Axial variation of wetting efficiency and liquid-solid mass transfer in long trickle bed columns

Elizabeth, L. du Toit, Rita Joubert, Francois Saayman, Willie Nicol*

Department of Chemical Engineering, University of Pretoria, South Africa

The following section gives a more detailed description of the experimental procedure used to generate the data given in the Research Note published under the title above

Experimental

Two separate clear PVC columns were used in this investigation. The first, with an internal diameter of 68 mm, was 1.6 m long and the second larger column had an internal diameter of 104 mm and was 5 m long. Both columns were operated at ambient conditions – i.e. at approximately 298 K and with gas and liquid outlet at ca. 87 kPa. The liquid phase was fed co-currently with the nitrogen gas phase through needle distributors. The liquid distributor in the smaller column used 1 mm inner diameter needles in a square pitch arrangement while 6.35 mm (¼″) needles were used in the pilot scale column. The orifice diameters were chosen to ensure sufficient pressure drop over the distributor plate. In both columns the liquid velocities at the orifice outlets were high enough to prevent any liquid stream agglomeration above the bed – even at the lowest liquid flow rates investigated. Furthermore the resultant drip point densities, 24507 points.m^{-2} and 10 280 points.m^{-2} in the small and pilot scale column respectively, exceed the minimum value of 5000 drips.m^{-2} recommended by Burghardt *et al.*[1] to ensure optimal liquid distribution in the column. The nitrogen was introduced below the liquid distributor plate and entered the 68 mm diameter column through a 12 mm inner diameter pipe, while the gas was introduced into the 104 mm diameter column through three ¼" stainless steel tubes spaced at 120° from each other.

The electrochemical cell technique developed by Reiss and Hanratty[2] and Mitchell and Hanratty[3] and specifically used by amongst others Chou[4] and Rao & Drinkenburg[5] for the measurement of local instantaneous LSMT in trickle bed reactors were adapted by Joubert and Nicol[6] for the simultaneous measurement of the corresponding wetted fraction of the electrode particles.   This technique was also used in this study. The electrolyte solution that was circulated through the columns, was an aqueous solution of 1M NaOH, 0.02M K$_4$Fe(CN)$_6$, 0.003M K$_3$Fe(CN)$_6$. The electrochemical reaction consisted of the reduction of Ferrycyanide on cathodes that consisted of multiple 4.5 mm diameter nickel coated bead

clusters, distributed along the length of each column, and the reverse reaction at the anode –
also a cluster of nickel coated particles at the bottom of each bed. At high enough voltages
the rate of the electrochemical reaction is fast enough to ensure that mass transfer is rate
controlling and the electrical current flowing in the solution between the electrodes is then a
direct measure of the rate of mass transfer and can be calculated using equation 1:

$$I = nCA_{cathode}\varphi k_{ls} \qquad (1)$$

The cathode area in this equation is based on a geometric calculation of the total area, while
φ is the fraction of the cathode that is actually in contact with the electrolyte – the cathode
wetted fraction. Joubert and Nicol[6] utilised the fact that the rate of the electrochemical
reaction becomes the rate limiting step at very low voltages in order to quantify the surface
area of the cathode that was exposed to the electrolyte solution. By varying the voltage
during the same experimental run, it is subsequently possible to simultaneously measure the
local LSMT coefficient and the wetting efficiency at each cathode. This allows one to
calculate the specific local LSMT coefficient (k_{ls}) based on the particle area that is actually in
contact with the liquid phase. Joubert and Nicol[6] determined that the electrochemical
reaction is rate limiting at voltages below 50 mV and subsequently a value of 20 mV was
used for the measurement of the wetting efficiency. A voltage of 1000 mV was shown to lie
in the centre of the mass transfer plateau and this value was used for all mass transfer
measurements.

In the 1.6 m long bed, the nickel coated clusters were more or less positioned at 0.2, 0.4, 0.5,
0.85 and 1.15 m (distances varied slightly each time the column was repacked) below the
liquid distributor (measured from the bottom of the cathode bead clusters) and in the 5 m bed
the clusters were placed 0.5, 2, 2.5, 3 and 3.5 m below the distributor. This corresponds to an
aspect ratio (z/D) range of between 2.94 and 33.3. The cathode bead clusters in the 1.6 m
column consisted of between 50 and 3500 beads, resulting in a geometric cathode surface
area of 0.00318 m^2 – 0.227 m^2, while cathodes consisting of 4000 beads ($A_{cathode}$ = 0.254 m^2)
were used in the 5 m column. The current/wetted area correlation was calibrated by
operating both columns under liquid flooded conditions while applying a low enough voltage
– 20 mV – to ensure that a change in superficial electrolyte velocity did not affect the current
reading. The single point calibration at different liquid velocities in the pilot scale column
followed the same straight line relationship previously reported for the smaller column[6] and
the independence of the wetted area measurement with liquid velocity was again confirmed.

The cathode clusters were separated from each other by sections of 4 mm glass beads. After each cluster of nickel beads was added to the bed, the column was tapped until a constant level was observed before the glass beads were added. Bed porosities in both columns varied between 0.37 and 0.4. A large section of nickel beads (8 times the size of the largest cathode) at the outlet of the column acted as the anode. This was to ensure that the anode reaction would not be the rate controlling step of the electrochemical reaction. The insulated copper wire used to complete the electrical circuit was soldered onto a single bead which was placed within the bottom quarter of the electrode height with the wire facing and descending directly downwards. The electrical current between a cathode and the anode under both applied voltage conditions, was measured with a NI PXI-4071 Digital Multi Meter with 7 ½ digit accuracy. In order to test whether the distance between the anode and each respective cathode may influence the measurements due to external effects, tests were performed in liquid flooded beds. The same values for wetting efficiency and mass transfer coefficients were obtained regardless of the distance between the cathode and the anode. This was considered to be sufficient proof that the ohmic resistance in the external circuit is negligible while the resistance of the flooded bed is very high.

The superficial gas velocity was controlled at a relatively low value of 20 mm/s by a Brooks Smart Mass Flow 5851S, while the superficial liquid phase velocities investigated were 3 mm/s and 5 mm/s as measured by an Electromagnetic Flow Measuring System (the PROline promag10H from Endress and Hauser). The liquid flow rate was adjusted by using a metering valve installed in parallel with a needle valve on the liquid supply line. In order to investigate the multiplicity behaviour of wetting efficiency and the local k_{ls}, the two different bed pre-treatment techniques that were determined by Loudon et al.[7] to be at the extremes of the flow hysteresis envelope were replicated. In the Kan pre-wetting mode, the liquid flow rate was increased until the pulsing regime was reached, after which the liquid flow rate was reduced and controlled at the desired set-point value. When the Levec pre-wetting procedure was followed, the bed was completely flooded by liquid and then drained for 30 minutes, after which the liquid and gas flow was introduced at a flow rate corresponding to the desired superficial velocity. In the 1.6 m column, each set of experiments were repeated four times – where a set consists of two velocities under the two pre-wetting conditions, while the experiments on the 5 m column were only repeated once. The cathodes were replaced after each set of repeat runs to guarantee the integrity of the coating. In order to prevent any possible decomposition of the electrolyte solution due to oxidation reactions, all the vessels in

the experiment were kept under a nitrogen atmosphere. Trivizadakis and Karabelas[8] measured the contact angles between the electrolyte solution and glass as well as nickel coated beads with a Kruess unit. They report similar values for both particle types. This was considered as sufficient proof that the physico-chemical interactions between the liquid/electrode beads and the liquid/glass beads in the rest of the bed may be assumed identical.

References

(1) Burghardt, A.; Bartelmus, G.; Jaroszyński, M.; Kolodziej, A. Hydrodynamics and mass transfer in a three-phase fixed-bed reactor with cocurrent gas-liquid downflow. *Chem. Eng. J.* **1995**, *58,* 83.

(2) Reiss, L.P.; Hanratty, T.J. Measurement of instantaneous rates of mass transfer to a small sink on a wall. *AIChE. J.* **1962**, *8*, 245.

(3) Mitchell, J.E.; Hanratty, J.T. A study of turbulence at a wall using an electrochemical wall shear meter. *J. Fluid Mec.* **1966**, *26*, 199.

(4) Chou, T. S.; Worley, F. L.; Luss, D. Local particle-liquid mass transfer fluctuations in mixed phase co-current down-flow through a fixed bed in the pulsing regime. *Ind. Eng. Chem. Fundam*. **1979***, 18,* 279.

(5) Rao, V. G.; Drinkenburg, A. A. H. Solid-liquid mass transfer in packed beds with co-current gas-liquid down flow. *AIChE J.* **1985**, *31,* 1059.

(6) Joubert, R.; Nicol, W. Trickle flow liquid–solid mass transfer and wetting efficiency in small diameter columns. *Can. J. Chem. Eng.* **2013**, *91*, 441.

(7) Loudon, D.; Van der Merwe, W.; Nicol, W. Multiple hydrodynamic states in trickle flow: Quantifying the extent of pressure drop, liquid holdup and gas–liquid mass transfer variation. *Chem. Eng. Sci.* **2006**, *26*, 7551.

(8) Trivizadakis, M. E.; Karabelas, A. J. A study of local liquid/solid mass transfer in packed beds under trickling and induced pulsing flow. *Chem. Eng. Sci.* **2006**, *61,* 7684.