Reinventing Rate Measurements by a Wetted Wall Column

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Abstract

Introduction. The absorption rate of a gaseous species by a liquid solvent can be measured using various apparatus, including stirred cell reactors [1], wetted sphere absorbers [2], laminar jet absorbers [3], string of disc contactors [4], stopped-flow apparatus [5], and wetted wall columns (WWC [6-14]). Each of these devices exhibits distinct mass transfer characteristics. Notably, the mass transfer properties and the geometry of the wetted wall column resemble those observed in reactive packed absorption columns, making it a useful tool for comparative analysis of absorption processes [8]. Another key advantage of the wetted wall is its versatility. It can operate over a wide range of temperatures, pressures, gas flowrates and liquid flowrates while also accommodating various solvent types, including aqueous amine solutions, nonaqueous CO_2-binding organic liquid [12] and biphasic solvents [13]. Furthermore, it is particularly well suited for measuring the overall liquid film mass transfer in systems involving fast chemical reactions.

WWC contactor and process diagram. Figure 1 shows the WWC contactor and process scheme available at the University of Texas (UT) at Austin, though alternative designs exist worldwide. This unit has been extensively used to evaluate the mass transfer coefficient of CO_2 in several amine systems. Consequently, CO_2 absorption in an amine-based solvent is the focus of the following analysis. However, by integrating the appropriate gas analyzer, the unit can also be used to study the mass transfer of other gaseous species in different solvents.
The liquid solvent enters the WWC through the bottom of the metal tube and overflows at the top forming a thin film on the outer surface of the tube, and exits from the bottom. The gas mixture (CO_2 and N_2) is introduced at the bottom of the reaction annulus and it flows upwards allowing absorption of absorbing gas in the liquid film. The stainless steel tube has an exposed height of 9.1 cm and an outer diameter of 1.26 cm and it is enclosed by a glass tube resulting in a hydraulic diameter of 0.44 cm and a cross-sectional for the gas flow of 1.3 cm^2. This contacting chamber is housed within a larger glass tube annulus filled with heating oil pumped from an external heater to control the temperature of the chamber. After contacting the gas phase, the solvent is pumped back to the liquid reservoir, which is about 1.1 L, forming a closed loop. A large solvent volume is required to provide a nearly constant loading during the experiments. Unlike the liquid solution, the gas is not recycled through the system. CO_2 and N_2 are mixed through mass flow controllers and the resulting gas blend is saturated with water at the operating temperature upstream of the WWC. This step prevents water mass transfer from the aqueous solvent to the gas stream in the reactive chamber. The gas exits from the top of the WWC and it is sent to a water knock out (an Erlenmeyer flask placed in a beaker filled with ice) followed by a

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drying column containing Drierite® Anhydrous Calcium Sulfate where the moisture is removed from the gas. The dry gas is then routed to the CO_2 analyzer (Horiba Infrared Detector VIA 510-A), where the concentration of CO_2 is measured. A bypass pathway on the gas line can be used to direct the saturate gas stream directly for concentration measurement without entering the contacting chamber. This bypass line can be used to determine the CO_2 concentration of the inlet gas into the WWC chamber. During the experiment, liquid samples can be taken from the solvent loop via the sample port downstream of the WWC. By measuring the outlet concentration of CO_2 in the gas phase and applying a material balance over the gas phase in the WWC, the CO_2 absorption flux, φ_{CO_2}, can be experimentally determined.

WWC design consideration. At the bottom of the stainless steel tube of the WWC a Teflon ring is placed to prevent the gas and liquid phases from mixing. In the UT design, there is only a single elevated inlet for the gas phase and a single outlet for the liquid stream. An improved design, developed by the Technical University of Denmark, DTU, features a Teflon ring with evenly distributed holes for three gas inlets and three liquid outlets [7]. This design allows for a more efficient liquid outflow from the reactive chamber, preventing the formation of a stagnant liquid film at the bottom of the WWC, which could introduce uncertainties in the evaluation of the gas-liquid contact area. Additionally, the configuration with 3 gas inlets is expected to promote a more even distribution of the gas phase on the cross section of the contact chamber. Another important consideration in WWC operation is ensuring a uniform liquid film coating the metal tube. The presence of dry spots or rippling phenomena can significantly impact the absorption rate, introducing modelling uncertainties. To address this, Luo [11] developed a hydraulic experiment using a high-speed camera to determine the optimal liquid flow rate range necessary to maintain a continuous, well-defined liquid film on its wetted wall (Norwegian University of Science & Technology, Trondheim), free from rippling and dry spots.
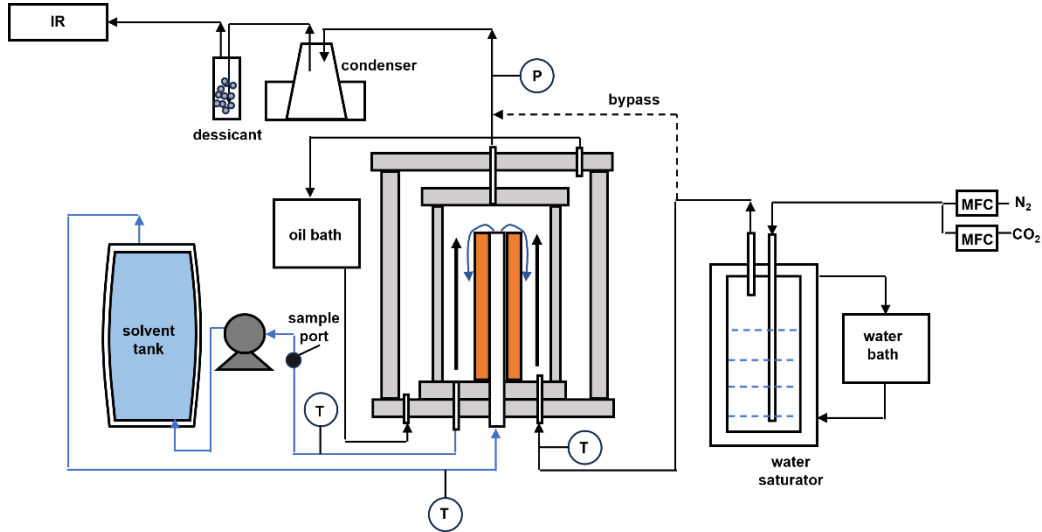

Figure 1. *Flowsheet of the wetted wall column experiment (setup available at the University of Texas).*

Data interpretation and design of experiments. By applying the two-film model and considering the continuity of the flux from the gas to the liquid, the absorbed CO_2 flux in the WWC can be described as $\varphi_{CO_2} = K_G \cdot \Delta P_{CO_2,LM}$, where K_G is the overall mass transfer coefficient, and $\Delta P_{CO_2,LM}$, is the overall logarithmic mean driving force between the top and the bottom of the column. In particular:

- $\Delta P_{CO_2,LM}$ can be evaluated as $\Delta P_{CO_2,LM} = \frac{(p_{CO_2}^{in} - p_{CO_2}^*) - (p_{CO_2}^{out} - p_{CO_2}^*)}{\ln\left(\frac{p_{CO_2}^{in} - p_{CO_2}^*}{p_{CO_2}^{out} - p_{CO_2}^*}\right)}$, where $p_{CO_2}^*$ is the partial pressure of the absorbing gas

  in equilibrium with the liquid bulk concentration and $p_{CO_2}^{in}$ and $p_{CO_2}^{out}$ are, respectively, the CO_2 partial pressure at the inlet and at the outlet of the WWC;

- K_G can be expressed as : $\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k_G'}$ (the series of resistance approach has been applied; the k_G and k_G' are the gas-side and liquid-side mass transfer coefficients with driving force in gas partial pressure unit, respectively).

During the experiment, six data points are collected at a steady-state CO_2 flux by varying the bulk gas CO_2 partial pressures between 0 (pure nitrogen) and twice the estimated $p_{CO_2}^*$. This approach enables both absorption and desorption with comparable CO_2 fluxes, allowing for the bracketing and determination of the $p_{CO_2}^*$ of the liquid solvent [8]. By plotting CO_2 flux against the driving force, as shown in Figure 2, the K_G is obtained as the slope of the fitted line, while the $p_{CO_2}^*$ value provides a 0 flux when the driving force

is 0. As a result, the experiment provides values for K_G and $p_{CO_2}^*$ at a given T for a solution of known amine concentration and CO_2 loading.
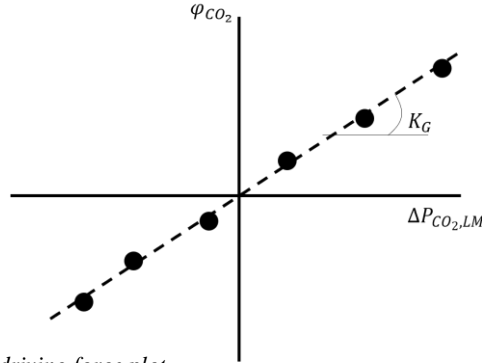

Figure 2. Example of a flux against driving force plot.

To get accurate estimates of K_G and $p_{CO_2}^*$, careful selection of gas and liquid flow rates, total pressure, and CO_2 driving force along the column is required.

- The ultimate goal of the experiment is to determine the CO_2 absorption/desorption performance of the solvent, i.e., k_G'. To achieve this, the gas phase resistance must be minimized, which is accomplished by selecting a high gas flowrate (in most of the experiments carried out in the WWC described above the total gas flowrate was set to 5 STLM). However, excessively high gas velocity can be detrimental. If the velocity is too high, the amount of CO_2 reacting in the chamber decreases, reducing the statistical accuracy of the difference between the inlet and the outlet gas phase CO_2 concentration. Additionally, excessive gas flow may disrupt the liquid film flowing down the contactor, potentially causing dry spots to form. Therefore an optimum gas flowrate has to be found for the specific WWC.
- A high liquid flowrate is generally recommended to prevent physical mass transfer in the liquid film from significantly affecting the measurements. This effect is embedded within the k_G' coefficient. To explicitly account for it, Dugas [8] applied the film resistance theory, representing the reaction and diffusion films in the liquid, and derived a complex expression for k_G': $\frac{1}{k_G'} = \frac{1}{k_G''} + \frac{1}{k_{L,prod}^0} \cdot \frac{\Delta P_{CO_2}^*}{\Delta[CO_2]_T} = \frac{1}{k_G''} + \frac{1}{k_{G,diff}'}$, where $\frac{1}{k_G''}$ represents the reaction resistance, characterized by the pseudo first order condition, $k_{G,diff}'$ describes the behavior within the diffusion film, which is expected to align with that of an instantaneous reaction regime (inside this term, $k_{L,prod}^0$ is the physical mass transfer coefficient for reactants and products and $\frac{\Delta P_{CO_2}^*}{\Delta[CO_2]_T}$ is the slope of the equilibrium line, which results from changing a concentration driving force to a partial pressure driving force). According to a fundamental model by Pigford [15], $k_{L,prod}^0$ is directly proportional to the liquid flowrate; therefore, increasing the liquid flowrate helps to minimize the impact of $\frac{1}{k_{G,diff}'}$ in the k_G' parameter. Typically, a liquid flowrate of 2 to 4 ml/s is used in the WWC experiments.
- High CO_2 driving forces along the WWC should also be avoided. When a higher driving force is present, a faster reaction is expected to occur, leading to increased depletion of the amine near the gas-liquid interface. This shifts the system into a mass transfer-controlled regime. Under these conditions, the data points in the CO_2 flux vs. driving force plot deviate from a linear trend because K_G becomes function of the CO_2 partial pressure/driving force in the WWC.
- Another point of concern is how the gas phase is modelled within the WWC. The conventional approach assumes it behaves as a plug flow. The validity of this assumption becomes more critical as the change in CO_2 gas concentration along the column increases. To minimize the impact of this assumption, the change in CO_2 concentration along the column should be kept within a range of 10–30%.

As mentioned, the ultimate objective is to use the WWC to obtain k_G', which is the key parameter for comparing different absorbent systems. To derive k_G' from the measured K_G, a correlation for estimating k_G is needed. Since k_G is highly dependent on the geometry of the specific WWC, an independent determination of k_G is required for each WWC configuration. These tests are conducted in a gas mass transfer limited regime using an absorbent with a known k_G'. Pacheco determined the k_G of the WWC at the University of Texas by applying the Hobler approach [16] to the study of CO_2 absorption in unloaded 2 M MEA (T between 25 and 90 °C, gas flow rate between 0.02 and 1.4 l/min, p = 100 psig). Later, the WWC at UT was retested, confirming the Pacheco correlation, using a 2 M PZ aqueous solution by Dugas (T = 40, 60 °C, p between 15 and 70 psig, and gas flowrate between 3 and 5 SLPM) [8] and by Bishnoi, who investigated SO_2 absorption in 0.1 M NaOH solution (gas flowrate 5, 6 SLPM) [14]. This latter system was also employed by Luo [11] for characterizing the k_G of the WWC at NTNU and by Gladis for the WWC at DTU [9]. In this case, the reaction can be assumed instantaneous and irreversible and the kG' resistance can be completely disregarded [11].

Since both solvents exhibit faster reaction kinetics than CO_2 absorption in MEA, these experiments should be more gas film-controlled. These are the correlations for the WWC at UT and at DTU:

$$Sh = 1.075 \cdot \left(Re \cdot Sc \cdot \frac{d_H}{h}\right)^{0.85}$$

$$Sh = 3.61 \cdot \left(Re \cdot Sc \cdot \frac{d_H}{h}\right)^{0.59}$$

where the dimensionless numbers are evaluated as: $\quad Sh = \frac{k_G \cdot d_H \cdot R \cdot T}{\wp_{CO_2}^G}, \quad Re = \frac{\rho_G \cdot d_H \cdot v_G}{\mu_G} \quad$, and $\quad Sc = \frac{\mu_G}{\rho_G \cdot \wp_{CO_2}^G}$

In the previous expression d_H is the hydraulic diameter of the annulus where the gas flows, h is the height of the WWC, ρ_G and μ_G are the density and viscosity of the gaseous mixture, respectively, v_G is the velocity of the gas in the WWC, $\wp_{CO_2}^G$ is the diffusion coefficient of CO_2 in the gas phase, and R is the gas constant.

Conclusions. This study has demonstrated the proper operation of a WWC apparatus to obtain reliable k_G' data. These data can be used to investigate the dependence of k_G' on reaction kinetics, equilibrium and the diffusion of reactants and products in the liquid film, but this falls beyond the scope of the present work, which is instead, identifying the most critical parameters for effectively operating the WWC. These guidelines will be applied to obtain new k_G' data for the 5 m Piperazine aqueous solution, addressing a gap in the scientific literature, which currently relies solely on the data collected by Dugas using the same WWC.

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