IEAGHG 8th Post Combustion Capture Conference

16th to 18th September 2025 Marseille, France

Modeling and mitigation of precipitation in PZ-based CO_2 capture solvents

Can Demir[a]*, Randi Neerup[a], Isaac Appelquist Løge[a], Jens Abildskov[b], Philip Loldrup Fosbøl[a]

[a]*Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Søltofts Plads 228A, 2800, Kgs. Lyngby, Denmark*

[b]*Process and System Engineering Center (PROSYS), Department of Chemical and Biochemical Engineering, Technical University of Denmark (DTU), Søltofts Plads 228A, 2800, Kgs. Lyngby, Denmark*

Abstract

Amine-based CO_2 capture remains a leading technology for decarbonizing hard-to-abate industries [1]. Novel piperazine (PZ)-based solvents are continuously benchmarked due to their enhanced CO_2 absorption rates and cyclic capacity to satisfy industrial scale CO_2 capture operations [2]. Among them, CESAR1, a 27 wt% 2-amino-2-methyl-1-propanol (AMP) and 13 wt% PZ blend, is currently replacing the traditional 30 wt% monoethanolamine (MEA) as the new benchmark due to its improved energy efficiency and stability [3]. However, PZ solubility limitations introduce operational challenges, particularly precipitation at low temperatures and CO_2 loadings. Managing precipitation is critical, as solid formation can lead to equipment damage, fouling, and eventually plant shutdowns [4]. This study presents the extended UNIQUAC thermodynamic model to accurately predict the solid formation behavior of aqueous PZ-based solvents loaded with CO_2, providing a strong foundation for accurate process simulations, validated at the pilot scale to mitigate precipitation risks at the industrial scale.

Keywords:Piperazine; Post combustion capture; Precipitation; Extended UNIQUAC; Solid-liquid equilibrium (SLE)

The extended UNIQUAC model is capable of representing a wide range of thermodynamic properties using a unique set of parameters, making it suitable for predicting solid-liquid equilibrium (SLE), vapor-liquid equilibrium (VLE), and heat of CO_2 absorption for aqueous amine solutions under various conditions [5]. Our extended UNIQUAC model for the PZ-water-CO_2 system accurately predicts the SLE, VLE, and heat of CO_2 absorption at varied temperatures, CO_2 loadings, and formulations. Precipitation temperature decreases and heat of CO_2 absorption increases as CO_2 loading increases. The model SLE predictions of the PZ-water-CO_2 system are shown with a strong agreement with the experimental data for the aqueous PZ system from Fosbøl et al. [6] in Figure 1. As seen, the precipitation temperature is pushed down with increasing CO_2 loadings.

* Corresponding author. Tel.: +45 91940689
E-mail address: cande@kt.dtu.dk

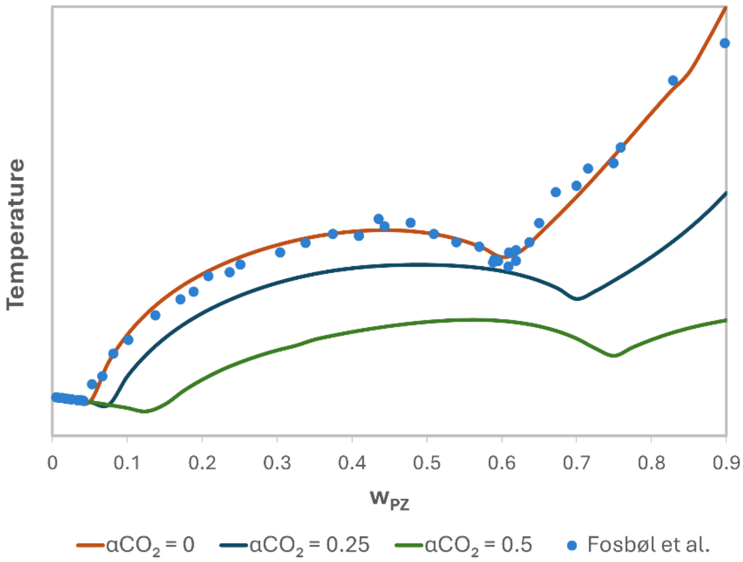

Figure 1: PZ precipitation temperature decreases with increasing CO_2 loading.

The validated SLE prediction for the PZ-water-CO_2 system suggests critical solvent management and operation strategies for the CO_2 capture plants that are planned to be installed in locations with colder climates such as Northern America and Europe. Higher lean loadings may be feasible in colder climates from a solvent management perspective, while cyclic loading optimization is necessary to avoid higher specific reboiler duty at elevated rich loadings.

Moreover, the validated extended UNIQUAC thermodynamic model for the PZ-water-CO_2 system provides a foundation for scaling up novel PZ-based solvents to the industrial scale. It enables more accurate precipitation risk assessment in CO_2 capture plants using these solvents. This study extends the model's application to process simulations with CESAR1 solvent. Despite being the new benchmark for amine-based CO_2 capture, CESAR1 still has significant knowledge gaps [7] and lacks a thermodynamic model validated by dedicated pilot scale data. Existing models, such as the electrolyte NTRL model proposed by Spek et al., are only validated within a limited range at the lab scale [8].

The extended UNIQUAC model will be integrated into an industry-standard process simulation tool such as Aspen Plus. This enables the validation of the model with eight months of pilot scale CO_2 capture data using CESAR1 from a cement plant flue gas [3]. The steady states obtained with various advanced configurations were tested at the pilot scale in 2023. These include intercooling, varied stripper pressure, and lean vapor compression to decrease the specific reboiler duty, as shown in Figure 2. As a result, precipitation behaviour can be predicted across various specific reboiler duty minimization strategies.

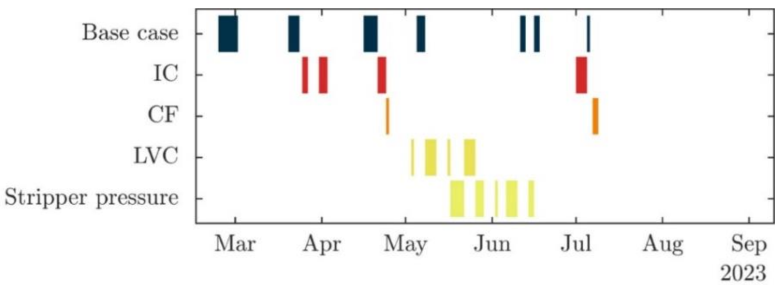

Figure 2: Overview of the experimental campaign, showing the dates for each tested process configuration [3]. **The configurations tested include IC, CF, LVC, and altered stripper pressure.**

The simulations provide key insights into operational limits, solvent cycling strategies, and heat integration measures to minimize precipitation risks while maintaining high CO_2 capture efficiency, validated at pilot scale. Additionally, the developed model supports both pilot and industrial scale studies by serving as a predictive tool for scaling up the novel PZ-based solvent systems. By evaluating steady state operation under different process configurations, it aids process optimization and reduces the need for extensive trial-and-error testing.

References

[1] G.T. Rochelle, Amine Scrubbing for CO2 Capture, Science (1979) 325 (2009) 1652–1654. https://doi.org/10.1126/science.1176731.

[2] G. Rochelle, E. Chen, S. Freeman, D. Van Wagener, Q. Xu, A. Voice, Aqueous piperazine as the new standard for CO2 capture technology, Chemical Engineering Journal 171 (2011) 725–733. https://doi.org/10.1016/j.cej.2011.02.011.

[3] I.A. Løge, C. Demir, S.H.B. Vinjarapu, R. Neerup, E. Hauge, J.K. Jørsboe, M. Dimitriadi, H. Halilov, C.F. Frøstrup, I. Gyorbiro, N. Kottaki, A.N. Jayan, S. Jensen, J.L. Karlsson, P. Fosbøl, Pilot-scale CO2 capture in a cement plant with CESAR1: Comparative analysis of specific reboiler duty across advanced process configurations, Chemical Engineering Journal (2025) 159429. https://doi.org/10.1016/j.cej.2025.159429.

[4] S.H.B. Vinjarapu, I.A. Løge, R. Neerup, A.H. Larsen, V.E. Rasmussen, J.K. Jørsboe, S.N.B. Villadsen, S. Jensen, J.L. Karlsson, J. Kappel, H. Lassen, P. Blinksbjerg, N. von Solms, P.L. Fosbøl, Learnings from up-scaling CO2 capture: Challenges and experiences with pilot work, Chem Eng Sci 300 (2024) 120576. https://doi.org/10.1016/j.ces.2024.120576.

[5] L. Faramarzi, G.M. Kontogeorgis, K. Thomsen, E.H. Stenby, Extended UNIQUAC model for thermodynamic modeling of CO2 absorption in aqueous alkanolamine solutions, Fluid Phase Equilib 282 (2009) 121–132. https://doi.org/10.1016/j.fluid.2009.05.002.

[6] P.L. Fosbøl, R. Neerup, M.W. Arshad, Z. Tecle, K. Thomsen, Aqueous Solubility of Piperazine and 2-Amino-2-methyl-1-propanol plus Their Mixtures Using an Improved Freezing-Point Depression Method, J Chem Eng Data 56 (2011) 5088–5093. https://doi.org/10.1021/je200959m.

[7] D. Morlando, V. Buvik, A. Delic, A. Hartono, H.F. Svendsen, H.M. Kvamsdal, E.F. da Silva, H.K. Knuutila, Available data and knowledge gaps of the CESAR1 solvent system, Carbon Capture Science & Technology 13 (2024) 100290. https://doi.org/10.1016/J.CCST.2024.100290.

[8] N. Yi, L. Herraiz, M. Fang, S. García, M. van der Spek, Open access, thermodynamically consistent, electrolyte NRTL model for piperazine, AMP, water, CO2 systems on Aspen Plus, Sep Purif Technol 350 (2024) 127924. https://doi.org/10.1016/j.seppur.2024.127924.