = u(0^-)(\rho c)_g T_a = u(0^+)(\rho c)_g \tilde{T}(0^+, t) - k\frac{\partial\tilde{T}(0^+, t)}{\partial x}. \quad (39)$$

[This unravels the mystery of  $C$  in Dantas,  $C = \rho_g$ . Note,  $k/(u(\rho c)_g L) \ll 1$  so it would seem sensible to neglect the axial conduction term, unless a very sharp boundary layer is expected.]

At the outlet we impose

$$\frac{\partial\tilde{T}(L^-, t)}{\partial x} = 0. \quad (40)$$

### 3.1 Comparison with previous models

Comparing the new equations with those of [4] highlights some clear differences. First, consider the solid heat equation. Dantas' version, equation (5), neglects diffusion through the solid. This is in keeping with the literature in general, see [2, 7, 12] for example. The derivation of this equation stems from a simple energy balance

for a single particle provided in [11] which is then generalised to the whole porous solid. For this reason there is no diffusion term to account for heat transfer between contacting particles. The heat exchange with the wall is missing and the gas exchange term has a different coefficient. This is not such an issue, the difference will be absorbed into the experimentally determined heat transfer coefficient. Finally the source term in (5) should sum all contributions.

The gas heat equation (4) contains the specific heats at both constant temperature and constant volume. If the  $\partial T_s/\partial t$  term is removed then the exchange between gas and solid reappears. The summation term makes it clear that the source term has been incorrectly written in the solid equation. The gas diffusion term is included where the conductivity is written as  $\lambda_L$ .

The void fraction has a typical value  $\epsilon = 0.5$ , so both gas and solid occupy approximately the same volume. Values for the thermal conductivity of various forms of activated carbon are given in [6], typically  $k_s \approx 0.4\text{W/m K}$ . For air  $k_g \approx 0.034\text{W/m K}$ . Since the solid conductivity is an order of magnitude greater than that of the gas, and they occupy the same volume it is surprising that the solid conduction is neglected while that in the gas is retained. Commonsense also indicates that gas advection must dominate over gas diffusion except for in extremely slow flows, no doubt non-dimensionalisation will verify this, hence gas diffusion is most likely negligible. Whereas with the solid there is no advection but the contact between particles provides an excellent route for heat transfer and this mechanism should be retained.

The sink term in previous models assume the density of adsorbed carbon matches that of the solid,  $\rho = 1140\text{kg/m}^3$ . In fact it is much lower,  $\rho_q \approx 300\text{kg/m}^3$ , see [1]. This means that the removal of  $\text{CO}_2$  will be too great, unless an incorrect adsorption rate is adopted to account for this. Similarly the heat increase will be too high unless it is adjusted for.

Authors often move between advection of the form  $(uC)_x$  and  $uC_x$ . The latter requires an assumption that only trace amounts of material are removed from the gas and so  $u$  may be treated as constant. In many examples around 20% of the gas is removed immediately, calling this assumption into question. However, it is clearly a sensible limit for preliminary studies.

## 4 Conclusion

During the MISG a set of equations was studied based on the 'seminal' work of Dantas et al [4]. Preliminary work led to a numerical solution which exhibited similarities to that published in the literature. A great deal of knowledge was also gained into the basics of carbon capture, such as the fact that all carbon is removed for the first few minutes in these devices. However, there appears to be a great number of published papers in this field, including reviews, with an incorrect set of governing equations. Although these equations can match experimental data (they

are after all simply advection-diffusion equations modelling an advection-diffusion experiment) the errors mean that the obtained parameter values will be incorrect. It will then prove impossible to scale up experiments, based on the incorrect equations and parameter values.

In the second half of this report we derived the correct equations describing carbon capture in a packed column. This directly answered the first question posed to the study group

*Can we improve current/develop new models?*

The new model will now form the basis for further studies. Once this is understood it should be possible to then determine improved strategies for carbon capture.

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