Reinventing Rate Measurements by a Wetted Wall Column

PCCC-8, 16th September 2025

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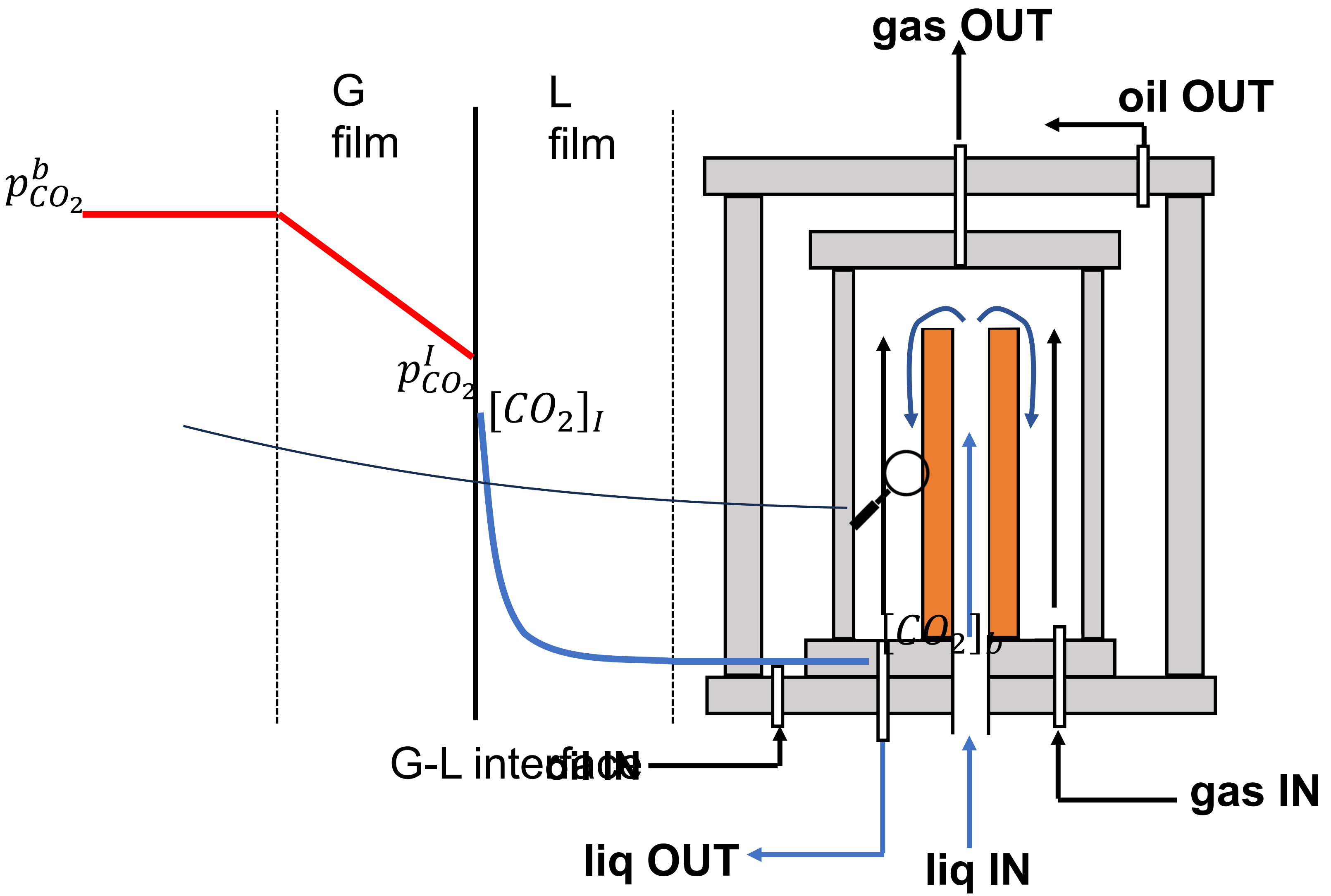
Why do we want to measure the reaction rate of CO_2 absorption? And why in a WWC?



Mass transfer contactors

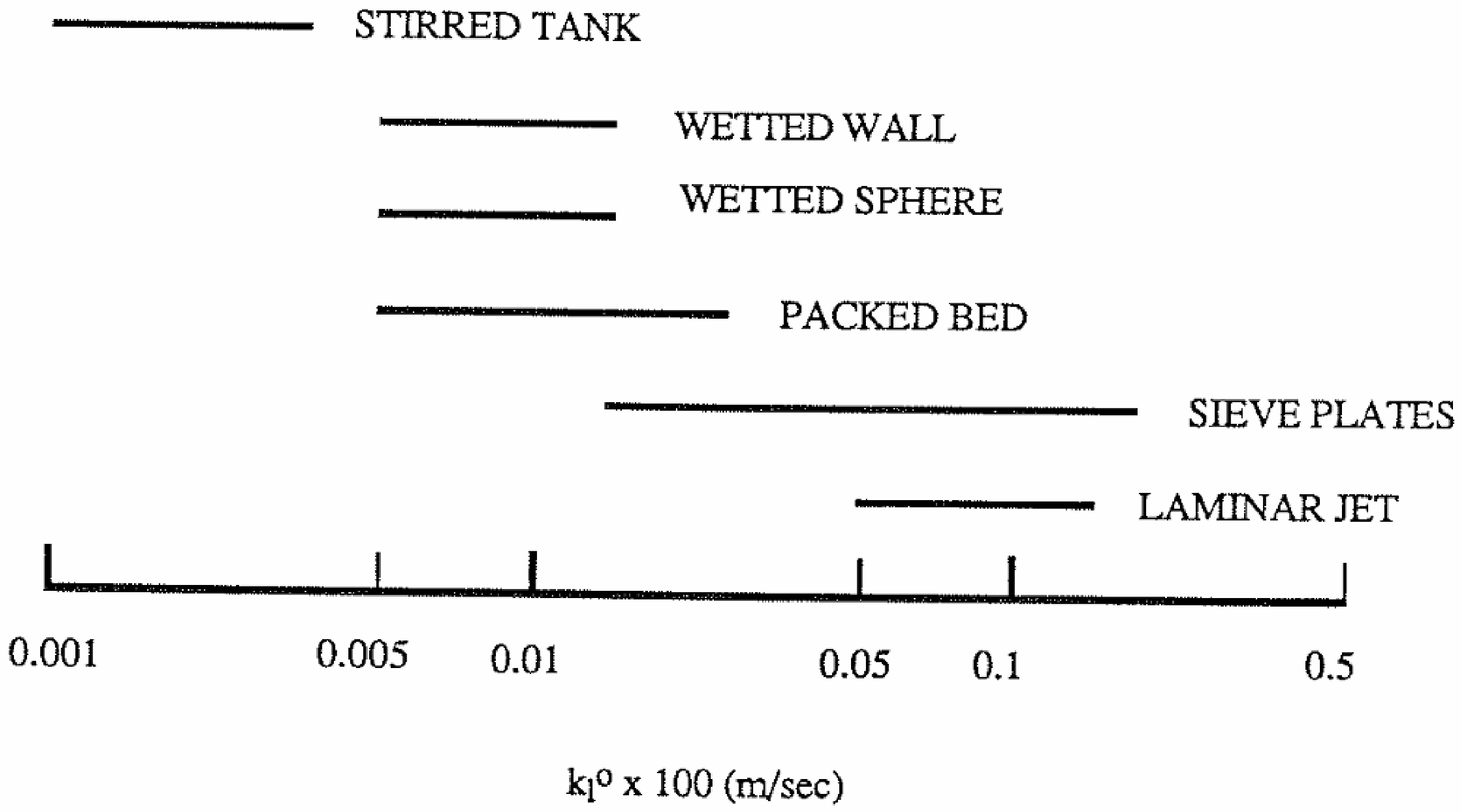
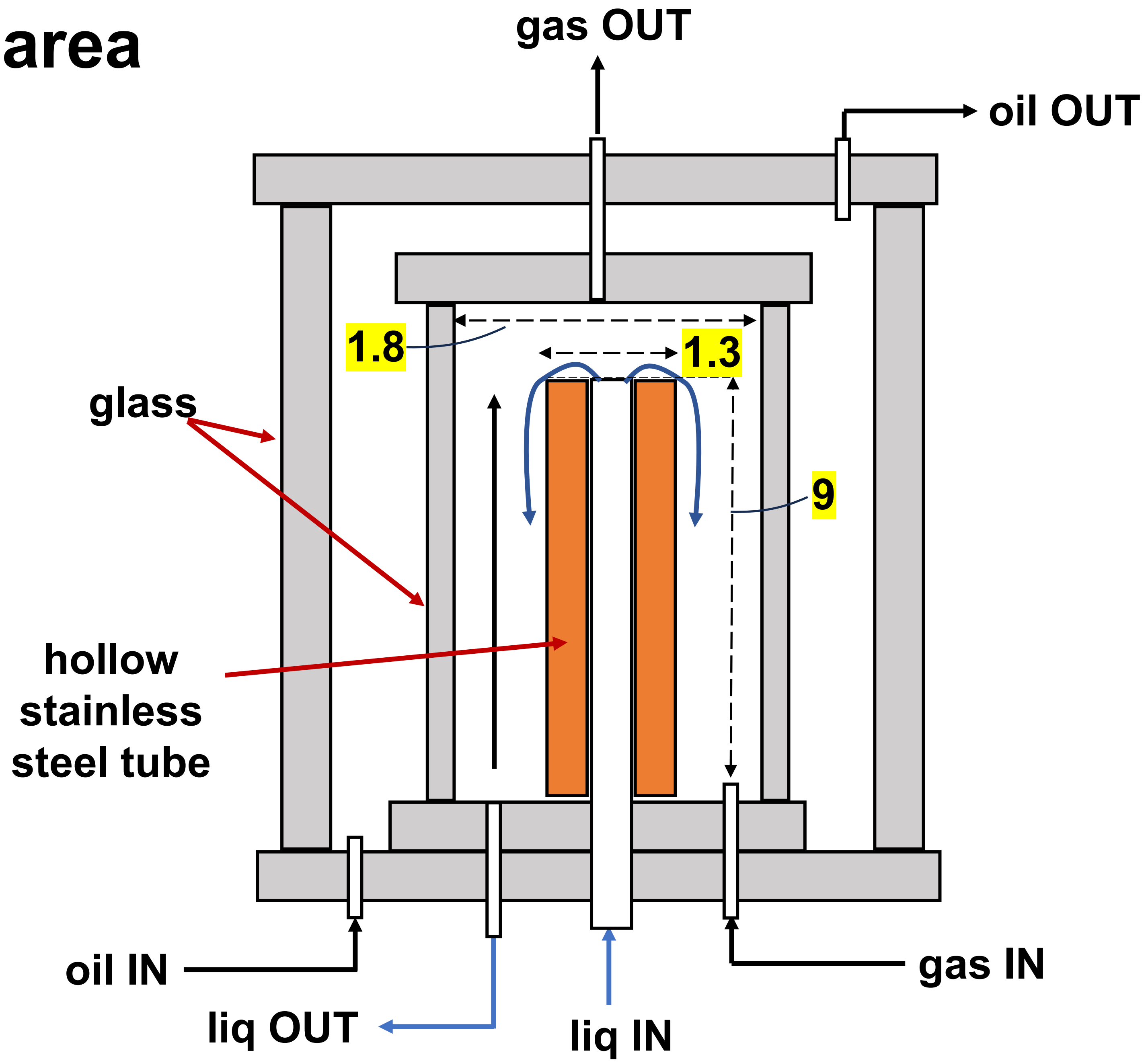


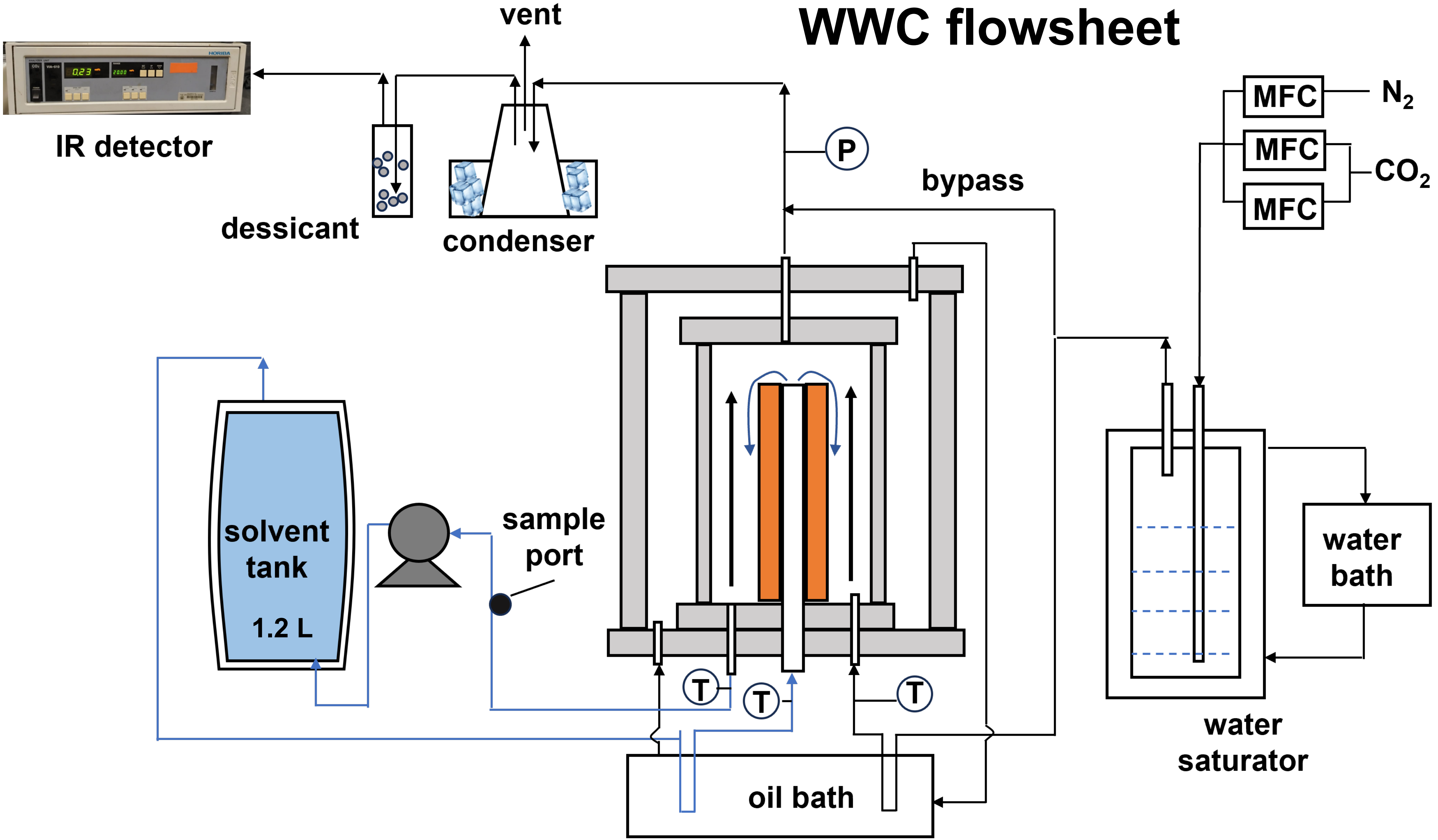
Figure 7.1 Liquid-Phase Mass Transfer Coefficients for Various Types of Equipment (Astarita et al., 1983; Fair, J., 1987)

Total contact area
= 39 cm^2

dimensions in cm

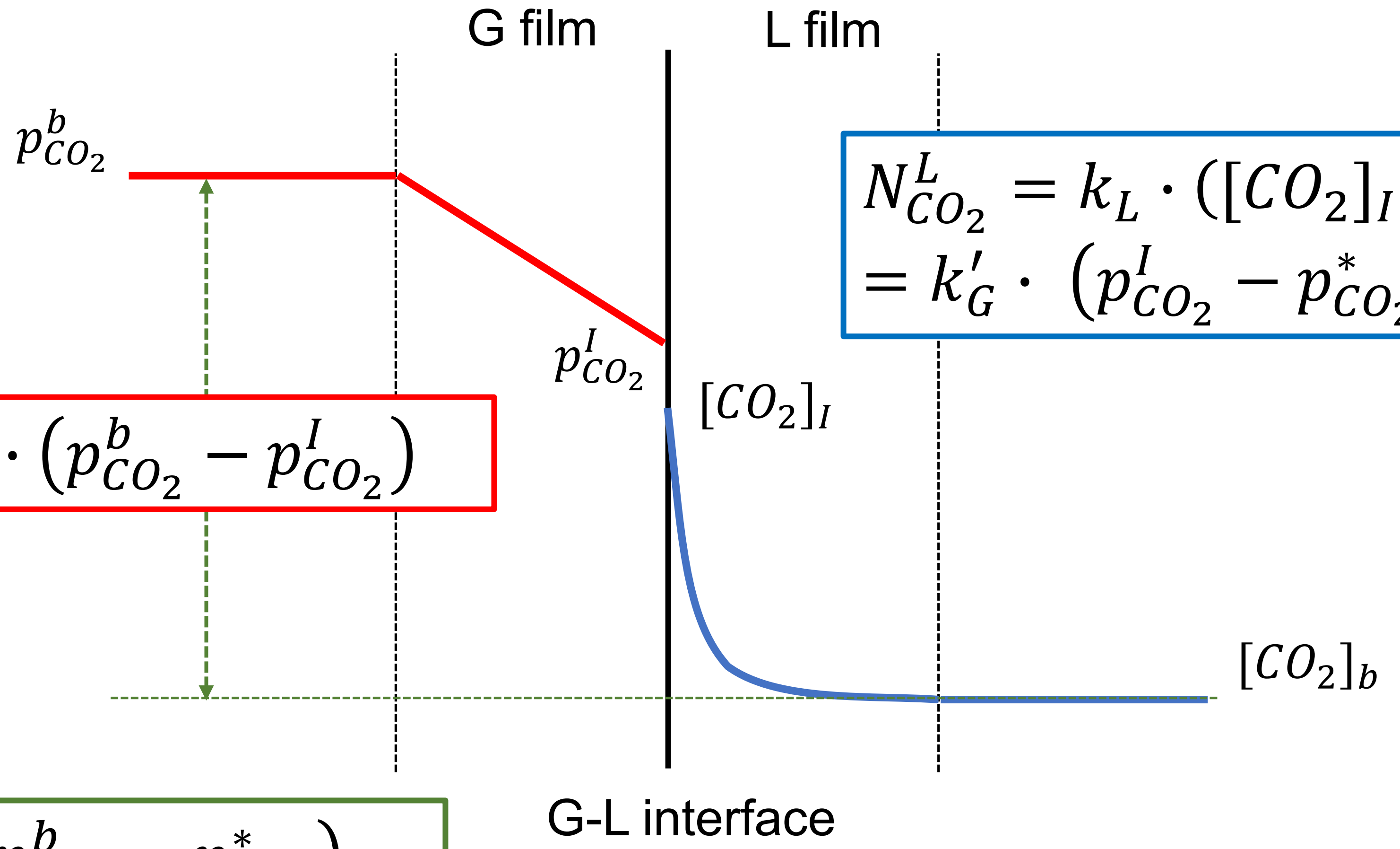


WWC flowsheet



Mass transfer: two-film theory

The mass transfer of CO_2 from the gas phase into the liquid phase can be described using the **two-film theory** (Lewis et al., 1924).



$$N^L_{CO_2} = k_L \cdot ([CO_2]_I - [CO_2]_b) = k'_G \cdot \left(p^I_{CO_2} - p^*_{CO_2}\right)$$

$$N^G_{CO_2} = k_G \cdot \left(p^b_{CO_2} - p^I_{CO_2}\right)$$

$$N_{CO_2} = K_G \cdot \left(p^b_{CO_2} - p^*_{CO_2}\right)$$

Mass transfer: two-film theory \2

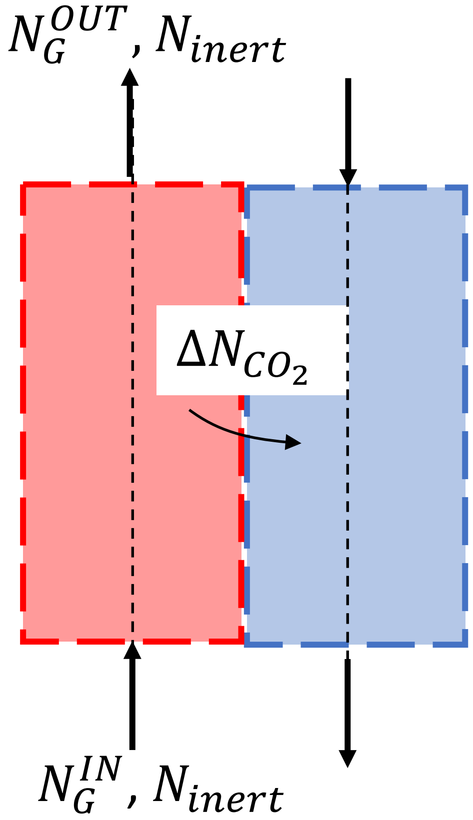
At steady-state, the fluxes across each mass transfer films are the same ($N^G_{CO_2} = N^L_{CO_2} = N_{CO_2}$) and the mass transfer coefficients can be written in the **series resistance form**:

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k'_G}$$

In a typical WWC experiment the steady-state N_{CO2} is measured and by defining the appropriate driving force along the WWC, it is possible to evaluate the K_G parameter.

HOW DO WE MEASURE N_{CO2} IN A WETTED WALL COLUMN?

N_{CO_2} → material balances for the gas phase



Material balance over the **gas phase**

HP: **Only CO_2 is transferred between the gas and liquid phases.**

$$N_G^{IN} - N_G^{OUT} = N_{CO_2}$$

$$N_{CO_2} = \left(N_{N_2} + \frac{N_{N_2} + N_{CO_2}^{IN}}{1 - \frac{p_{H_2O}^{sat}(T)}{p}} \cdot \left(\frac{p_{H_2O}^{sat}(T)}{p} \right) \right) \cdot \frac{\left(y_{CO_2}^{IN} - y_{CO_2}^{OUT} \right)}{\left(1 - y_{CO_2}^{IN} \right) \cdot \left(1 - y_{CO_2}^{OUT} \right)}$$

Overall mass transfer coefficient, K_G

$$N_{CO_2} = K_G \cdot \left(p^b_{CO_2} - p^*_{CO_2}\right)$$

?

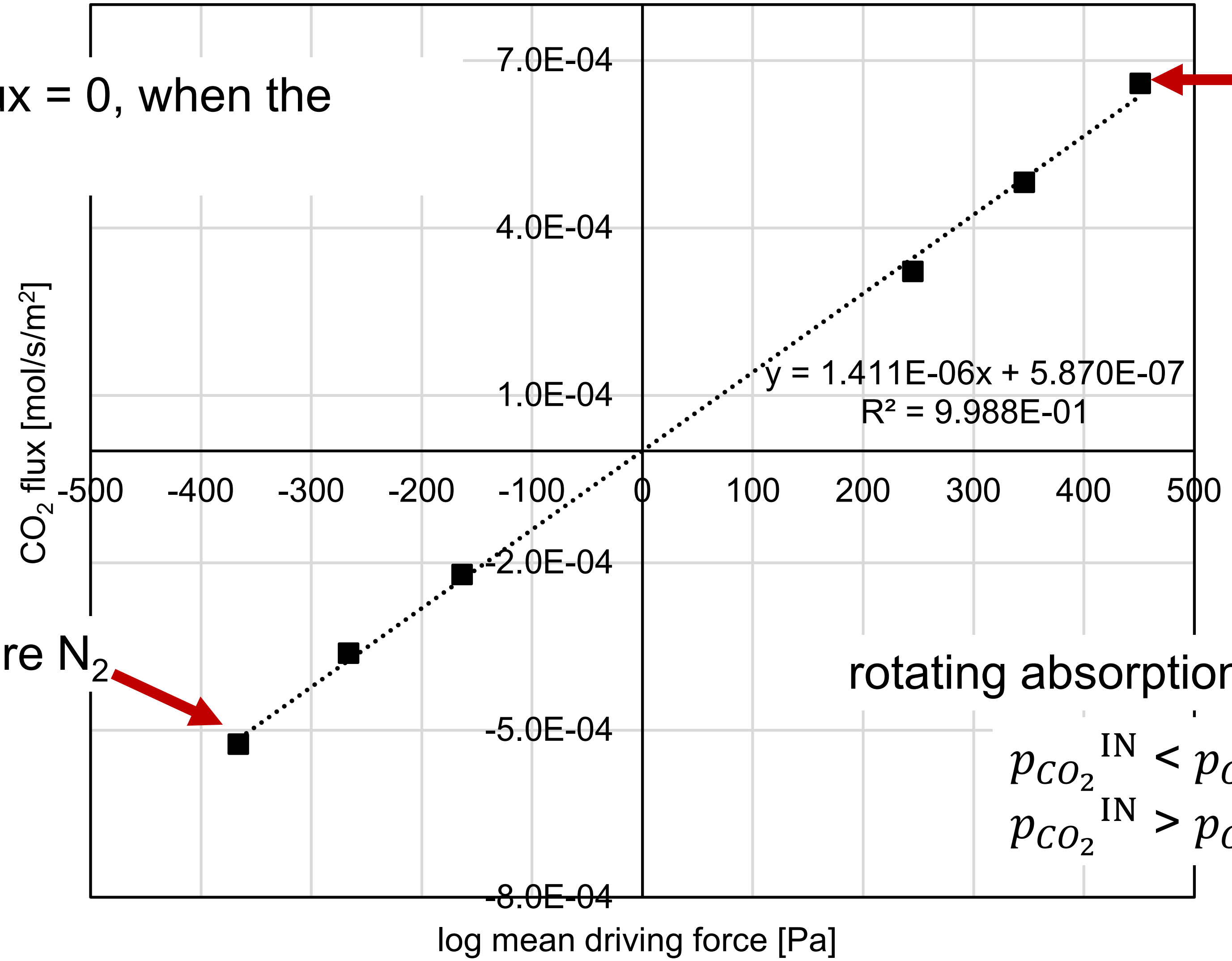
CO_2 profile in the gas phase is expected to have a **curved or** somewhat **asymptotic shape** (**gas** phase modelled **as a pfr**) ←→ **log mean driving force** gives a better weighted average of the driving forces along present along the WWC.

$$\left({p_{CO_2}}^b - {p_{CO_2}}^*\right)_{LM} = \frac{\left({p_{CO_2}}^{IN} - {p_{CO_2}}^*\right) - \left({p_{CO_2}}^{OUT} - {p_{CO_2}}^*\right)}{\ln\left(\frac{{p_{CO_2}}^{IN} - {p_{CO_2}}^*}{{p_{CO_2}}^{OUT} - {p_{CO_2}}^*}\right)}$$

$$\cancel{K_G = \frac{N_{CO_2}}{\left({p_{CO_2}}^b - {p_{CO_2}}^*\right)_{LM}}}$$

Overall mass transfer coefficient, K_G \2

$p_{CO_2}{}^*$ ← the CO_2 flux = 0, when the driving force is 0



$2 \cdot p_{CO_2}{}^*$

pure N_2

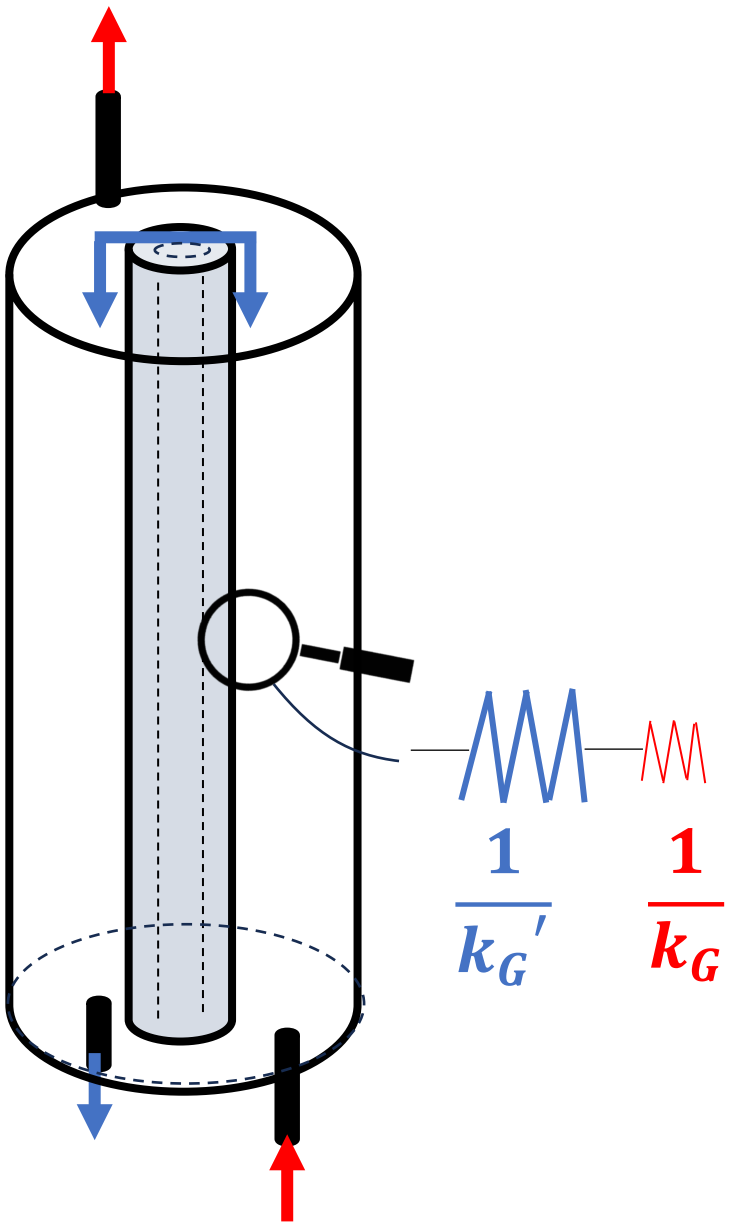
rotating absorption/desorption experiments

$p_{CO_2}{}^{\mathrm{IN}} < p_{CO_2}{}^*$ desorption

$p_{CO_2}{}^{\mathrm{IN}} > p_{CO_2}{}^*$ absorption

T = 40 °C, p = 24 psig, 5m PZ, loading = 0.310 [$molCO_2/mol_{Alk}$], total gas flowrate = 4.5 [Nl/min] (all the same for each of the six runs).

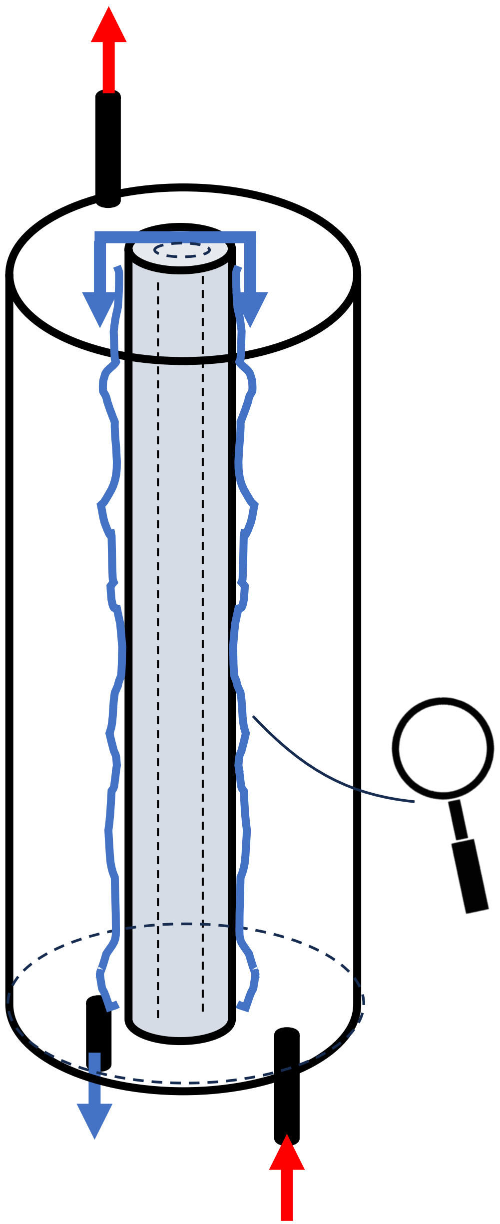
1. Gas film mass transfer resistance



gas flowrate ↑	
$1/k_G$	↓
$\Delta p_{CO2}\|_{WWC}$	↓
liquid film stability	↓

gas flowrate ≈ 5 Nl/min

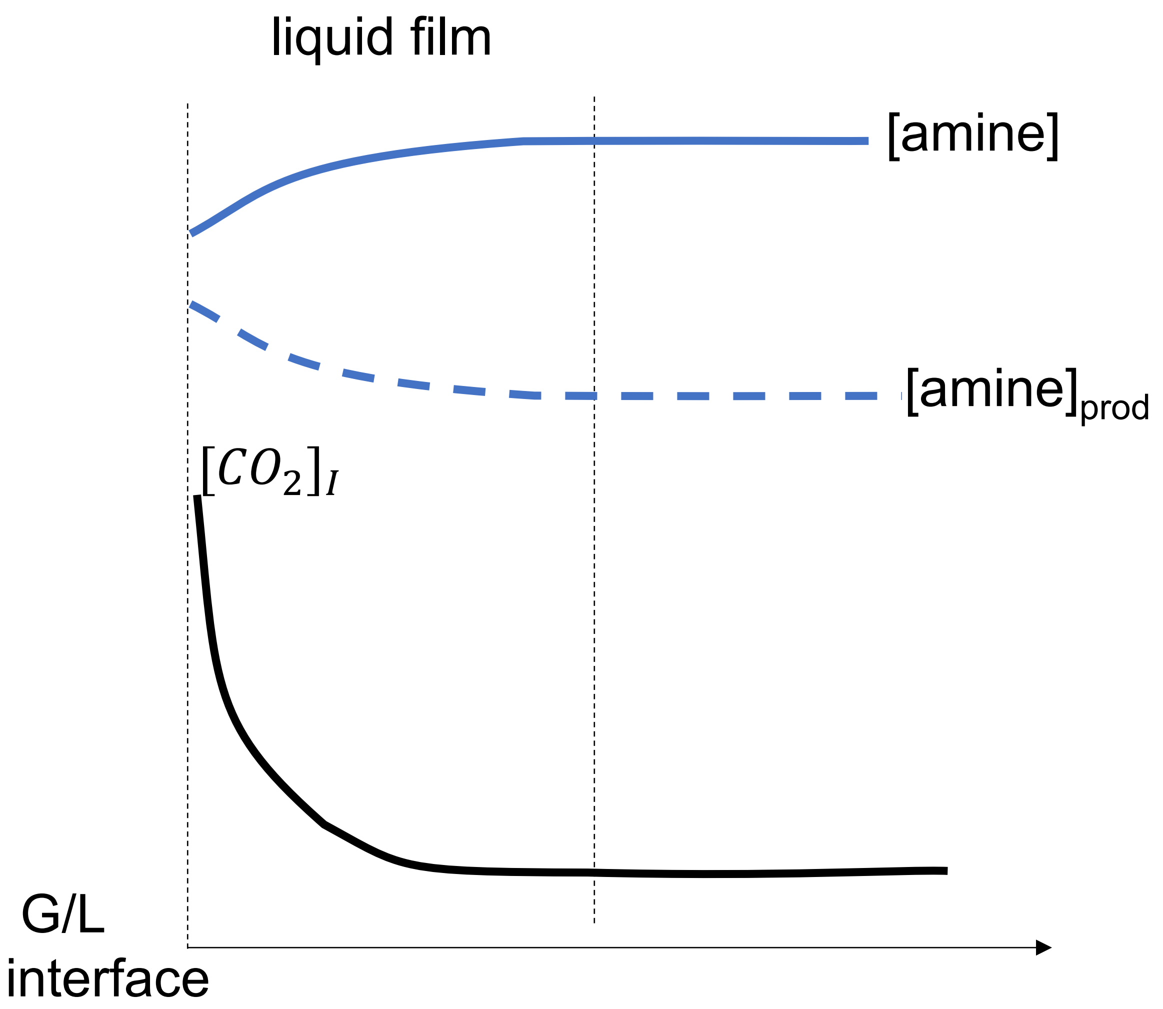
2. Liquid film diffusional resistance



liquid flowrate ↑	
k_L^0	↑
liquid film stability	↓

liquid flowrate ≈ 2 - 4 ml/s

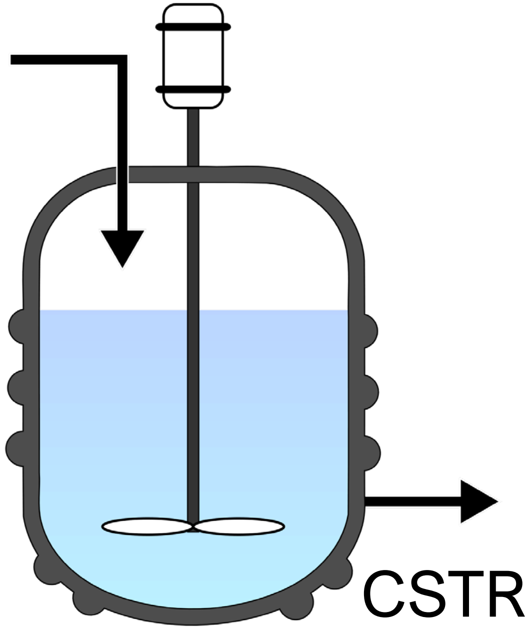
3. Mass transfer limited regime

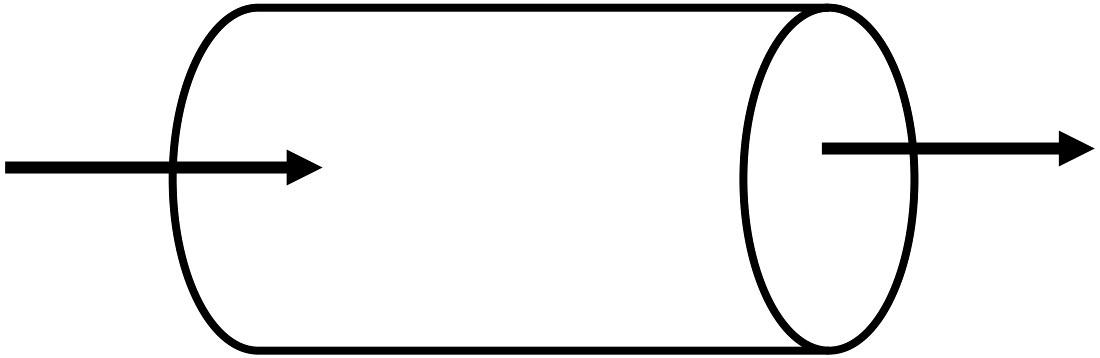


$\nabla p_{CO_2} \downarrow$

${p_{CO_2}}^{IN}$ not too different from ${p_{CO_2}}^{*}$

4. Gas phase modelling





change in p_{CO_2} along the column ≈ 10 – 30%

5. Pressure

jacketed bubbling saturator

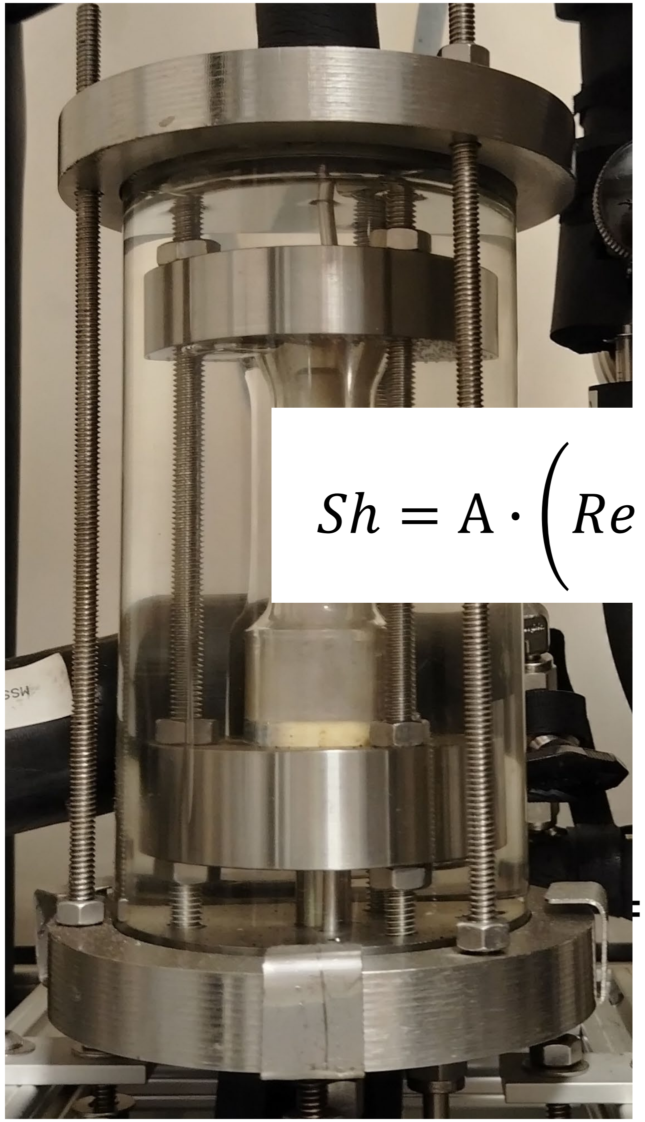
$$p \geq 20\,psig$$

Max pressure → 110 psig (PSV)

Gas film mass transfer coefficient, k_G

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k'_G}$$

?



$$Sh = A \cdot \left(Re \cdot Sc \cdot \frac{d_H}{h_{WWC}} \right)^B$$

Luo: A = 2.0006, B … = 3.61, B = 0.59

Pacheco: A = 1.075, B = 0.85

WWC at UT.

Liquid film mass transfer coefficient, k_G'

$$\frac{1}{K_G} = \frac{1}{k_G} + \frac{1}{k'_G}$$

?

Solvent → **5m PZ solution**

Why?

1. the **extensive experimental work conducted by Rochelle's group demonstrated that 5m PZ solution is the best compromise between CO_2 absorption capacity and viscosity:** 5m PZ solution is 50% less viscous than 8m PZ, which enhances heat and mass transfer;

2. Dugas, 2009: measured the k_G' of this solvent and his data can be used for comparison.

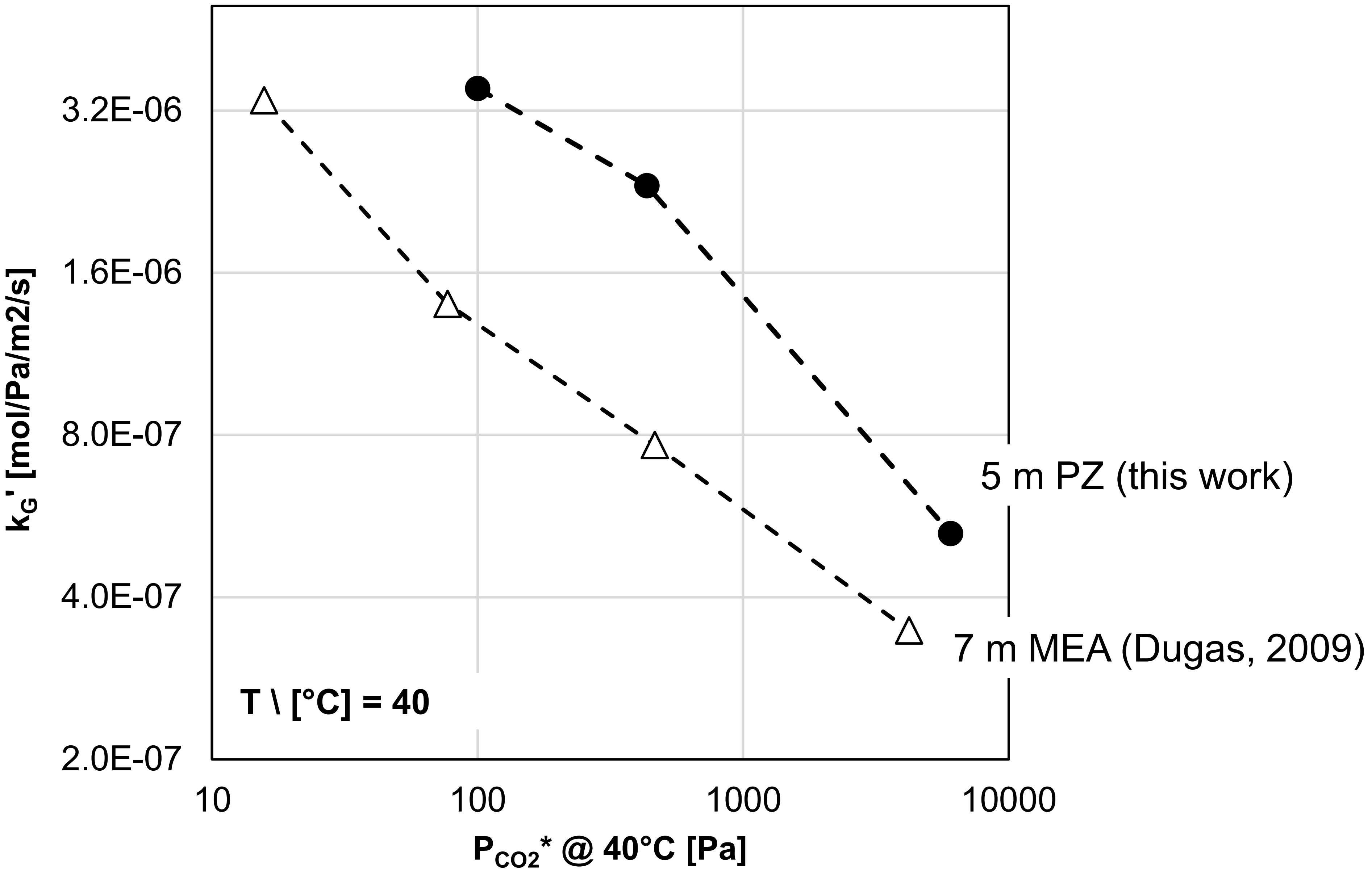
Experimental conditions: temperature (30 – 80 [°C]), loading (0.236, 0.310, 0.404 [mol CO_2/mol $_{Alk}$])

Loading measured via TIC (Total Inorganic Carbon) + titration

[kg CO_2/kg $_{solution}$]

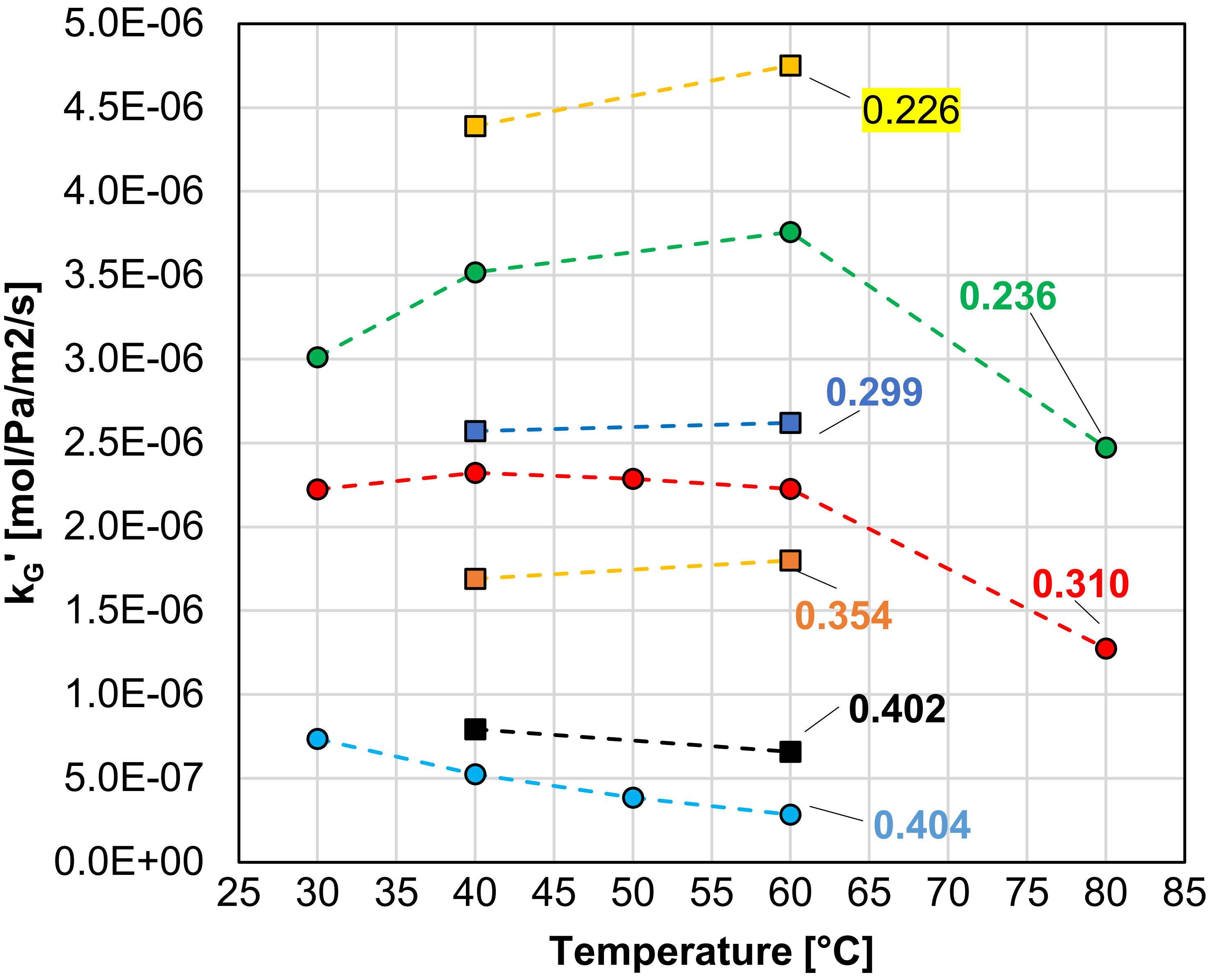
[kg PZ/kg $_{solution}$]

Results



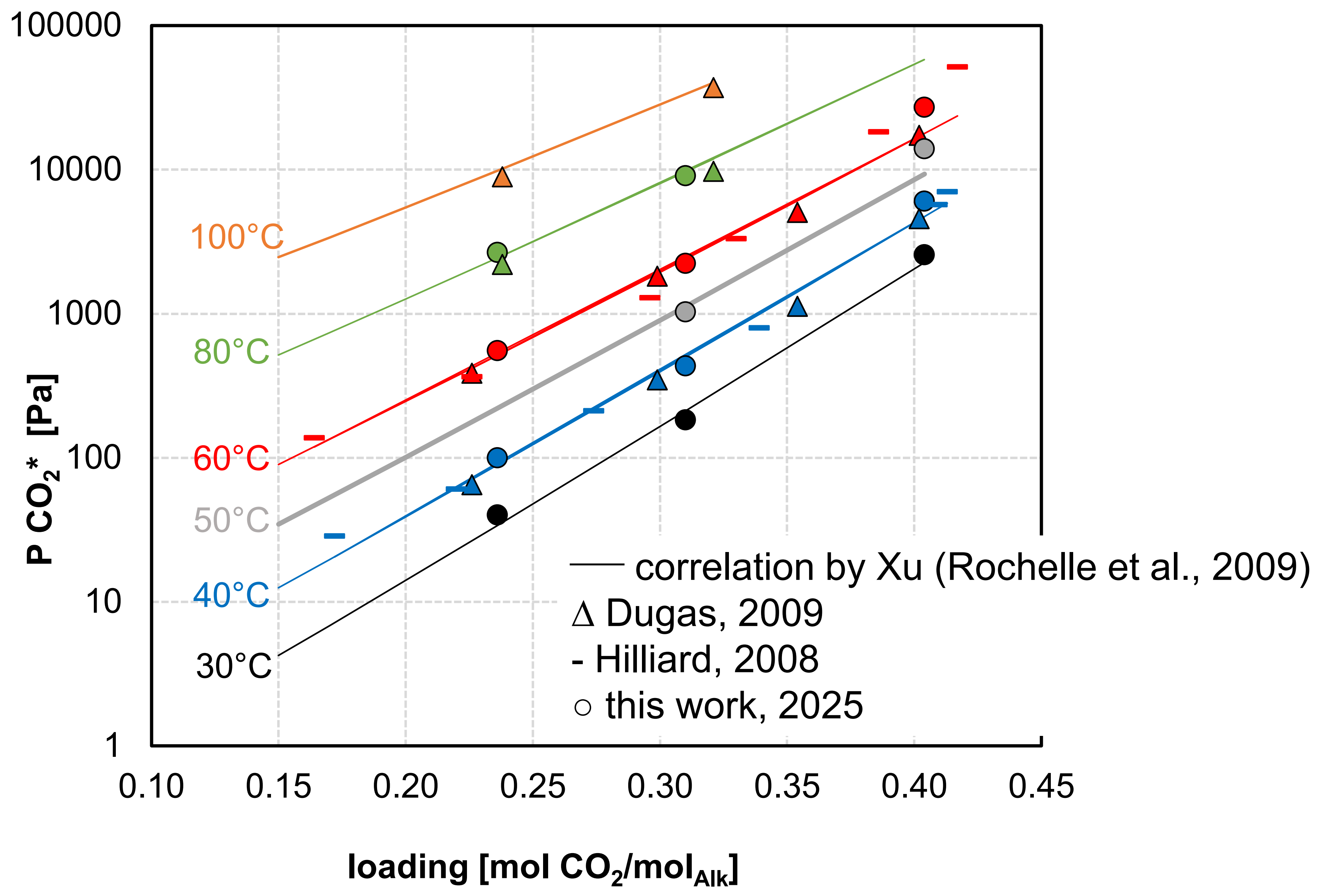
5 m PZ and 7 m MEA mass transfer rate comparison at 40 [°C].

Results \2



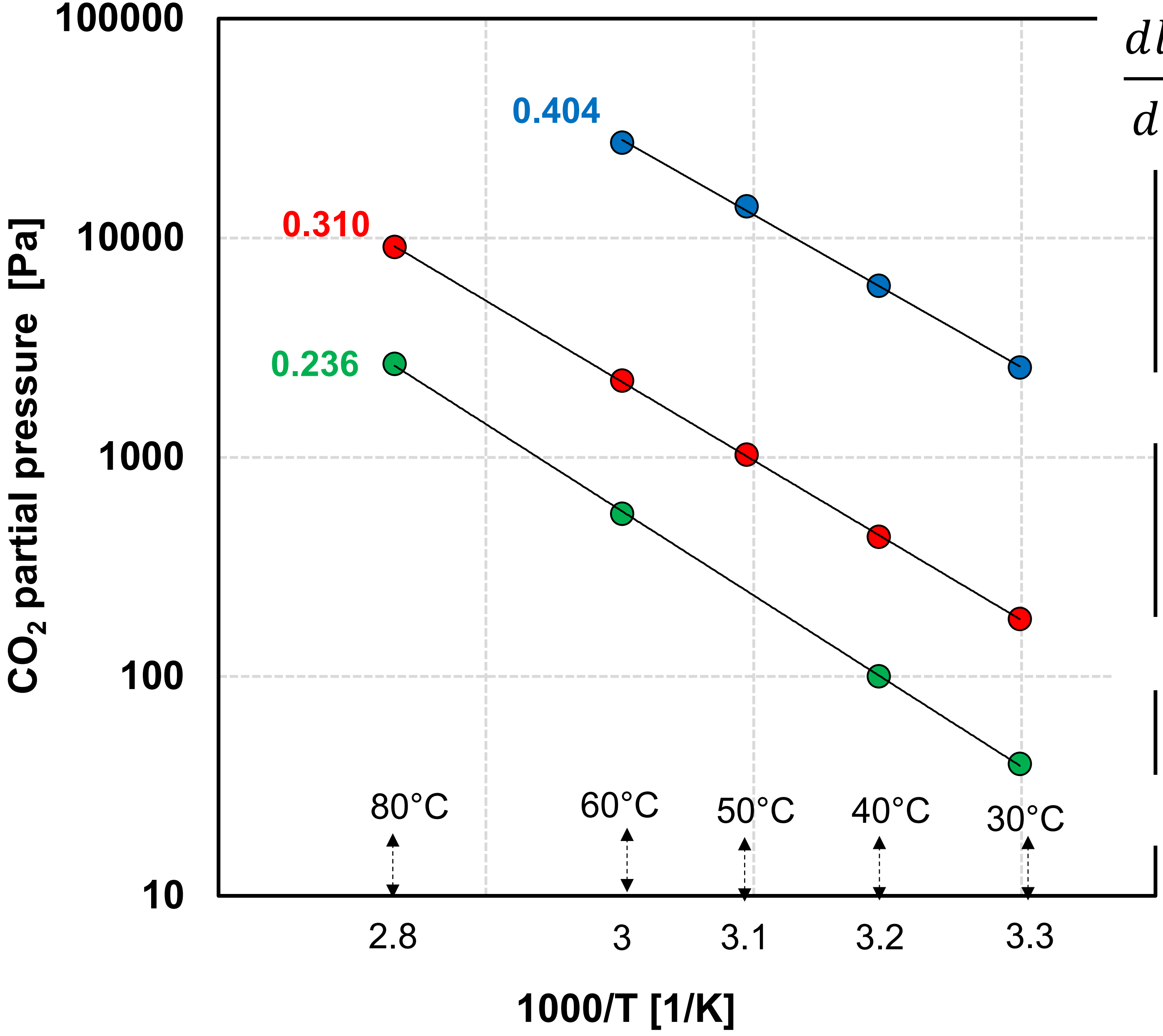
k_G' for 5 m PZ as a function of loading and temperature, data by this work (○) and Dugas, 2009 (□).

Results \3



100000
10000
1000
100
10
1
P CO_2* [Pa]
100°C
80°C
60°C
50°C
40°C
30°C
0.10
0.15
0.20
0.25
0.30
0.35
0.40
0.45
correlation by Xu (Rochelle et al., 2009)
Δ Dugas, 2009
- Hilliard, 2008
○ this work, 2025
loading [mol CO_2/mol_{Alk}]

Results \4



$$\frac{d\ln p_{CO_2}}{d\left(1/T\right)} = \frac{-\Delta H_{abs}}{R}$$

$-\Delta H_{abs} = 67\ kJ/mol$

$-\Delta H_{abs} = 70\ kJ/mol$

$-\Delta H_{abs} = 75\ kJ/mol$

Conclusions

1. **replicate data** by **Dugas for 5m PZ;**

2. **k_G'** show **a weak temperature dependence;**

3. **k_G'** show **a stronger loading dependence;**

4. the measured **k_G' [mol/m^2/s/Pa]** at **p_{CO2}* ≈ 0.1 kPa was 3.52E-06 for 5 m PZ, compared to 1.40E-06 for 7 m MEA.**

Outlook

Apply the guidelines to characterize a new generation solvent in a nearly built WWC available at the Eni S.p.A. laboratories in San Donato Milanese, Milan, Italy.

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References

Conversano A, Gatti M, Scazzabarozzi R, Martelli E, Ali I, Moure G, Consonni S, "Techno economic assessment of novel vs. standard 5m piperazine CCS absorption processes for conventional and high-efficiency NGCC power plants." 14th International Conference on Greenhouse gas control technologies, GHGT-14.

Darde V. *CO_2 capture using aqueous ammonia.* Technical University of Denmark. Ph.D. Dissertation. 2011.

Dugas RE. *Carbon Dioxide Absorption, Desorption, and Diffusion in Aqueous Piperazine and Monoethanolamine.* The University of Texas at Austin. Ph.D. Dissertation. 2009.

Freeman SA. *Thermal degradation and oxidation of aqueous piperazine for carbon dioxide capture*. The University of Texas at Austin. Ph.D. Dissertation. 2011.

Gladis AB *Upscaling of enzyme enhanced CO_2 capture.* Technical University of Denmark. Ph.D. Dissertation. 2017.

Glasscock DA. *Modelling and experimental study of carbon dioxide absorption into aqueous alkanolamines.* The University of Texas at Austin. Ph.D. Dissertation. 1990.

Hilliard MD. *A Predictive Thermodynamic Model for an Aqueous Blend of Potassium Carbonate, Piperazine, and Monoethanolamine for Carbon Dioxide Capture from Flue Gas.* The University of Texas at Austin. Ph.D. Dissertation. 2008.

Hobler T. *Mass transfer and absorbers*. Oxford: Pergament press., 1966.

Luo X. *Experimental and numerical study of carbon dioxide mass transfer and kinetics in amine solutions.* Norwegian University of Science and Technology. Ph.D. Dissertation. 2012.

Pacheco MA. *Mass Transfer, Kinetics, and Rate-based Modeling of Reactive Absorption*. The University of Texas at Austin. Ph.D. Dissertation. 1998.

Patek J, Hruby J, Klomfar J, Souckova M, Harvey AH. "Reference correlations for thermophysical properties of liquid water at 0.1 MPa". *J. Phys. Chem. Ref. Data.* 2009;38(1):21–29.

References

Pigford RL. *Counter-diffusion in a Wetted Wall Column*. The University of Illinois, Urbana, Illinois. Ph.D. Dissertation. 1941.

Pinto DDD, Monteiro GM-S, Johnsen B, Svendsen HF, Knuutila H. "Density measurements and modelling of loaded and unloaded aqueous solutions of MDEA (N-methyldiethanolamine), DMEA (N,N-dimethylethanolamine), DEEA (diethylethanolamine) and MAPA (N-methyl-1,3-diaminopropane)". *Int. J. Greenhouse Gas Control*. 2014;25:173–185.

Poling BE, Prausnitz JM, O'Connell JP. *The properties of gases and liquids*. McGraw-Hill, 2001.

Rochelle GT, Chen X, et al., "CO_2 capture by aqueous absorption – 2nd Quaterly progress report 2009

Versteeg GF, Van Swaaij WPM. "Solubility and diffusivity of acid gases (CO_2, N_2O) in aqueous alkanolamine solutions". J. Chem. Eng Data. 1988;33(1):29–34.