Measuring the liquid-solid mass transfer coefficient in packed beds using $T_2 - T_2$ relaxation exchange NMR

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Abstract

Direct measurement of the liquid-solid mass transfer coefficient in packed beds is achieved using $T_2 - T_2$ relaxation exchange NMR. This method directly probes molecular exchange between intra- and inter-pellet fluid, rather than requiring a net flux between phases as in conventional methods. Mass transfer coefficients measured using the NMR method are compared with literature values and two widely used correlations. For Reynolds number, Re, less than 0.2, the mass transfer coefficients measured using NMR show excellent agreement with the correlations over the flow conditions for which they were developed. The approach also enables the quantification of mass transfer in the limit of, and at, zero flow. At $Re = 0$, the Sherwood number in packed beds with voidage of 0.41 determined by NMR is found to approach 9, in good agreement with previously reported results, but significantly greater than that predicted by extrapolating well-known correlations beyond their range of validity to $Re = 0$.

1. Introduction

In packed bed operations, mass transfer from the bulk fluid to the pellet surface is an important consideration, and mass transfer limitations must be quantified to design and model packed beds. Due to the random structure of packed beds, and the resulting complex hydrodynamics, rather than solving the advection-diffusion equation to quantify the mass transfer in the bed, the mass transfer is commonly described using an averaged transport coefficient. The fluid-solid mass transport coefficient, k, is a proportionality constant linking the flux between the pellet surface and bulk fluid with the driving force producing the flux (typically the concentration difference between the pellet surface and the bulk).

Due to its importance, mass transfer in packed beds has been extensively studied since it was first investigated over 75 years ago (Gamson et al., 1943). Despite this, directly obtaining k for the specific fluids, pellets, and conditions used in real processes can be challenging. Numerous methods to measure k have been developed, where most commonly measurements are made on a simplified model system that displays mass transfer resistance (*ex situ* methods). Examples include dissolution methods (Kumar et al., 1977; Williamson et al., 1963; Wilson and Geankoplis, 1966), evaporation methods (Bradshaw and Myers, 1963; Gamson et al., 1943; Gupta and Thodos, 1963), ion exchange methods (Selke et al., 1956), electrochemical methods (Coeuret, 1976; Karabelas et al., 1971; Olive and Lacoste, 1979), and transient pulse methods (Miyauchi et al., 1975, 1976; Wakao et al., 1976). Additionally, due to the analogy between heat and mass transfer (Chilton and Colburn, 1934), measurements of heat transfer in packed beds can be used to determine the mass transfer. Inevitably, a disadvantage of these methods is that measurements are made on an analogue system, and not using the process fluids or pellets of interest, and results must be nondimensionalized and extrapolated for

use. Further, at low Péclet number, Pe, (and thus low Reynolds number, Re) complications arise making the accurate determination of k using conventional *ex situ* methods difficult. To determine the true rate of mass transfer, care must be taken to account for the effect of axial dispersion at low Pe (Fedkiw and Newman, 1978; Rexwinkel et al., 1997), often requiring the use of empirical correlations. Also, free convection effects, due to density differences of different species, may become significant and can corrupt the measurement of k at low Pe (Wakao and Funazkri, 1978). Furthermore, saturation of the outlet stream due to the long residence time at low Pe makes accurate measurement of the mass transfer coefficient difficult for these conditions. Alternatively, *in situ* methods for measuring k have been used in trickle bed reactors whereby conversion data from the operating process of interest are directly used to estimate the mass transfer. A reaction kinetics model and a relationship between the flow rate and mass transfer coefficient are assumed, and k is obtained by fitting reaction results to a model of the transport and reaction occurring in the reactor (Morlta and Smith, 1978; van Houwelingen and Nicol, 2011). Although *in situ* methods are closer to a direct measurement, a clear disadvantage of these *in situ* methods is the need to assume reaction kinetics and a dependency between flow rate and k. Zheng et al. (Zheng et al., 2017) developed a novel *operando* method for measuring the liquid-solid mass transfer coefficient in an operating trickle bed reactor during 1-octene hydrogenation by measuring the intra- and inter-pellet composition during reaction using nuclear magnetic resonance (NMR). While this method provides a means of quantifying k by directly measuring both the driving force for mass transfer and the conversion, the method assumes internal transport resistance is negligible and the experimental measurement and associated analysis require expertise in state-of-the-art magnetic resonance imaging techniques. In summary, conventional experimental methods for obtaining k commonly employ systems far simplified from those used in practice and/or make use of restrictive assumptions and empirical correlations to extract k from the underlying data. Furthermore, the measurement of the true rate of mass transfer at low Pe is difficult using conventional methods. More recently, computational fluid

dynamics (CFD) has been employed to simulate mass and heat transfer in packed beds, and extract the relevant transport coefficients (Bale et al., 2019; Das et al., 2017; Zhu et al., 2019). These methods can be used to evaluate the transport properties in beds of different pellet shapes and rapidly evaluate transport properties over a range of conditions. However, a number of inputs and assumptions are required for CFD based methods. Most notably, the bed structure must be numerically generated, and assumptions are required to appropriately define bulk and surface concentration/temperature in order to compute the transport coefficient. It is the purpose of the present work to demonstrate a method for experimentally measuring k by directly quantifying the molecular self-exchange between intra- and inter-pellet fluid in a packed bed using $T_2 - T_2$ exchange NMR. This novel method for measuring k does not make restrictive assumptions about internal transport or reaction kinetics, does not require corrections for dispersion or convection effects at low Pe, and can be conducted using the real porous pellets and fluids employed in heterogeneous catalysis. Moreover, it can be conducted at relevant process conditions.

The $T_2 - T_2$ NMR experiment is based on the measurement of the so-called spin-spin nuclear relaxation time, of the nuclear spin system of interest. Most commonly, that spin is ^{1}H, associated with the hydrogen atoms in the fluid of interest. The transverse nuclear magnetic relaxation time, T_2, is an exponential time constant describing the decay of the NMR signal following excitation of the spin system using a radio-frequency (r.f.) pulse. T_2 is dependent on molecular rotational dynamics, and is sharply reduced for molecules interacting with a solid surface, allowing it to serve as a contrast mechanism for differentiating populations of molecules existing within regions of different pore size (Mitchell et al., 2007), such as intra- and inter-pellet fluid in a packed bed. The $T_2 - T_2$ exchange experiment, first developed by Lee et al. (Lee et al., 1993), can be used to probe molecular exchange between different relaxation environments. $T_2 - T_2$ exchange has been applied extensively to study both structure and molecular exchange dynamics in a wide variety of heterogeneous systems

including cements (Song et al., 2012), metal organic frameworks (Chen et al., 2015), alumina pellets and powders (d'Eurydice et al., 2016; Terenzi et al., 2019), surfactant solutions (Griffith et al., 2009), polysaccharide solutions (Kolz et al., 2010), rocks (Washburn and Callaghan, 2006), articular cartilage (Mailhiot et al., 2018), and spruce wood (Cox et al., 2010), among others. Exchange rates between different relaxation environments are quantified from $T_2 - T_2$ exchange results by conducting the experiment over a range of mixing times (t_{mix}). These exchange rates can be used to provide information about the molecular residence time of the molecule of interest in each environment (Washburn and Callaghan, 2006), and have been shown to be related to the characteristic diffusive exchange distance in heterogeneous porous media (Mitchell et al., 2007). Despite the extensive application of $T_2 - T_2$ exchange to study heterogeneous systems, to date it has found little application in the study of transport in packed beds. Olaru et al. (Olaru et al., 2012) investigated the effect of flow on the two-dimensional (2D) T_2 distribution obtained from the $T_2 - T_2$ exchange experiment for flow through a pack of non-porous soda lime glass spheres, finding a decrease in relaxation time and a shifting of cross peaks as Pe increased. Robinson et al. (Robinson et al., 2020) used $T_2 - T_2$ exchange to investigate molecular exchange in a packed bed of commercial zeolite pellets. The model of Washburn and Callaghan (2006) was used to quantify pore-pore and pore-bulk exchange rates, however mass transfer coefficients were not estimated from these data. To date, no studies have reported the use of $T_2 - T_2$ exchange measurements for quantifying the mass transfer coefficient in packed beds.

A quantitative analysis of the 2D T_2 distributions are required to extract and quantify exchange kinetics from $T_2 - T_2$ exchange. Models of varying degrees of complexity have been developed for this purpose, from the straightforward exponential model of Washburn and Callaghan (Washburn and Callaghan, 2006) to the more complex models of Dortch et al. (Dortch et al., 2009) and van Landeghem et al. (van Landeghem et al., 2010) who consider the effect of relaxation and fast exchange during implementation of the pulse sequence. Taking an alternative approach, Olaru et al.

(Olaru et al., 2012) modelled the $T_2 - T_2$ exchange for flow through a bead pack by considering the magnetization transport (Bloch-Torrey equation) and including appropriate terms for advection and diffusive exchange between different relaxation environments. Each of the aforementioned models treat exchange as a first order Poisson process where the probability of a molecule exchanging is independent of position (Fieremans et al., 2010). This is a reasonable assumption for systems where transport resistance lies predominantly at an interface, or where only a characteristic length or timescale is desired from the exchange model. However, for exchange between intra- and inter-pellet fluid in a packed bed, the exchange processes is clearly non-Poissonian as there is transport resistance within the pellet; fluid near the pellet surface is more likely to exchange with the inter-pellet fluid than fluid near the centre of the pellet. To accurately obtain k from a $T_2 - T_2$ exchange experiment, a model of the magnetization transport during the experiment is therefore required that accounts for internal diffusive transport within the pellet, such that k correctly describes the external mass transport in the bed and does not contain the influences of internal transport resistance.

This paper describes the development of a model for magnetization transport during the $T_2 - T_2$ exchange experiment in a packed bed of porous pellets using the Bloch-Torrey equation, considering both intra-pellet diffusion and mass transfer between the intra- and inter-pellet fluid. By conducting the $T_2 - T_2$ exchange experiment over a range of mixing times and regressing the magnetization transport model onto the experimental results it is possible to obtain k. The NMR method directly measures the molecular self-exchange between intra- and inter-pellet fluid, and does not require a net flux, hence no correction for dispersion or density-driven convection are required at low flow rates as in conventional methods. As a result, obtaining k at zero flow is possible, enabling the investigation of the limiting mass transfer rate in packed beds. Mass transport coefficients are measured using $T_2 - T_2$ exchange for water flow through packed beds of porous silica and titania spheres over a range of

flow conditions ($0 \leq Re \leq 38.6$). The dimensionless results are then compared to previously reported data and two extensively-used correlations.

2. Theory and Model Development

Central to this work is relating the molecular exchange process probed by the $T_2 - T_2$ experiment to the mass transfer coefficient as defined and used in chemical engineering. The NMR pulse sequence for the $T_2 - T_2$ experiment is shown in Figure 1a. T_2 is first encoded for using a variable length Carr-Purcell-Meiboom-Gill (CPMG) echo train (Carr and Purcell, 1954; Meiboom and Gill, 1958), followed by storage of the magnetization along the longitudinal axis for duration t_{mix} during which molecular exchange between different relaxation environments occurs (Lee et al., 1993; Washburn and Callaghan, 2006). Following the mixing period, the magnetization is recalled to the transverse plane and a CPMG train is used to encode for T_2 again. The resulting NMR signal can be expressed as:

$$M(t_{\mathrm{e}}^{\mathrm{A}}, t_{\mathrm{e}}^{\mathrm{B}}; t_{\mathrm{mix}}) = \iint P\left(T_2^{\mathrm{A}}, T_2^{\mathrm{B}}; t_{\mathrm{mix}}\right) exp\left(-\frac{t_{\mathrm{e}}^{\mathrm{A}}}{T_2^{\mathrm{A}}} - \frac{t_{\mathrm{e}}^{\mathrm{B}}}{T_2^{\mathrm{B}}}\right) dT_2^{\mathrm{A}} dT_2^{\mathrm{B}}\,, \tag{1}$$

where M is the magnetization (acquired NMR signal), P is the 2D T_2 probability distribution for a given mixing time t_{mix}, t_{e} is the encoding time of the CPMG sequence during which the magnetization is subject to T_2 relaxation , T_2 is the transverse relaxation time, and the superscripts A and B denote the first and second encoding intervals, before and after the mixing time, respectively. An example of the 2D time-domain magnetization decay resulting from the $T_2 - T_2$ experiment for two exchanging populations is shown in Figure 1b. The 2D T_2 distribution, P, is obtained from the acquired signal, M, through a 2D inverse Laplace transform (ILT) of Equation (1), an example of which is shown in Figure 1c. In the absence of exchange, P will only have peaks on the diagonal with $T_2^{\mathrm{A}} = T_2^{\mathrm{B}}$. Molecular exchange between regions (phases) with different T_2 (such as intra- and inter-pellet) gives rise to off-diagonal peaks in P with $T_2^{\mathrm{A}} \neq T_2^{\mathrm{B}}$, as seen in Figure 1c. For two site

exchange between phases i and j with relaxation times T_2^i and T_2^j, the ratio between the intensity of cross (off-diagonal) peaks, I_{XP}, and the total peak intensity, I_{TP}, is:

$$\frac{I_{\mathrm{XP}}}{I_{\mathrm{TP}}}(t_{\mathrm{mix}}) = \frac{P\left(T_2^{\mathrm{A}} = T_2^i, T_2^{\mathrm{B}} = T_2^j;\ t_{\mathrm{mix}}\right) + P\left(T_2^{\mathrm{A}} = T_2^j, T_2^{\mathrm{B}} = T_2^i;\ t_{\mathrm{mix}}\right)}{\iint P\left(T_2^{\mathrm{A}}, T_2^{\mathrm{B}}; t_{\mathrm{mix}}\right) dT_2^{\mathrm{A}} dT_2^{\mathrm{B}}}, \tag{2}$$

and is related to the fraction of molecules that have exchanged between phases i and j during t_{mix}. Indeed, when the longitudinal relaxation of both phases are similar ($T_1^i \approx T_1^j$) and exchange is slow compared to T_2 such that negligible exchange occurs during encoding periods $t_{\mathrm{e}}^{\mathrm{A}}$ and $t_{\mathrm{e}}^{\mathrm{B}}$, $I_{\mathrm{XP}}/I_{\mathrm{TP}}$ quantitatively represents the fraction of molecules that have exchanged during t_{mix} (e.g. the fraction of molecules that started in phase i and ended in phase j, and vice-versa). When these assumptions do not hold, $I_{\mathrm{XP}}/I_{\mathrm{TP}}$ is confounded with the effects of T_1 relaxation weighting and fast exchange (van Landeghem et al., 2010). However, if effects of fast exchange and T_1 weighting are accounted for through mathematical modelling, the evolution of $I_{\mathrm{XP}}/I_{\mathrm{TP}}(t_{\mathrm{mix}})$ can be used to investigate the molecular exchange dynamics between phases i and j.

To model the results from the $T_2 - T_2$ exchange experiment applied to a packed bed with porous pellets, drawing on the approach used by Olaru et al. (Olaru et al., 2012), the magnetization transport is considered using the Bloch-Torrey equation:

$$\frac{\partial \mathbf{M}}{\partial t} = \gamma \mathbf{M} \times \mathbf{B} - \bar{\bar{R}}(\mathbf{M} - \mathbf{M}^{\mathrm{eq}}) + D\nabla^2 \mathbf{M} - \boldsymbol{v} \cdot \nabla \mathbf{M} \tag{3}$$

where $\mathbf{M}$ is the (net) magnetization density vector, $\mathbf{B}$ is the magnetic field, $\mathbf{M}^{\mathrm{eq}}$ is the magnetization at thermal equilibrium, $\bar{\bar{R}}$ is the relaxation rate tensor, D is the diffusion coefficient, and $\boldsymbol{v}$ is the velocity. The terms in the above account for (i) precession under the magnetic field, (ii) relaxation, (iii) diffusion, and (iv) advection. The magnitude of the NMR signal is related to the total signal in

the transverse plane, $M = |M_x + iM_y|$. Simplifying Equation (3) to describe M, the magnetization density giving rise to the final NMR signal, gives:

$$\frac{\partial M}{\partial t} = -\boldsymbol{v} \cdot \nabla M + D\nabla^2 M - R_{1.2}(M - M^{eq}) , \tag{4}$$

where $R_{1,2}$ describes the appropriate relaxation rate when the magnetization is along the longitudinal axis (and subject to T_1 relaxation) or in the transverse plane (and subject to T_2 relaxation), respectively. Equation (4) represents an advection-diffusion-reaction equation describing the transport and relaxation of nuclear magnetism. Solving Equation (4) for a general system presents a formidable challenge requiring complete knowledge of the flow field and spatial dependence of the relaxation rate. For a packed bed, when the relaxation is uniform in both the intra- and inter-pellet phases (being described by relaxation times T_1^{intra}, T_2^{intra} and T_1^{inter}, T_2^{inter}), Equation (4) can be greatly simplified by considering the intra- and inter-pellet magnetization separately and linking the flux between intra- and inter-pellet using the mass transfer coefficient. Assuming advection is negligible inside the pellet, and that the pellet has uniform porosity, ϕ and intra-pellet diffusivity, D^{intra}, Equation (4) for the intra-pellet phase becomes:

$$\begin{cases} \dfrac{\partial M^{intra}}{\partial t} = D^{intra}\,\nabla^2 M^{intra} - R_{1.2}^{intra}\left(M^{intra} - M^{eq}\right) \\ M^{intra}(t=0) = M_0^{intra} \\ \left.\dfrac{\partial M^{intra}}{\partial r}\right|_{r=0} = 0 \\ \left. -D^{intra}\dfrac{\partial M^{intra}}{\partial r}\right|_{r=R} \phi = k\left(M_s^{inter} - M^{inter}\right) \end{cases} , \tag{5}$$

where M_0^{inter} is the constant (uniform) initial magnetization density in the intra-pellet phase (due to the assumed uniform porosity ϕ), M_s^{inter} is the magnetization density at the pellet surface in the inter-pellet phase, M^{inter} is the bulk (well-mixed) magnetization density in the inter-pellet phase, and k is the mass transfer coefficient. The no-flux boundary condition at the centre results from the symmetry

of the pellet, while the boundary condition describing the flux at the surface results from equating the diffusive intra-pellet flux at the surface to the mass transfer flux from the bulk to the surface. To close Equation (5), expressions for M_s^{inter} and M^{inter} are needed. Assuming the fluid density to be the same in the intra- and inter-pellet phases, $M_s^{\text{inter}} = M^{\text{intra}}(r = R)$. A material balance on the inter-pellet phase is used to express the evolution of M^{inter}:

$$\frac{\partial M^{\text{inter}}}{\partial \text{t}} = \frac{Ak}{V^{\text{inter}}}\left(M_s^{\text{inter}} - M^{\text{inter}}\right) - \frac{Q}{V^{\text{inter}}}M^{\text{inter}} - R_{1.2}^{\text{inter}}\left(M^{\text{inter}} - M^{\text{eq}}\right), \tag{6}$$

with initial condition $M^{\text{inter}}(t = 0) = M_0$. V^{inter} is the volume of fluid in the inter-pellet phase, A is the total pellet surface area in the bed, and Q is the volumetric flow rate. Note that only the ratio of surface area to inter-pellet volume, A/V^{inter}, is needed, which for a bed of known dimensions and voidage can be determined using simple geometrical arguments. The loss of magnetization due to magnetized spins flowing out of the NMR coil region (so-called inflow/outflow effects) are accounted for through the outflow term (term 2 on the LHS). Together, Equations (5) and (6) describe the evolution of magnetization density in a packed bed during the NMR experiment. Different relaxation rates in the intra- and inter-pellet phases lead to a gradient in magnetization density. Internal diffusion causes intra-pellet transport of magnetization density, and mass transfer results in flux between the intra- and inter-pellet phases. The total magnetization, measured during the NMR experiment is a sum of the intra- and inter-pellet magnetization density weighted by the fraction of each phase and is expressed as:

$$M^{\text{total}} = \frac{\epsilon}{\epsilon + (1-\epsilon)\phi}M^{\text{inter}} + \frac{(1-\epsilon)\phi}{\epsilon + (1-\epsilon)\phi}\overline{M^{\text{intra}}}, \tag{7}$$

where ϵ is the bed voidage (using the conventional definition $\epsilon = V^{\text{inter}}/V^{\text{bed}}$), and $\overline{M^{\text{intra}}}$ is the spatially averaged intra-pellet magnetization density, $\overline{M^{\text{intra}}} = \int_0^R 4\pi r^2 M^{\text{intra}} dr \,/\, \frac{4}{3}\pi R^3$.

By appropriately solving Equations (5)-(7), the magnitude of the NMR signal during an experiment studying flow through a packed bed is modelled. Specifically, the NMR signal during the $T_2 - T_2$ exchange experiment is modelled by appropriately defining the relaxation rate for phase i used in Equations (5)-(7):

$$R_{1,2}^{i}(t) = \begin{cases} T_2^{i\,-1}, & 0 < t < t_{\mathrm{e}}^{\mathrm{A}} \\ T_1^{i\,-1}, & t_{\mathrm{e}}^{\mathrm{A}} \le t < t_{\mathrm{e}}^{\mathrm{A}} + t_{\mathrm{mix}} \\ T_2^{i\,-1}, & t_{\mathrm{e}}^{\mathrm{A}} + t_{\mathrm{mix}} \le t < t_{\mathrm{e}}^{\mathrm{A}} + t_{\mathrm{mix}} + t_{\mathrm{e}}^{\mathrm{B}} \end{cases}, \tag{8}$$

for both the intra- and inter-pellet phases. The magnetization from the entire $T_2 - T_2$ exchange experiment, $M(t_{\mathrm{e}}^{\mathrm{A}}, t_{\mathrm{e}}^{\mathrm{B}}; t_{\mathrm{mix}})$, can be simulated for a given t_{mix} by independently stepping both $t_{\mathrm{e}}^{\mathrm{A}}$ and $t_{\mathrm{e}}^{\mathrm{B}}$ and subsequently solving Equations (5)-(7). Since the magnetization transport is modelled for all portions of the pulse sequence, the effect of fast exchange on the resulting bulk magnetization is accounted for. Therefore, the use of Equations (5)-(7), when combined with the relaxation rate scheme given in Equation 8, are appropriate in general, and not merely in the limit when exchange is slow compared to T_2. To extract the mass transfer coefficient, k, the magnetization transport model is solved and compared to experimental $T_2 - T_2$ exchange results. Rather than directly compare the magnetization, M, from model and experiment, the approach selected here is to apply a 2D ILT to the measured and simulated signal to recover both experimental and simulated 2D T_2 distributions (Equation (1)). The cross peaks, being indicative of exchange, are then integrated (Equation (2)) and compared. By conducting $T_2 - T_2$ exchange experiments and modelling over a range of t_{mix}, the cross peak evolution can be used to extract k using non-linear least squares fitting of the simulated and measured cross-peak intensity, $I_{\mathrm{XP}}(t_{\mathrm{mix}})$. Given that the bed properties, pellet properties and flow conditions are known (ϕ, ϵ, R, Q) and the intra-pellet diffusion and nuclear spin relaxation properties of both phases are also known (readily measured using standard NMR methods), the only unknown parameter is k. Therefore, the reported magnetization transport model is a 1-parameter model to quantify the mass transfer coefficient, k, using $T_2 - T_2$ exchange data. The model workflow

to extract k from experimental $T_2 - T_2$ exchange data is shown in Figure 2. To summarize, the model workflow is as follows:

(i) Solve Equations (5)-(7) for a range of $t_{\mathrm{e}}^{\mathrm{A}}, t_{\mathrm{e}}^{\mathrm{B}}$ and constant t_{mix} consistent with experimental conditions to obtain simulated 2D time-domain magnetization decay, $M(t_{\mathrm{e}}^{\mathrm{A}}, t_{\mathrm{e}}^{\mathrm{B}}; t_{\mathrm{mix}})$.

(ii) 2D ILT of $M(t_{\mathrm{e}}^{\mathrm{A}}, t_{\mathrm{e}}^{\mathrm{B}}; t_{\mathrm{mix}})$ to recover a simulated 2D T_2 distribution.

(iii) Quantify the cross peaks intensity $I_{\mathrm{XP}}/I_{\mathrm{TP}}$ from the simulated distribution using Equation (2).

(iv) Repeat (i-iii) for variable t_{mix} consistent with experimental conditions.

(v) Minimize the least squares difference between simulated and experimental cross peak intensity profile by iterating (i-iv) using k as a fitting parameter.

Here, it is worth pointing out the simplicity of the $T_2 - T_2$ exchange method for measuring k. The $T_2 - T_2$ NMR exchange experiment directly probes molecular exchange between different relaxation environments. When combined with the magnetization transport model reported above, the measurements of molecular exchange can be converted into the mass transfer coefficient, without the need for calibrations or empirical / semi-empirical models to fit the data.

3. Experimental and Data Processing

3.1 Materials and experimental setup

A schematic of the experimental setup used to conduct $T_2 - T_2$ exchange experiments of flow through a packed bed is shown in Figure 3. A 15.7 mm inner diameter plastic pipe was packed with porous pellets. The bed was packed with glass ballotini on both ends of the packing of porous pellets, and placed vertically through the bore of the NMR spectrometer. A peristaltic pump (Watson Marlow

505S) provided the driving force for flow through the packed bed with a 2 L vessel used at the outlet to dampen flow oscillations and provide steady flow through the packed bed. Silicon rubber tubing of outer diameter 10 mm was used to facilitate flow through the flow loop. Deionized water (Elga PureLab Option DV-25) was used as the working fluid for all experiments. Experiments were conducted using two different pellet types in order to demonstrate that the NMR method can be used to measure the mass transfer coefficient on various porous support materials. Porous silica (Q50) spheres (Fuji Silysia) of mean diameter 1.3 mm and porous anatase titania spheres (Saint-Gobain) of mean diameter 3.1 mm were used for this purpose. The median pore size of the titania pellets was 40 nm and the mean pore size of the silica pellets was 50 nm, as provided by the respective suppliers. Experiments were conducted over a range of flow conditions by varying the flow rate through the bed with Re ranging from 0 – 2.7 for the silica spheres and 0 – 38.6 for the titania spheres.

3.2 Magnetic resonance experiments

All NMR experiments were conducted using a super-wide bore Bruker AV300 7.1 T superconducting magnet equipped with a 3-axis gradient strengths providing gradient strengths up to 0.8 T m^{-1}. A 40 mm diameter birdcage ^{1}H r.f. coil tuned to 300.87 MHz was used for signal excitation and acquisition with a typical 90˚ hard pulse duration of 20 μs.

$T_2 - T_2$ exchange experiments were conducted using the standard pulse sequence shown in Figure 1a, consisting of two CPMG encoding periods separated by mixing time t_{mix} (Lee et al., 1993; Washburn and Callaghan, 2006). For experiments with the silica pellets, the inter-echo spacing for both CPMG loops was 6 ms. The number of echoes in the first CPMG loop was stepped from 1 to 256 in 32 (uneven) steps with 512 echoes being acquired from the second CPMG loop for each increment of the first loop. For experiments with titania pellets, due to the shorter intra-pellet T_2, the

inter-echo spacing was reduced to 2 ms and the first CPMG loop stepped from 1 to 512 in 32 (uneven) steps with 1024 echoes being acquired from the second CPMG loop. A 50 ms homospoil gradient at a strength of 0.08 T m^{-1} was applied in the x and z directions during the storage period t_{mix} in order to eliminate any unwanted coherences. To capture the cross peak evolution, t_{mix} was varied between 0.1 s to 3.75 s; in 6 increments for the silica pellets, and 5 increments for the titania pellets. A repetition time of 12 s was used with 16 averages to complete the full 16 step cycle used, resulting in an acquisition time of ~ 2.5 h for a single t_{mix}.

In order to acquire the diffusion and relaxation parameters needed by the magnetization transport model, $D - T_2$ correlation and $T_1 - T_2$ correlation experiments were conducted using standard APGSTE-CPMG and inversion recovery – CPMG sequences, respectively (Hürlimann and Venkataramanan, 2002). The parameters for the CPMG encoding were identical to those used for $T_2 - T_2$ exchange. For T_1 encoding using inversion recovery, the storage time was incremented from 1 ms to 8 s in 32 (uneven) steps. For diffusion encoding using APGSTE, $\delta = 1$ ms, $\Delta = 75$ ms, and the gradient strength was stepped from 0.006 T m^{-1} to 0.56 T m^{-1} in 32 linear steps. Data processing was conducted in a similar manner to that used for $T_2 - T_2$ exchange using a 2D ILT (see Section 3.3) to recover 2D correlation maps. The resulting 2D $D - T_2$ and $T_1 - T_2$ correlation maps were used to determine the intra-pellet diffusivity D^{intra} and T_1 of both phases, by taking the logarithmic mean D and T_1, respectively, from the well separated intra-and inter-pellet peaks.

3.3 Data processing and modelling

As-acquired magnetization decay data from $T_2 - T_2$ exchange experiments were 0$^{\mathrm{th}}$-order phase corrected and the real part of the phase-corrected decay from even echoes was retained. A fast 2D ILT algorithm based on singular value decomposition (SVD) (Hürlimann and Venkataramanan,

2002; Venkataramanan et al., 2002) was used to recover $T_2 - T_2$ distributions from the magnetization decays. The points retained following SVD typically spanned three orders of magnitude, with smaller values being truncated, consistent with the work of Venkataramanan *et al*. (Venkataramanan et al., 2002). Tikhonov regularization was used to give stable inversions, with generalized cross-validation (GCV) used to optimize the smoothing parameter (Golub et al., 1979). Cross peak intensity, $I_{\mathrm{XP}}/I_{\mathrm{TP}}$, was calculated by integrating the resulting $T_2 - T_2$ distributions using rectangular regions manually selected to capture the cross peaks. The manually selected integration bounds were increased and decreased and the resulting variation in peak intensity was taken as the error in $I_{\mathrm{XP}}/I_{\mathrm{TP}}$ since the selection of integration bounds has previously been shown to be the dominant contribution to error in cross peak intensity (Mitchell et al., 2007).

The magnetization transport model given by Equations (5)-(7), was solved numerically to simulate the cross peak evolution. The PDE model was solved using the method of lines (Schiesser and Griffiths, 2009) whereby the spatial dimension was discretized into 250 points and the resulting system of ODEs was solved. Model results were fit to the experimentally obtained $I_{\mathrm{XP}}/I_{\mathrm{TP}}(t_{\mathrm{mix}})$ profile using the Levenberg-Marquardt algorithm with the mass transfer coefficient, k, as the sole fitting parameter. The pellet and bed properties used to solve the magnetization transport model are reported in Table 1. Pellet porosity, ϕ, was obtained from mercury intrusion porosimetry conducted by the respective suppliers. Bed voidage, ϵ, was obtained by measuring the bed loading density. The diffusion and relaxation parameters were determined through $D - T_2$ and $T_1 - T_2$ correlation experiments, as described in Section 3.2.

4. Results and Discussion

4.1 Measurement of the mass transfer coefficient using $T_2 - T_2$ exchange NMR

$T_2 - T_2$ exchange results for water flow through the bed of silica spheres over a range of mixing times, t_{mix}, and Reynolds number, Re, are shown in Figure 4. $T_2 - T_2$ results from the bed of titania spheres are similarly reported in Figure 5. Consistent with previous studies of mass transfer in packed beds, the Reynolds number used here is defined as $Re = \rho d_{\mathrm{p}} u_{\mathrm{s}}/\mu$, where u_s is the superficial liquid velocity through the bed. Looking first at the data from the silica spheres in Figure 4, at $t_{\mathrm{mix}} = 0.1$ s, two peaks are seen along the diagonal at approximately $T_2 \sim 0.1$ s and $T_2 \sim 1.2$ s, corresponding to intra- and inter-pellet water, respectively. Both lie on the diagonal, $T_2^{\mathrm{A}} = T_2^{\mathrm{B}}$, and no significant cross-peaks are apparent, indicating that the amount of exchange between intra- and inter-pellet fluid on the shortest timescale studied ($t_{\mathrm{mix}} = 0.1$ s) is negligible. As t_{mix} increases for a given Re, cross peaks are observed to form at approximately $T_2^{\mathrm{A}}, T_2^{\mathrm{B}}$ = 0.1 s, 1.2 s and $T_2^{\mathrm{A}}, T_2^{\mathrm{B}}$ = 1.2 s, 0.1 s. As discussed in Section 2, these cross peaks are indicative of molecules that have exchanged between the intra- and inter-pellet phases during t_{mix}. The cross peaks visually increase in intensity as t_{mix} increases, as is expected, due to the increased amount of molecular exchange that occurs between the intra- and inter-pellet phases during the longer mixing time. While the cross peaks appear qualitatively similar for different Re at a given t_{mix}, it is difficult to gauge any quantitative trends visually. To quantify exchange, and ultimately the mass transfer coefficient, the cross peaks from each distribution in Figure 4 are quantified by integration, with typical integration bounds shown by the red boxes in the upper rightmost distribution.

The $T_2 - T_2$ results for the titania spheres shown in Figure 5 similarly show diagonal peaks, and cross peaks that increase in intensity with increasing t_{mix}. The peaks in the titania $T_2 - T_2$ distributions are much broader than those observed for silica, potentially due to the faster intra-pellet

relaxation and/or internal magnetic field gradients in the titania pellets. Qualitatively, for a given t_{mix} the cross peaks appear to increase in intensity with increasing Re. The broadening, and occasional merging, of peaks makes accurately and objectively quantifying the cross peaks slightly more difficult in this case. In order to make the cross peak quantification as objective as possible, integration regions were defined (as shown by the red boxes in Figure 5) and held constant, with the exception cases where the cross peak position shifted significantly ($Re = 0.0$, $t_{\mathrm{mix}} = 2.25$ s) where the bounds were then shifted to capture the peak centre. To quantify the error from the somewhat arbitrary definition of the integration bounds, the integration bounds were increased / decreased by ~ $\pm$ 5% and the resulting difference in cross peak intensity was taken as the error.

The evolution of cross peak intensity, $I_{\mathrm{XP}}/I_{\mathrm{TP}}(t_{\mathrm{mix}})$, as determined by integration of the cross peaks in Figure 4 and Figure 5, is shown in Figure 6 as well as the evolution of the simulated cross peak intensity profile obtained from solving the magnetization transport model (Equations (5)-(7), Figure 2). The resulting mass transfer coefficients extracted from the model are reported in Table 2. As expected, Figure 2 shows that when Re increases, $I_{\mathrm{XP}}/I_{\mathrm{TP}}$ increases faster, indicative of faster mass transfer between the intra- and inter-pellet phases. This is indeed the case when k is quantified through solving the magnetization transport model, as shown in Table 2, where the resulting k obtained from least squares fitting increases with Re for both beds. The magnetization transport model describes the evolution profiles of the exchange peak for both silica and titania with only a single fitting parameter (k), thus enabling the quantification of the mass transfer coefficient in the bed. In contrast to previously developed models (Dortch et al., 2009; Olaru et al., 2012; Washburn and Callaghan, 2006) which treat exchange as a first order Poissonian process (Fieremans et al., 2010), the model developed in this work applies the definition of the mass transfer coefficient to directly model the magnetization transport in the packed bed during the $T_2 - T_2$ exchange experiment. This enables the $T_2 - T_2$ exchange experiment, which directly probes molecular

exchange, to be used for direct measurement of the mass transfer coefficient for the first time. It is noted that the need to acquire a 2D dataset during the $T_2 - T_2$ exchange experiment is quite laborious given that only the cross peak intensity is needed. In future work, it may be possible to implement a data analysis method to extract the cross peak intensity from a subset of the data (Song et al., 2016), thus accelerating the measurement of k.

4.2 Comparison of the NMR measured mass transfer coefficients with literature data and existing correlations

Dimensionless correlations of mass transfer in packed beds relate the rate of mass transfer to flow conditions, and fluid and bed properties through correlations of the form $Sh = f(Re, Sc, geometry)$ (Rexwinkel et al., 1997), where the Schmidt number is defined as $Sc = \mu/\rho D$ and the Sherwood number is defined as $Sh = kd_{\mathrm{p}}/D$. Ranz and Marshall (1952) showed analytically that for laminar flow around a single sphere, $Sh = 2 + 0.6Re^{1/2}Sc^{1/3}$. Many correlations for mass transfer in packed beds are simply modified versions of the single-sphere Ranz-Marshall correlation (Coeuret, 1976; Dwivedi and Upadhyay, 1977; Olive and Lacoste, 1979; Wakao and Funazkri, 1978; Williamson et al., 1963; Wilson and Geankoplis, 1966). Wakao and Funazkri (Wakao and Funazkri, 1978) compiled mass transfer data from numerous packed bed studies in the literature and, after correcting for the effect of dispersion, proposed the correlation $Sh = 2 + 1.1Re^{3/5}Sc^{1/3}$, which has found extensive use in packed bed design and analysis. The dimensionless NMR mass transfer data, along with the data used by Wakao and Funazkri (Wakao and Funazkri, 1978) and the resulting correlation, along with a correlation developed by Wilson and Geankoplis (Wilson and Geankoplis, 1966) are shown in Figure 7. Additionally, low Re data obtained by Miyauchi et al. (Miyauchi et al., 1976) using a transient ion exchange method are shown. Note that while the NMR mass transfer coefficients were measured at constant $Sc = 468$, the reported

literature data were collected over a wide range of Sc. For $Re > 1$ ($Re^{3/5}\ Sc^{1/3} > 7.7$), the NMR measured mass transfer coefficients fall within the range reported in the literature as summarized by Wakao and Funazkri (Wakao and Funazkri, 1978). Additionally, the results obtained for the silica spheres for $0.2 \leq Re \leq 2.7$ ($3.0 \leq Re^{3/5}\ Sc^{1/3} \leq 14.1$), fall into the range reported by Miyauchi et al. (Miyauchi et al., 1976). It is therefore clearly demonstrated that the mass transfer coefficients obtained using the NMR method are consistent with those obtained using conventional methods for measuring mass transfer. However, unlike with conventional methods, the NMR method can be used directly to measure the mass transfer coefficients of real pellets employed in packed bed processes, allowing this method to be used for the optimisation of pellet shape and porosity for particular process applications.

With the exception of the measurement at $Re = 0$, the mass transfer coefficients measured using NMR show good overall agreement with both correlations. For $Re > 1$ ($Re^{3/5}\ Sc^{1/3} > 7.7$), the NMR values agree very well with the correlation of Wakao and Funazkri, which was developed using a survey of literature results over the range of $3 < Re < 10000$. Similarly, the NMR measurements agree reasonably well (with the exception of the measurements at $Re = 0$) with the correlation of Wilson and Geankoplis, which was developed using the dissolution method over $0.0016 < Re < 55$. Due to the lower Re studied by Wilson and Geankoplis, this correlation gives better agreement with the silica data at $Re = 0.2$ ($Re^{3/5}\ Sc^{1/3} = 3.0$) as compared to the correlation of Wakao and Funazkri, which is being extrapolated for this point. At $Re = 0$, the limiting value of Sh obtained from NMR was found to be 9 ± 2 for the titania pellets, and 8.7 ± 0.7 for the silica pellets. The agreement between pellets at identical flow conditions suggests that the NMR method is able to successfully measure the mass transfer independent of the pellet material. Extrapolating the correlations, limiting values of $Sh = 2$ and $Sh = 0$ at zero flow are predicted by the correlations of Wakao and Funazkri, and Wilson and Geankoplis, respectively.

4.3 Limiting behaviour of Sh in packed beds

The limiting value of Sh in packed beds as $Pe \to 0$ (where the Péclet number is defined as $Pe = u_s d_p/D$) has been extensively debated in the packed bed mass transfer literature (Scala, 2013), with some studies suggesting that Sh decreases linearly with Pe (Bar-llan and Resnick, 1957; Petrovic and Thodos, 1968) while others suggest that Sh reaches an asymptotic value as Pe decreases (Gunn and de Souza, 1974; Littman et al., 1968; Miyauchi et al., 1975, 1976). The source of these discrepancies has been primarily attributed to the effect of dispersion (axial mixing) (Fedkiw and Newman, 1978; Glicksman and Joos, 1980) and the selection of the reference concentration difference (the driving force for mass transfer) (Scala, 2013). Accounting for, or neglecting, dispersion when conventional methods are used to measure mass transfer can subtly change the definition and meaning of the mass transfer coefficient. As discussed by Fedkiw and Newman (Fedkiw and Newman, 1978), when the mass transfer coefficient is defined taking axial dispersion into account, the mass transfer coefficient (termed the film, or local, mass transfer coefficient) quantifies the flux between the bulk fluid and surface and reaches an asymptotic value at low Pe. However, when axial dispersion is neglected, the mass transfer coefficient links the log mean driving force to the concentration difference between the inlet and the outlet, thus representing an effective mass transfer coefficient. At large Pe (and thus Re) the difference between the two definitions is negligible, however for low Pe conditions, the distinction is important. Fedkiw and Newman (Fedkiw and Newman, 1978) showed through the use of a 1D transport model that when dispersion is neglected, Sh decreases linearly with Pe, however when dispersion is accounted for the mass transfer coefficient approaches a constant value at low Pe. This difference can easily be understood by considering the bed at zero flow conditions. Due to molecular diffusion, in the limit of zero flow rate there is a finite rate of mass transfer between the intra- and inter-pellet phases. However, due to

axial dispersion (diffusion in this case), the concentration at the inlet and outlet will approach equal values, thus giving an effective mass transfer coefficient of zero if axial dispersion is neglected. Although the mass transfer coefficients obtained with/without neglecting dispersion are mathematically linked (Fedkiw and Newman, 1978), the significance of the mass transfer coefficient as a parameter quantifying the total transport between two phases is obscured when dispersion is neglected. Since the NMR measured mass transfer coefficient is defined through a source term in the magnetization model (Equation (6)), and the $T_2 - T_2$ exchange experiment quantifies the total molecular exchange between intra- and inter-pellet phases, the NMR measurement is consistent with the film (also termed local) mass transfer coefficient. The NMR measurement is thus able to quantify the true rate of mass transfer between the intra- and inter-pellet regions, which is needed to design and model packed bed processes, without requiring knowledge of the dispersion coefficient which often must be obtained from empirical correlations.

As previously discussed, the difficulties in measuring the mass transfer coefficient at very low flow rates with conventional methods contribute to the uncertainty and debate surrounding the limiting value of the mass transfer coefficient in packed beds (Scala, 2013). Many empirical correlations, as a result of neglecting dispersion (and thus obtaining the effective mass transfer coefficient) or due to the inability to make accurate measurements at sufficiently low flows take the form $Sh = \alpha Re^{\beta} Sc^{1/3}$, implying that Sh reaches zero as $Re \to 0$ (Dwivedi and Upadhyay, 1977; Petrovic and Thodos, 1968; Wilson and Geankoplis, 1966). The correlation developed by Wakao and Funazkri (1978), which accounted for the effect of dispersion, simply selected the same limiting Sh as that of a single sphere ($Sh = 2$) because the authors elected to exclude $Re < 3$ data from their analysis due to the possibility of free convection effects confounding measurements at low Re.

Table 3 shows the limiting value of Sh for flow in packed beds reported in a number of previous experimental and numerical studies, as well as the values measured in this work. Some authors have taken great care to experimentally investigate the limiting behaviour of Sh at low Pe (thus low Re), by both accounting for the effect of dispersion and using transient pulse methods to ensure the outlet stream did not become saturated. These results could then be used to estimate the limiting Sh in packed beds by extrapolating the results to $Re = 0$. Miyauchi et al. suggested a limiting value of Sh =12.5 for gas flow through a packed bed (ϵ~0.5) and 16.7 for liquid flow (ϵ~0.4) (Miyauchi et al., 1975, 1976). The data for liquid flow from Miyauchi et al. (Miyauchi et al., 1975) are shown in Figure 7 and are seen to follow a similar trend to the NMR data for the low Re points. Similarly, Gunn and de Souza (Gunn and de Souza, 1974) used an experimental approach to study gas flow through a packed bed (ϵ~0.4) at flows as low as $Re = 0.05$ and suggested a limiting value of $Sh =$ 10, closely corresponding with the NMR measurements at $Re = 0$. The large range of previous experimental estimates of the limiting value of Sh in packed beds is likely due to the complicated data analysis required for the transient pulse methods that have been employed, as well as the fact that these results must be extrapolated to $Re = 0$ as a direct measurement at zero flow is not possible. To the authors' knowledge, the present study is the first reported direct measurement of the limiting value of Sh.

Numerical approaches have also been used to compute the limiting value of Sh in packed beds, with two previously reported numerical results shown in Table 3. Sorensen and Stewart (Sørensen and Stewart, 1974) analytically solved the velocity profile in a unit cell of simple cubic packing analytically and subsequently solved the convection diffusion equation to numerically compute the limiting value of Sh at $Re = 0$. Fedkiw and Newman showed that these calculations result in a limiting value of the film mass transfer coefficient of $Sh = 7.1$ for a simple cubic packing ($\epsilon = 0.48$)

(note that the $Sh = 3.89$ result originally reported by Sorenson and Stewart is based on a log-mean average driving force and is not the limiting film transfer coefficient, see (Fedkiw and Newman, 1978) for further discussion). Scaling the result of Sorensen and Stewart to be consistent with the average voidage of the beds in this work suggests a limiting Sherwood number of $Sh = 7.1 \times (0.48/0.41) = 8.3$ for the beds studied here, which is within error of the NMR values from both pellets at $Re = 0$. Further, Pfeffer and Happel (Pfeffer and Happel, 1964) analytically solved a free surface model of mass transfer in a packed bed, which yielded $Sh = 12$ for a bed of $\epsilon = 0.4$ at zero flow, which is also reasonably close to the NMR measured values.

In summary, the limiting value of Sh obtained by NMR is in close agreement with previous results obtained analytically (Pfeffer and Happel, 1964; Sørensen and Stewart, 1974) and from asymptotic trends in experimental data (Gunn and de Souza, 1974; Miyauchi et al., 1975, 1976). Significant under-prediction of the mass transfer coefficient at low Re is obtained by extrapolating existing correlations to flow rates lower than the ranges for which they were developed.

5. Conclusions

In this work, we have introduced a novel method for measuring the liquid-solid mass transfer coefficient in packed beds by directly measuring molecular exchange between intra- and inter-pellet fluid using $T_2 - T_2$ relaxation exchange NMR. The molecular exchange measured with $T_2 - T_2$ relaxation exchange is used to extract the mass transfer coefficient through a magnetization transport model developed in this work. The $T_2 - T_2$ exchange method was applied to measure the mass transfer coefficient for water flowing through beds of porous silica and titania spherical pellets over the range $0 \leq Re \leq 38.6$. The dimensionless results were in good agreement with values previously reported in the literature measured using conventional methods, as well as with the predictions of two

correlations over the range of flow conditions for which they were developed. Because the NMR method directly measures molecular exchange between the intra- and inter-pellet, it was possible to measure the limiting mass transfer coefficient at $Re = 0$, giving $Sh \sim 9$ for both titania and silica pellets. This result is in close agreement with the trends from previous studies conducted at low Re and previous analytical calculations, and suggests that extrapolations of correlations commonly-used to characterise mass transfer beyond the flow rates for which they were developed under-predict the limiting value of Sh. Being the first direct experimental measurement of Sh in packed beds at zero flow, this result aids in resolving the debate in the literature regarding the limiting rate of mass transfer in packed beds.

Whereas most conventional methods for measuring transfer make use of analogue systems, measurements on the porous pellets employed in practice in packed beds are possible with the $T_2 - T_2$ exchange NMR method. As a result, this method can be used for quantifying the mass transfer properties of real porous catalysts and hence enables the optimization of pellet characteristics and process operating conditions. Further, the spatial and chemical resolution modalities of NMR can be readily combined with this method to further investigate and quantify mass transfer in packed bed processes. In particular, spatial variation of mass transfer characteristics at different positions within a bed can be studied, and followed as a function of time-on-stream. The ability to add chemical resolution to the measurements enables molecular species-specific measurements to be made in the case of multi-component transfer processes.

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Figure Captions

Figure 1. (a) Schematic of the $T_2 - T_2$ pulse sequence. (b) Example of typical 2D time-domain magnetization decay resulting from the $T_2 - T_2$ experiment for two exchanging populations. (c) 2D T_2 distribution, P, obtained from a 2D ILT of the time-domain magnetization decay data shown in (b). Off-diagonal peaks identify the nature and extent of molecular exchange between populations during the mixing period t_{mix}. Note that the signal in (b) was numerically generated using Equation (1) and assuming a theoretical 2D T_2 distribution, with Gaussian diagonal and cross peaks, as shown in (c).

Figure 2. Algorithm flowchart showing how the mass transfer coefficient is determined from experimental $T_2 - T_2$ exchange data using the magnetization transport model.

Figure 3. Schematic of rig used to conduct $T_2 - T_2$ exchange experiments. (a) Schematic of magnet and flow loop: (1) 20 L holding tank, (2) peristaltic pump, (3) 2 L vessel, (4) clamp valve, (5) ceramic monolith flow distributor, (6) r.f. probe, (7) 15.7 mm ID packed bed, (8) 7.1 T superconducting magnet, (9) volumetric cylinder for flow measurements. (b) Detailed schematic of packed bed, active region of spectrometer shown by red box.

Figure 4. 2D T_2 distributions from $T_2 - T_2$ exchange experiments for water flowing through a bed of 1.3 mm diameter spherical silica pellets over a range of mixing times, t_{mix}, and Re. The cross peak integration regions are shown by the red boxes in the upper rightmost plot.

Figure 5. 2D T_2 distributions from $T_2 - T_2$ exchange experiments for water flowing through a bed of 3.1 mm diameter spherical titania pellets over a range of mixing times, t_{mix}, and Re. Typical cross peak integration regions are shown by the red boxes.

Figure 6. $T_2 - T_2$ cross peak evolution profiles and the fits of the data to the magnetization model for (a) the bed of 1.3 mm spherical silica pellets, and (b) the bed of 3.1 mm spherical titania pellets. For both beds the NMR data are shown by the circular symbols (•). Error bars represent the variation of I_{XP}/I_{TP} when the integration bounds were varied. Simulations were only run at the discrete values of t_{mix} used experimentally. These results are plotted as individual points (×), connected by a solid line (—) to guide the eye.

Figure 7. Dimensionless mass transfer coefficients, measured using the NMR method, compared with existing literature data and two selected correlations. Sh is plotted as a function of $Re^{3/5}Sc^{1/3}$ to enable comparison with the survey of dispersion-corrected literature data compiled by Wakao and Funazkri (Wakao and Funazkri, 1978). Data points shown are: (★) NMR 3.1 mm titania spheres, (■) NMR 1.3 mm silica spheres, (×) data from Miyauchi et al.(Miyauchi et al., 1975) , and (•) mass transfer data from many sources compiled and corrected for dispersion effects by Wakao and Funazkri (Wakao and Funazkri, 1978). The correlation of correlation of Wakao and Funazkri (—), and the correlation of Wilson and Geankoplis (Wilson and Geankoplis, 1966) evaluated at $Sc = 468$ consistent with the conditions used in the present work (—) are also shown. The correlation of Wakao and Funazkri (Wakao and Funazkri, 1978) is shown as a dashed line where it is being extrapolated beyond the flow conditions (lower Re) for which it was developed.

Tables

Table 1. Pellet and bed properties used to solve the magnetization transport model

	SiO_2	TiO_2
d_p [mm]	1.3	3.1
$D^{intra} \times 10^9$ [m^2 s^{-1}]	1.25	1.41
ϵ [-]	0.4	0.42
ϕ [-]	0.69	0.68
T_1^{intra} [s]	1.2	2.0
T_1^{inter} [s]	2.7	2.4
T_2^{intra} [s]	0.14	0.009
T_2^{inter} [s]	1.23	1.81

Table 2. Mass transfer coefficients extracted from the fit of the magnetization transport model to the experimental $T_2 - T_2$ exchange data. Error bars represent the 95% parameter confidence interval for k obtained from non-linear least squares regression.

Pellet	Re [-]	$k \times 10^5$ [m s^{-1}]
SiO_2	0	1.3 ± 0.1
SiO_2	0.2	1.5 ± 0.2
SiO_2	1.1	2.0 ± 0.3
SiO_2	2.7	2.9 ± 0.01
TiO_2	0	0.6 ± 0.1
TiO_2	10.1	1.7 ± 0.4
TiO_2	17.5	2.7 ± 0.3
TiO_2	38.6	6.5 ± 1.7

Table 3. Limiting values of Sh for flow in packed beds as $Re \to 0$ reported in previous experimental and numerical studies, along with the direct experimental NMR measurement of Sh at $Re = 0$ reported in this work. *note that the $Sh = 3.89$ result originally reported by Sorenson and Stewart is based on a log-mean average driving force and is not the limiting film transfer coefficient, see (Fedkiw and Newman, 1978) for further discussion.

method	$\lim_{Re \to 0} Sh$	voidage, ϵ	reference
experimental, extrapolation from low Re	12.5	~0.5	(Miyauchi et al., 1976)
	16.7	~0.4	(Miyauchi et al., 1975)
	10	~0.4	(Gunn and de Souza, 1974)
numerical	7.1*	0.48	(Sørensen and Stewart, 1974)
	12	0.4	(Pfeffer and Happel, 1964)
experimental, direct	8.7 ± 0.7	0.40	this work (SiO_2)
	9 ± 2	0.42	this work (TiO_2)