

EFFICIENT MODELLING OF FAST CYCLE ADSORPTION FOR THE SEPARATION OF CO₂

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Introduction

The urgency behind finding economically viable methods of separating and capturing CO₂ has never been greater [1]. A significant improvement in separation efficiency in the case of, for example, emissions from power stations, where separation represents 50% of the total sequestration cost, would be a major breakthrough [2]. Currently all commercial CO₂ separations are performed using an expensive chemical absorption process with a MEA solvent [3]. Fig. 1 below shows the variety of alternatives available and their relative merits.

Method	Comment	Effective?	Operating Cost	Capital Cost
<i>Absorption</i>	Proven technology - low risk	Yes	High	High
<i>Membranes</i>	Not useful alone	No	Low	High
<i>Cryogenics</i>	Only for high concentrations	No	Low	High
<i>PSA</i>	Low throughput & high energy cost	Yes	High	Low

Fig. 1. CO₂ separation technologies [4].

In this study we will consider how the PSA option can be made more attractive. A traditional PSA system consists of many beds packed with adsorbent, which preferentially adsorbs CO₂ at pressure. By cyclically varying the pressure over a bed CO₂ can be made to adsorb and desorb as required. A four bed system is shown below in fig. 2.

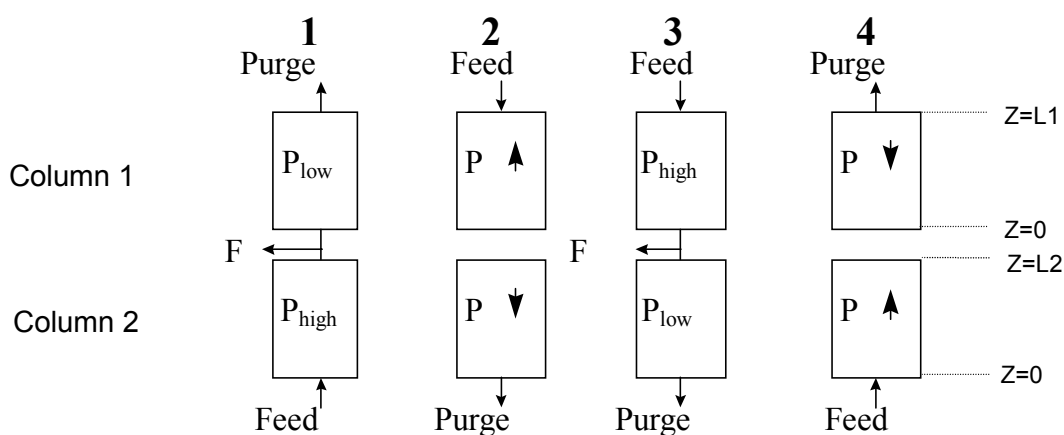


Fig. 2. A schematic diagram of a simple Skarstrom PSA cycle [5]

To enhance the performance of a PSA system improvements can be made by using structured packings, such as parallel passage contactors [6], which reduce pressure drop. Furthermore the high energy usage associated with gas compression can also be addressed if a dual piston driven PSA system can be utilised [7]. Such a technology employs coupled pistons at each end of a single column to affect pressure changes; expansion in one piston can help drive compression in the other. Savings are made both in terms of energy and fixed costs. In this study we address specifically how accurate and computationally efficient modelling of a PSA system operating at fast cycle times can be achieved, since by increasing the rate of cycling major increases in throughput can also be achieved.

Objective

Modelling a PSA system is inherently complex and hence our aim is to find valid simplifying assumptions that reduce complexity but do not compromise accuracy. One such assumption is the Linear Driving Force (LDF) model, used to represent mass transfer in adsorption systems. The LDF model, derived by Glueckauf [8], may be used to replace the diffusion equation in which concentration depends on adsorbent particle radius or plate thickness. A lumped mass transfer coefficient can then be used to find an averaged concentration, which is independent of adsorbent dimensions.

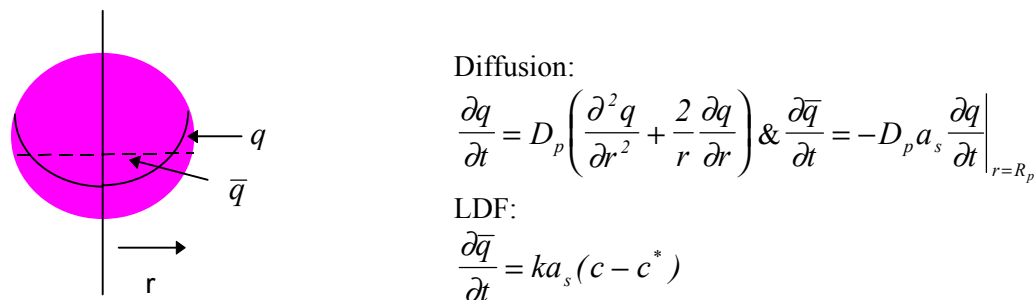


Fig 3. Average and distributed concentration profiles in a spherical particle.

When cyclic adsorption processes are considered, the lumped parameter is found to vary with cycle time [9-11]. Concentrations vary cyclically both within the particle and in the bulk. Since in the piston driven system, our interest lies in optimising the piston movements to achieve maximum separation we must obtain an accurate prediction of the bulk concentration profile. Therefore our aim, in conjunction with previous studies, is to develop an LDF model, with cycle time dependent parameters where necessary, which may be used with confidence in place of the diffusion model in the design of any fast cycle adsorption process at cyclic steady state.

Approach

In order to achieve our objectives we have investigated three approaches; a pure numerical simulation, a frequency response study to analytically derive the solution to the cyclic steady state problem and full analytical solution of the dynamic equations. The latter of these techniques was used to look at transient behaviour, which will be examined in a later communication. The approach used by Suzuki [10] involves matching the average adsorbed concentration in a single particle, subject to instantaneous equilibration at the surface, using the LDF and the diffusion model at

cyclic steady state . A parameter, η , is used to evaluate the LDF coefficient, $ka_s = \eta D_p / R_p^2$, as a function of the dimensionless half-cycle time, a .

Since our interest lies in adsorbed and bulk concentrations, we tested the LDF approximation using a perfectly mixed cell, which represents the limiting behaviour of a full column dispersed plug flow model. The model remains simple but allows analysis of the relevant concentration profiles. To obtain a cyclic process a sinusoidal inlet concentration is assumed.

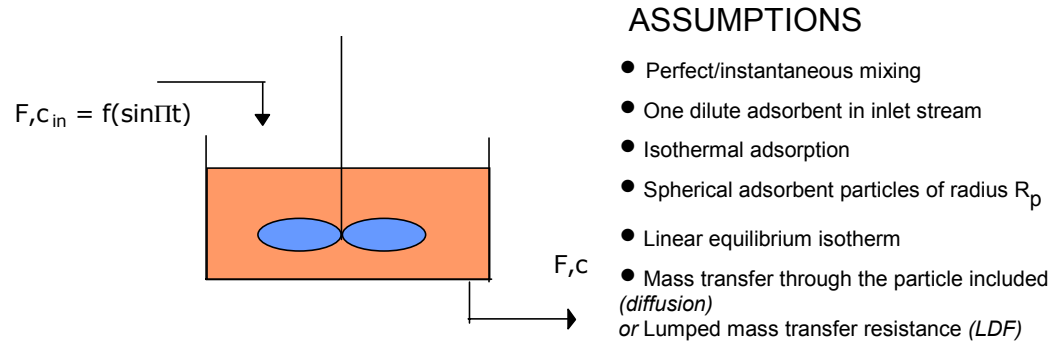


Fig.4. Simple CSTR model

Dimensionless mathematical models were derived and solved computationally, using gPROMS [12], to find the solutions for the bulk and adsorbed concentrations using the diffusion and LDF models.

Mass balance in fluid:

$$\psi \frac{dC}{d\tau} + \frac{d\bar{Q}}{d\tau} = 3L(C_{in} - C)$$

Mass balance in solid -

LDF:

$$\frac{d\bar{Q}}{d\tau} = \eta(\bar{Q} - Q_{eq})$$

Cyclic inlet concentration:

$$C_{in} = \frac{1}{2} \left(1 + \sin \frac{\pi\tau}{a} \right)$$

Mass balance in solid - Diffusion:

$$\frac{\partial Q}{\partial \tau} = \left(\frac{\partial^2 Q}{\partial \xi^2} + \frac{2}{\xi} \frac{\partial Q}{\partial \xi} \right) \text{ where } \frac{d\bar{Q}}{d\tau} = 3 \frac{\partial Q}{\partial \xi} \Big|_{\xi=1} \text{ and}$$

$$\bar{Q} = 3 \int_0^1 Q \xi^2 d\xi$$

Boundary conditions:

$$\frac{\partial Q}{\partial \xi} \Big|_{\xi=0} = 0 \text{ and } Q \Big|_{\xi=1} = C$$

Fig. 5 Dimensionless CSTR models

Additionally a technique was employed by which direct calculation of cyclic steady state cycle could be obtained. This involved removing the automatic time domain and distributing equations and variables over our own domain, defined by the dimensionless cycle time. To obtain one cycle of steady state behaviour periodicity conditions were set (by definition, this implies the value of the parameters were the same at the end and beginning of the cycle [13,14]).

The numerical approach showed that using Suzuki's method the adsorbed phase concentration could be approximated while a phase shift was present in the calculated gas phase concentration.

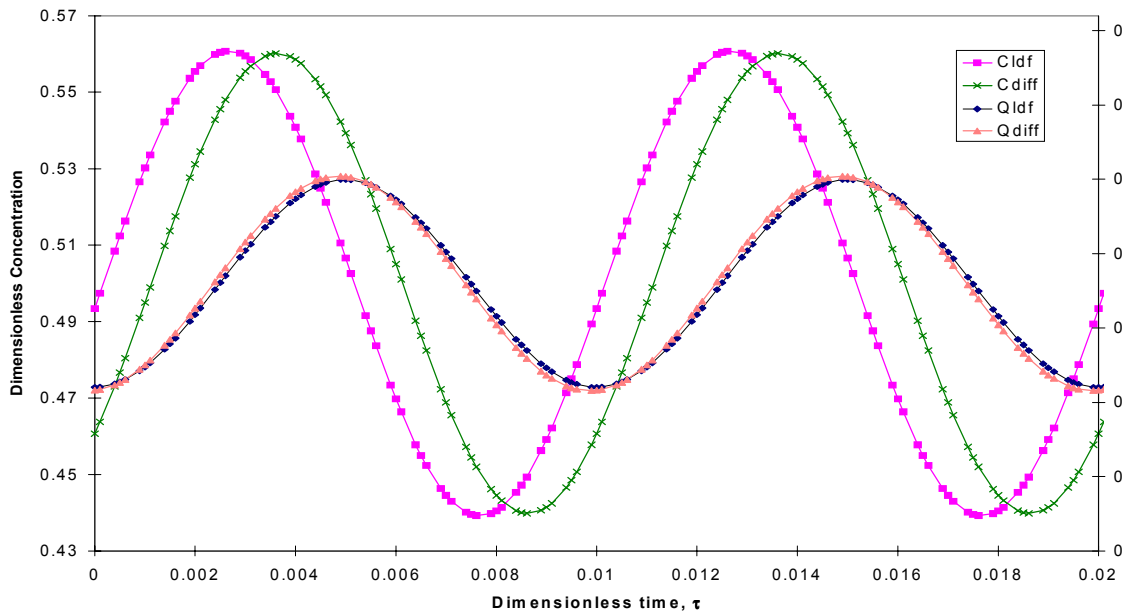


Fig. 6. Comparison between adsorbed and bulk concentration profiles using diffusion and Suzuki-corrected LDF models ($a=0.005$)

We therefore proceeded using the frequency response method to derive the analytical solution to the cyclic steady state problem.

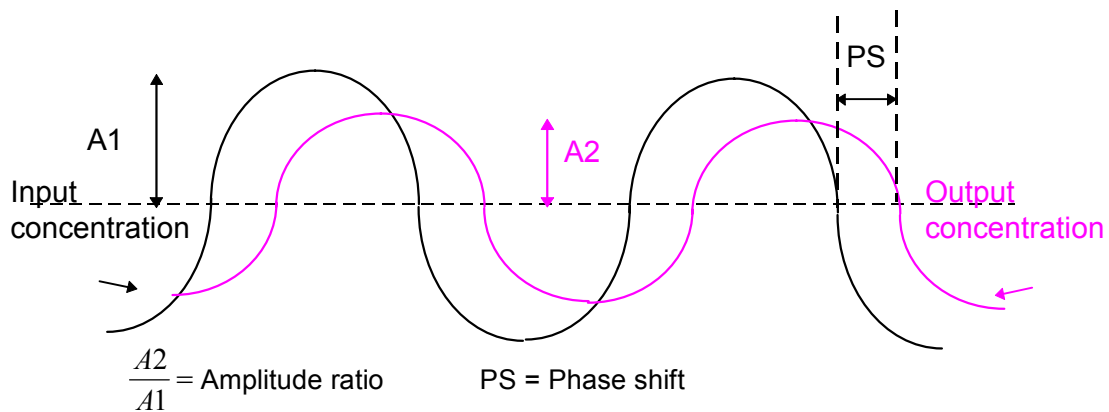


Fig. 7 Steady state cyclic concentration profiles and the relevance of the frequency response technique.

In this study the output and input waves of fig. 7 represent either external or adsorbed concentrations, where the output curve is given by the solution to the LDF or diffusion equation at steady state. For the single particle model, we calculated the parameter η needed to match the amplitude ratio, η_{AR} , or the phase shift, η_{PS} , and the results are shown in figure 8.

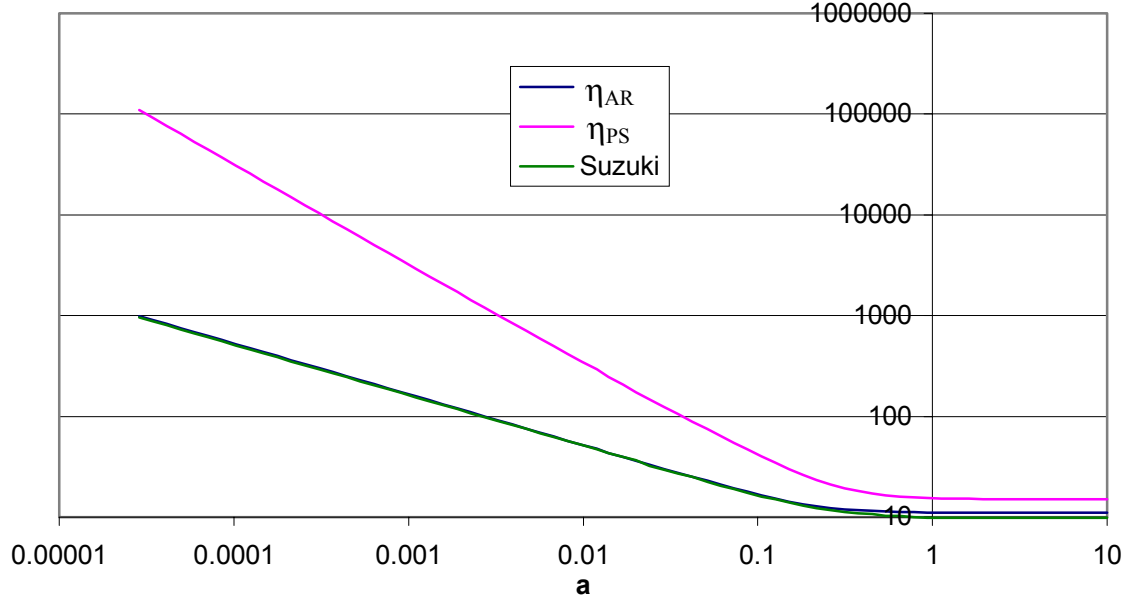


Fig 8. Correction factor divergence.

From above we see that as cycle times become shorter, the η values diverge. Interestingly the η_{AR} profile is very similar to Suzuki's [10] solution for η , both showing a dependence on $1/\sqrt{a}$. The small difference between the two similar profiles can be attributed to the type of perturbation used to affect cyclic behaviour; Suzuki [10] used a square wave perturbation whereas we use a sinusoidal variation. The η_{PS} profile, for fast cycle times, shows a dependence on $1/a$.

What is clear is that, as noted by Rodrigues [15], solving for η using amplitude ratio and phase shift leads to two different values, where either the phase shift or amplitude are matched, but not both. Simply adjusting the mass transfer coefficient will not lead to full matching. We therefore investigated an alternative formulation of the LDF model capable of resolving this difficulty.

Results

Using the frequency response method we can derive a new additional correction parameter as

$$\eta' = \frac{\bar{Q}_{ldf}}{Q_{diff}} = \frac{a\eta}{(a\eta + i\pi) \frac{3a}{i\pi} \left(\sqrt{\frac{i\pi}{a}} \coth \sqrt{\frac{i\pi}{a}} - 1 \right)}$$

This new parameter when combined with the mass transfer correction factor based on matching the phase shift for the single particle case yields a LDF equivalent model capable of correctly representing the amplitude ratios and phase shifts of both adsorbed and gas phase concentrations.

To have an insight into the physical meaning of the new parameter η' we have to consider the two the limiting cases: for $a \gg 1$ then Glueckauf's [9] limit is found;

$$\eta = 15 \text{ and } \eta' = 1; \text{ for } a \ll 1 \text{ then } \eta' = \frac{1}{3} \sqrt{\frac{\pi}{2a}}.$$

The parameter η' is the ratio of the effective volumes. Thus the inverse of η' gives an indication of the use of the adsorbent material. For $a \ll 1$, regardless of the geometry, the dimensionless penetration depth is $\delta = \sqrt{\frac{2a}{\pi}}$ and $\frac{1}{\eta'} = 3\sqrt{\frac{2a}{\pi}} = \frac{4\pi R_p^2 \delta R_p}{\frac{4}{3}\pi R_p^3} = 3\delta$

To confirm the validity of the new approach we have extensively tested it in the computational CSTR model and excellent results are found. A representative example is shown in figure 9.

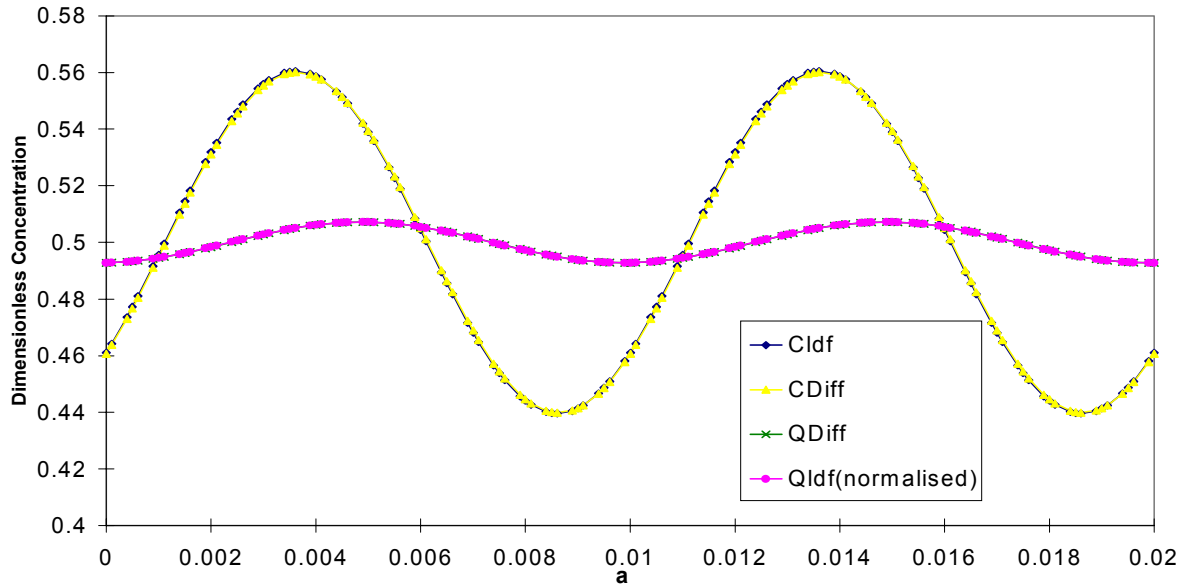


Fig.9. Comparisons for adsorbed and bulk concentrations using diffusion and corrected LDF models for $a = 0.005$ ($\eta = 628.32$, $\eta' = 5.91$)

To verify the applicability of the method to the simulation of a full PSA process we have also considered the “heatless drier“ of Raghavan et al. [16].

The PSA model

Initially concentration profiles were generated for the diffusion model and the LDF models using various values of η to try and achieve matching; the same technique Raghavan [16] employed.

The results shown in fig.10 below reveal that even after 55 half cycles cyclic steady state is not reached. Furthermore, calculating the penetration depth shows that the particles are only penetrated up to a dimensionless depth of 0.02. This means that for an accurate representation of the diffusion model we need to have a large number of radial collocation points, as can be seen from the difference between the two solutions of the diffusion equations.

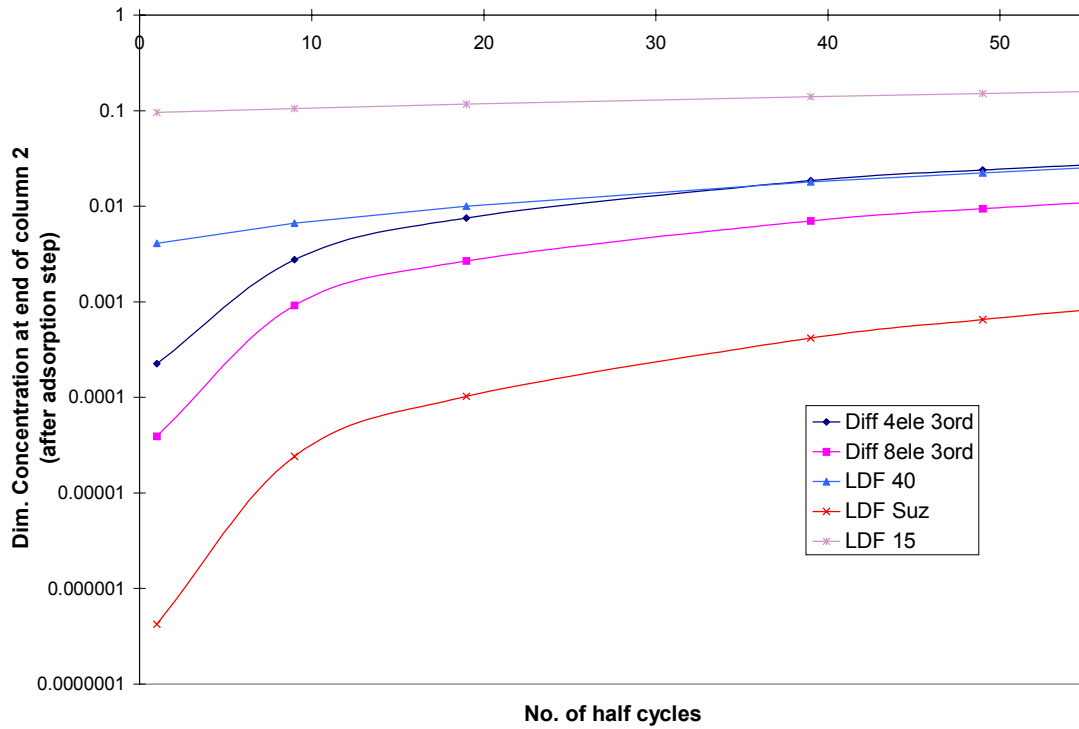


Fig. 10 Product concentration profiles from column 2 ($a = 0.00076$) for 55 half cycles

Extending the simulation to over 300 cycles we found extremely good agreement at the true steady state, between the diffusion model and the LDF with the predicted correction factors. For comparison we also include the solution of the LDF model using Suzuki's [10] parameter and the value suggested by Raghavan et al. [16].

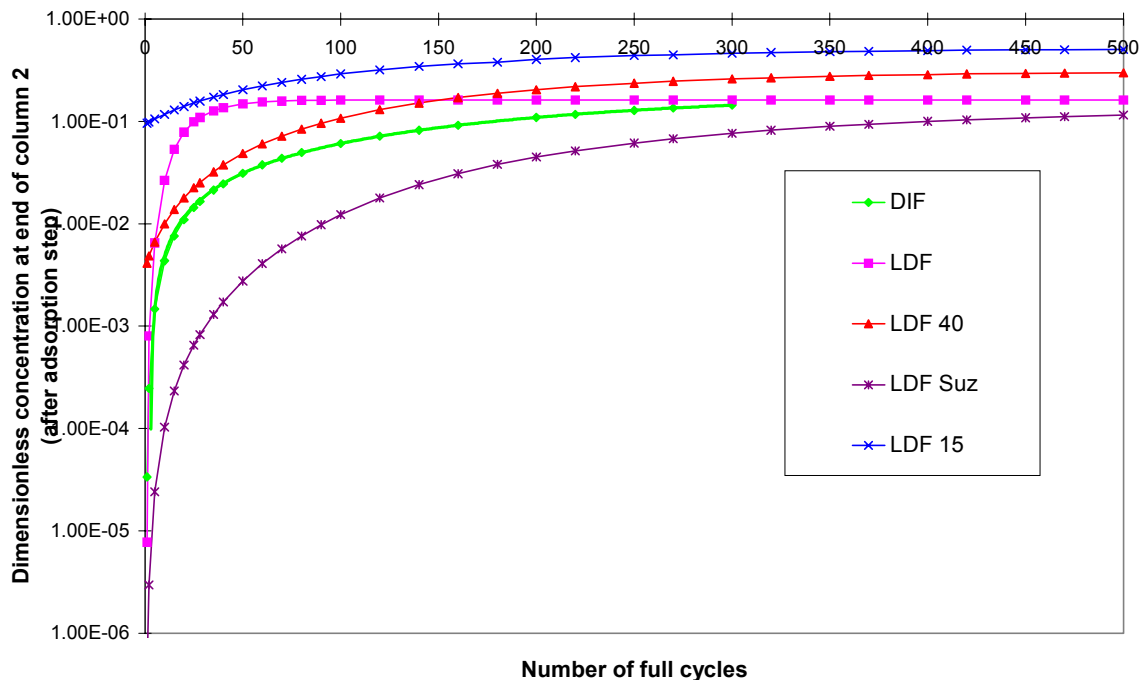


Fig. 11 Product concentration profiles from column 2 ($a = 0.00076$) for 500 complete cycles ($\eta = 4.21 \times 10^3$, and $\eta' = 15.452$)

An interesting point is that the number of cycles required to reach cyclic steady state with the proposed LDF approximation is, in this case, an order of magnitude less than the full diffusion model, therefore the numerical problem is reduced both in terms of the number of equations to solve and also in the time needed for the simulation to converge to the cyclic steady state solution.

	LDF PSA model	Diffusion PSA model
Discretisation across column axis	3 rd order 10 element orthogonal collocation	3 rd order 10 element orthogonal collocation
Discretisation across particle radius	-----	3 rd order 6 element orthogonal collocation
Number of variables	252	2546
Time to simulate 30 cycles*	~ 2 ¹ / ₂ hours	~ 125 hours

Fig.12. Comparison between LDF and diffusion simulations (the same computer was used for both runs)*

The indicative results shown above demonstrate that even with a fairly conservative number of elements across the particle radius the number of variables in the diffusion case is ten times that of the LDF case. The result is that the simulation time is hugely increased.

Benefits

This study has shown the clear advantages of using the two parameter corrector approach as applied to the LDF equation to model fast cycle adsorption processes. These can be summarised as follows.

- Using the LDF model and employing the two derived coefficients external concentrations at steady state can be found with a high degree of accuracy.
- Finding and applying the correctors is simple. The modeller can either use the derived correlations at the fast cycle time limit or, for increased accuracy, full graphical solutions.
- Since the correctors have proven to depend on cycle time alone, they are non-system specific and are equally valid for a single particle or a PSA system.
- The geometry of adsorbent is also of no issue as it may be incorporated into the mathematical model and the correction factors changed respectively.
- A cyclic adsorption system may be subjected to various types of perturbation. We have been able to show that the two parameter corrector approach may be used for both sinusoidal (CSTR case) and square wave (PSA case) perturbations.
- Including more than one resistance to mass transfer across an adsorbent particle is easily achieved. Raghavan et al.[16] suggested resistance to mass transfer occurs in the external fluid film and in the particle macropores. This premise was incorporated into a lumped coefficient for the PSA case and correction factors were applied accordingly.

- The equilibrium or volume corrector is very useful for calculating penetration depth. In terms of modelling this meant we could ensure enough collocations points were distributed across the particle to give accurate results. In a commercial sense the implication is that particles or slabs may be developed with outer coatings of costly adsorbent, the thickness of the penetration depth and inexpensive inert centres.
- Using the LDF model gives immensely improved computational efficiency. In the PSA case the corrected model is 50 times faster than the diffusion case.

All of these benefits can be taken forward into developing a dual piston driven PSA system for CO₂ separations. We anticipate that our findings regarding the LDF model will prove an extremely powerful modelling tool in the study of the design and optimisation of PSA processes.

Future Activities

The long term aim of this project is to establish an experimentally verified mathematical representation of a dual piston driven pressure swing adsorption system. Therefore the next step is to introduce pressure changes induced by piston movement into the model. Additionally the issue of large pressure drops, created by randomly packed columns, is to be addressed by investigating the feasibility of parallel passage contactors. Studies by Farooq [17] and Ruthven [6] are encouraging but further work is needed to refine simulation accuracy.

Heat effects are a major issue for investigation. Studies undertaken to date have shown inconclusive evidence of whether isothermal models are adequate for representing behaviour of fast cycle adsorption systems. In the case of the piston driven system, heat effects may be prominent since not only must the heat of adsorption be considered but also the heat due to friction in the pistons. Further work will be designed to reveal whether heat effects are significant and therefore whether alterations are needed to the derived correction factors for mass transfer. To attempt to confirm all the findings in this study and test hypothesis regarding heat, experimental work will be undertaken using a dual piston driven system.

References

1. US Department of Energy. **Working paper on carbon sequestration science and technology. Chap. 2 Separation and capture of carbon dioxide.** February, 1999.
2. Wildenborg A.F.B., Floris F., van Wees J.D., Hendriks C. **Costs of CO₂ sequestration by underground storage.** Paper presented at the *Special Session on CO₂*, EAGE Conference, Glasgow UK, May 2000.
3. Herzog. Howard, **An Introduction to CO₂ Separation and Capture Technologies.** August 1999.
4. IEA Greenhouse Gas R&D Programme, **Carbon Dioxide Capture from Power Stations.**
5. Ruthven D.M., Farooq S., Knaebel K.S. **Pressure swing adsorption.** VCH, New York, 1994.
6. Ruthven D.M., Thaeron C. **Performance of a parallel passage adsorbent contactor.** *Separation & Purification Technology*, 1997, 43-60.

7. G.E. Keller, C-H.A.Kuo. **Enhanced air separation by selective adsorption**. US Patent 4,354,859, assigned to Union Carbide Corporation, 1982.
8. Glueckauf, E. & Coates, J.I.E. **Theory of chromatography, Part 4. The influence of incomplete equilibrium on the front boundary of chromatogram and on the effectiveness of separation**. *J. Chem. Soc.*, 1947, 1315-1321
9. Glueckauf, E. **Theory of chromatography, Part 10. Formula for diffusion into spheres and their application to chromatography**. *Trans. Faraday Soc.*, 1955, **51**, 1540-1511
10. Nakao, S. & Suzuki, M. **Mass transfer coefficient in cyclic adsorption and desorption**. *J. Chem. Eng. Japan*, 1983, **16**, 114-119
11. Alpay, E & Scott, D.M. **The linear driving force model for fast-cycle adsorption and desorption in a spherical particle**. *Chem. Eng. Sci.*, 1992, **47**, 499-502
12. Process Systems Enterprise Ltd., **gPROMS Advanced User Guide**, London, 1999.
13. Nilchan S, Pantelides CC, **On the optimisation of periodic adsorption processes**, *Adsorption*, 1998, **4**, 113-147.
14. Schmidt, F.W & Willmott, A.J, **Thermal Energy Storage and Regeneration** (Chapter 6), Hemisphere Publishing Corporation, New York, 1981.
15. Rodrigues, A.E. & Dias, M.M. **Linear driving force approximation in cyclic adsorption processes: Simple results from system dynamics based on frequency response analysis**. *Chem. Eng. & Proc.*, 1998, **37**, 489-502
16. Raghavan, N.S., Hassan, M.M. & Ruthven, D.M. **Numerical Simulation of a PSA System Using a Pore Diffusion Model**. *Chem. Eng. Sci.*, 1986, **41**, 2787-2793
17. Farooq, S., Tharon, C. & Ruthven, D.M. **Numerical simulation of a parallel passage piston-driven PSA unit**. *Separation & Purification Technology*, 1998, **13**, 181-193

Nomenclature

a	dimensionless cycle time	q	adsorbed phase concn. ($F(r)$)
\bar{A}_1	input amplitude	\bar{q}	average adsorbed phase concn
\bar{A}_2	output amplitude	$Q, Q_{..}$	dimensionless adsorbed concns.
a_s	external surface area per particle	r	radial direction
c	bulk/external concentration	R_p	particle radius
		t	time
c^*	equilibrium (external) concn.	Z_1, Z_2	axial direction
C_{in}	inlet concentration ($f(t)$)	Z, Z_1, Z_2	dimensionless axial direction
$C_{in}, C_{eq..}$	dimensionless bulk concentrations		
D_p	homogenous particle diff. coeff.	δ	penetration thickness
F	flowrate	η	Suzuki correction factor (m.t)
i	imaginary number	η'	correction factor (eqm)
k	lumped mass transfer coeff.	η_{AR}	correction factor from amplitude ratio (m.t)
L	dimensionless parameter	η_{PS}	correction factor from phase shift (m.t.)
	$FR_p^2/3V_sD_pK$		
L_1, L_2	column length	τ	dimensionless time
PS	phase shift	ω	frequency
P_{high}, P_{low}	high/low pressure in PSA process	ξ	dimensionless radial direction
		ψ	dimensionless parameter
			$\epsilon/(1-\epsilon)K$

Acknowledgements: The financial contributions from the EPSRC, BP and The Leverhulme Trust are gratefully acknowledged.