

Theoretical and experimental study of the mass transfer inside silica **gel for flue gas drying** <u>A. Houzé</u>⁽¹⁾, N. Heymans ⁽¹⁾, G. De Weireld ⁽¹⁾

⁽¹⁾ Thermodynamics and Mathematical Physics Unit, University of Mons (UMONS), Place du parc 20, 7000 Mons, Belgium.

adrien.houze@umons.ac.be

Numerous studies are emerging on different capture and/or gas purification methods, among which adsorption appears to be an efficient technology. Various designs have been considered, particularly based on regeneration methods, cycle steps, and adsorbent types. However, in most adsorption process development studies, obtaining the fundamental parameters for describing the adsorbent is challenging and complex; in particularly for estimating mass transfer due to the complex phenomena that contribute to it. Although some specific equipment is designed for such measurements, it is rarely available in laboratories and is also costly [1]. Another alternative in adsorption studies is to estimate transfer coefficients from purely theoretical considerations [2]. However, it requires parameters that are difficult to estimate theoretically or determine experimentally. Finally, a simplified yet very imprecise approach is the use of breakthrough curves.

The aim of this study is to develop a hybrid method for determining mass transfer by combining experimental measurements with theoretical representations of the physical phenomena involved. This work is part of greenhouse gas capture efforts focused on the drying of flue gases, and thus the compounds considered will be carbon dioxide, nitrogen, and water. To avoid the issue of cross-effects between heat and mass transfer resulting from breakthrough curve measurements, uptake curves on small scale sample were measured. These are carried out on gravimetric (or volumetric) equipment, where the variation of the adsorbent mass (or the cell's pressure) is recorded over time. These measurements are conducted for a given pure compound, at a given temperature, and a specified pressure step. For water, the uptake curves were recorded using a gravimetric installation, Dynamic Vapor Sorption (DVS) from Surface Measurement Systems. For N₂ and CO₂, due to their faster adsorption kinetics, the measurements were carried out in a home-made volumetric/manometric apparatus.

Uptake curves were measured on a BASF silica gel (Sorbead R2050) from 30 to 60°C and from 5 to 85% of the saturation vapor pressure for water. For CO₂ and N₂, a range of 20 to 40°C and 0 to 15 bar was chosen. These experimental uptake curves were then incorporated into a fitting with the linear driving force (LDF) model, yielding a transfer coefficient for each temperature and pressure condition. Part of the results for water are shown in Figure 1. The quality of the fitting allowed an assessment of the LDF model towards its representation of the adsorption from low to high surface coverage. Further, the rate-limiting resistance in the diffusion within the silica gel was investigated. The LDF model considers film transfer, macropore diffusion, and micropore diffusion lumped into a single coefficient. If the film transfer is rate-limiting, the value obtained from theoretical models should approach the experimental value. Assuming the macropore diffusion is rate-limiting, the uptake curve can be represented with an alternative theoretical expression [3]. A macropore diffusion coefficient was thus fitted and compared to that of the LDF's model. If both values are of the same order of magnitude, it is reasonable to assume that the rate-limiting transfer occurs within the macropores. Otherwise, it resides either within the micropores or as a combination of multiple resistances. For a rate-limiting transfer in the macropores, it is then possible to determine the contributions of various diffusion mechanisms (molecular, Knudsen, Poiseuille, and surface diffusion) and to fit typically inaccessible theoretical parameters, such as the surface diffusion activation energy, using the experimental diffusion coefficient [4]. Finally, with temperature and pressure screening, an empirical expression can be derived to represent the mass transfer coefficient. This expression can ultimately be validated by comparing simulated breakthrough curves with those obtained experimentally.



Figure 1. Fitting of the LDF model (in blue) with the experimental uptake curve (in red) for three different pressure.



Resulting from this study, a $k_{LDF}(T,p)$ was determined for each of the three compounds. As an illustration, the values for water are shown in Figure 2. As expected, it appears that the kinetics are enhanced with increasing temperature. A parabolic behavior is observed with respect to pressure, reflecting the influence of surface coverage on kinetics, as seen in other studies [5]. For all three compounds, it seems that the macropore resistance is rate-limiting. Theoretical regression further suggests that surface diffusion is the primary mechanism for water, while molecular and Knudsen diffusion combine as the dominant mechanisms for nitrogen and carbon dioxide. This finding aligns with experimental results showing that temperature has a more pronounced effect on water compared to the other two gases. Surface diffusion, in particular, is characterized by a stronger dependence on temperature than other mechanisms. For modeling purposes, an Arrhenius law for temperature combined with a second-degree polynomial for pressure was determined for each compound. Finally, validation was achieved by comparing experimental breakthrough curves (for dry and humid CO_2/N_2) with those simulated.

This study demonstrates the feasibility of accurately determining and representing mass transfer within an adsorbent using a coupling of experimental measurements and theoretical models. This method avoids the limitations of breakthrough curves, which are susceptible to cross-effects with thermal phenomena. The LDF model can also be validated and applied to derive a transfer coefficient as a function of temperature and pressure. Finally, this combined approach provides fundamental insights into the diffusion phenomena occurring within the porosity of the adsorbent.



Figure 2. Evolution of the mass transfer coefficient of water on silica gel Sorbead R2050 (BASF) with temperature and pressure

References

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