



Analysis of the K_2CO_3 - NH_3 solvent properties for carbon capture applications

Stefano Lillia¹ Davide Bonalumi¹ Philip Fosbøl²
Kay Thomsen² Gianluca Valenti¹ Indira Jayaweera³

¹Politecnico di Milano – Dipartimento di Energia, Via R. Lambruschini 4, Milano, Italy

²Technical University of Denmark, Department of Chemical Engineering, Center for Energy Resource Engineering, Søtofts Plads, 2800, Kgs. Lyngby, Denmark

³SRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA

Abstract

Absorption-based systems that typically employ amines such as monoethanolamine (MEA) are in commercial use for scrubbing CO_2 from industrial flue and process gases. However, many challenges must be overcome when applying amine-based technology for the treatment of pulverized coal-fired power plants such as toxicity, degradation, high energy consumption associated with regeneration of the solvent, low regeneration pressure and cost of the chemicals. Other solvents such as aqueous solutions of ammonia (NH_3) (Chilled Ammonia Process) and aqueous solution of potassium carbonate (K_2CO_3) are mature non-amine alternatives to the state-of-the-art MEA technology. Technology based on NH_3 is capable of capturing CO_2 at high loadings compared with MEA-based technology. In addition, NH_3 -based technology can strip CO_2 at high pressure, thereby reducing CO_2 compression costs and it has a kinetic of absorption comparable to the amine technologies at temperatures around $25^\circ C$. However, this process requires gas washing to reduce the NH_3 emissions in the scrubbed flue gas [1-2]. The K_2CO_3 -based process has lower regeneration energy requirements and no emission issues. However, it has a low kinetic of absorption, a very low loading capacity, and low-pressure of CO_2 regeneration. Both the solvents (NH_3 and K_2CO_3) have no problems of degradation and toxicity and they have low costs compared to the amines [3].

The aim of this work is the study of the thermodynamic properties and the kinetic of absorption of the mixture between the NH_3 and K_2CO_3 in the same solvent in order to investigate a solution with low heat duty of regeneration reducing the ammonia slip and maintaining a higher regeneration pressure [4].

The novelty is the analysis of the thermodynamic and the kinetic of absorption of the Mixed-salt Technology solvent for the carbon capture application applied on the pulverized coal-fired exhausts with 13% of CO_2 concentration. The thermodynamic analysis of the properties is conducted with the Extended UNIQUAC thermodynamic model proposed by Thomsen and Rasmussen [5] in its new version calibrated with both the experimental data of the ternary systems NH_3 - CO_2 - H_2O and K_2CO_3 - CO_2 - H_2O , while the kinetic of absorption is studied experimentally with the Wetted Wall Column.

- *Thermodynamic Analysis*

Because of primary importance, the heat of CO₂ desorption is evaluated as a function of (i) the capacity of the solvent (sum of the NH₃ and K₂CO₃ molality) and (ii) the composition of the NH₃ and K₂CO₃ in the solvent. Figure 1 shows the trend of the heat of CO₂ desorption as a function of the cited parameters. The curves are drawn for a range of composition where the salts do not precipitate, since the salt precipitation does not allow the use of the packed column for the CO₂ absorption. The chart highlights that the solvent with only K₂CO₃ has a heat of desorption lower than all the solvents with NH₃ and K₂CO₃. Moreover, when the iso-capacity reaches an amount of K₂CO₃ around 1 [mol/kg_{H2O}], the hHeat duty decreases with the increment of the concentration of K₂CO₃. The most promising iso-capacity is iso-cap 4 molal since the NH₃ and K₂CO₃ are not too much diluted and the salt precipitation is not an issue for a wide range of composition between NH₃ and K₂CO₃.

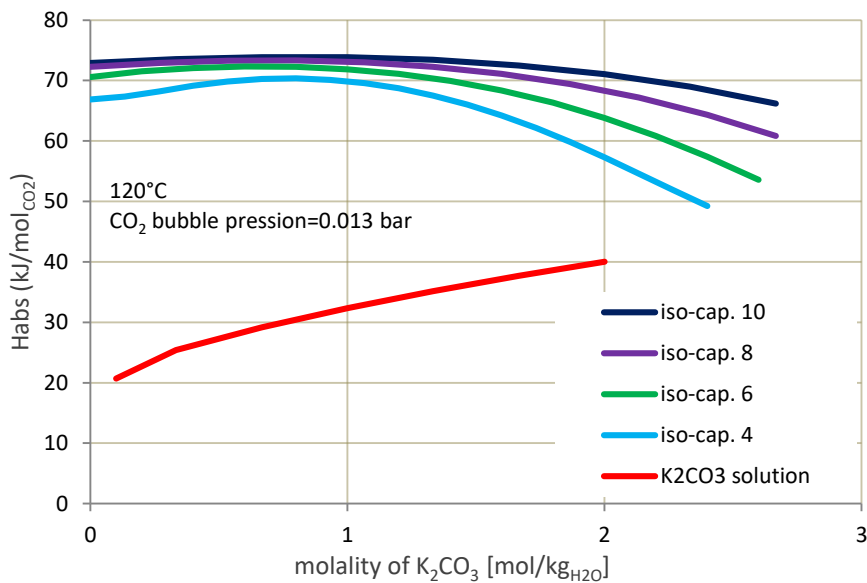


Figure 1. The chart presents the heat of CO₂ absorption at 120°C as a function of the solvent composition at different values of iso-capacity. The curves are interrupted when the salts deposition occurs.

A second property evaluated is the partial pressure of NH₃ at the absorption pressure in order to study the impact of the K₂CO₃ on the ammonia slips. Figure 2 (Left) shows the partial pressure of ammonia at constant CO₂ partial pressure (0.013) and at varying initial ammonia concentration at 25 °C as a function of the K₂CO₃ content. Figure 2 (Right) depicts the concentration of species for the solvent with an initial concentration of 4 molal ammonia as a function of the K₂CO₃ content in the solvent. The results do not show a significant variation of the ammonia partial pressure with rising K₂CO₃ fraction. Indeed, as described by the speciation chart, the free ammonia in the liquid phase, NH_{3(aq)}, is almost constant with varying K₂CO₃ content. This fact is a benefit for the solvent as the ammonia slip remains constant while increasing the capacity of the solvent.

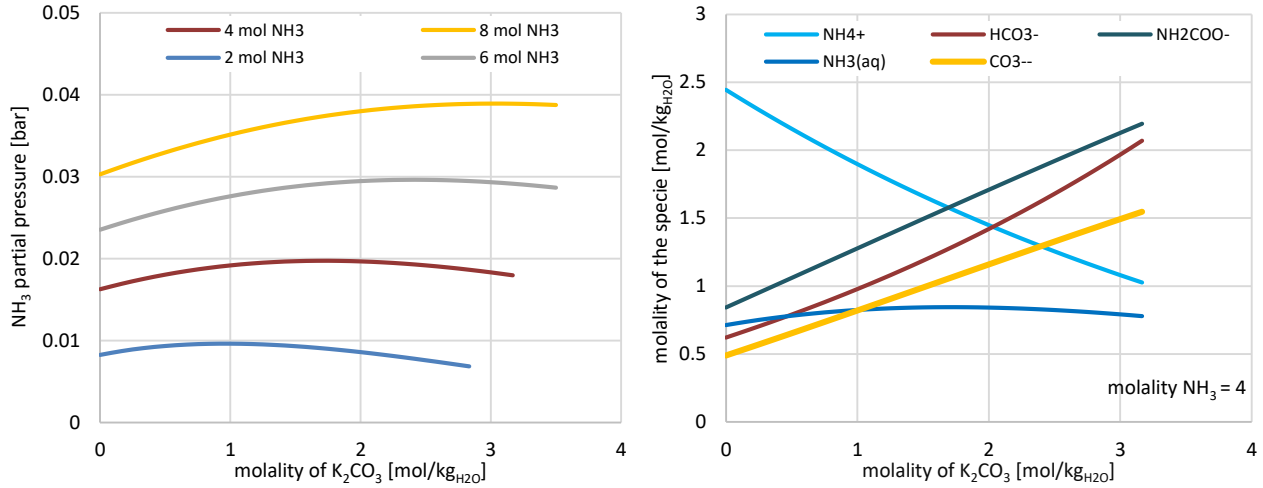


Figure 2. (Left) Ammonia partial pressure as a function of the K₂CO₃ concentration for different ammonia initial concentration. The partial pressure of CO₂ is constant, 0.013 bar, and the temperature is 25 °C. (Right) Molality of every specie in the solvent for a solvent with an initial ammonia molality of 4. In both charts the lines are interrupted when salt precipitation starts.

- *Rate of CO₂ absorption measurement with the Wetted Wall Column*

After the thermodynamic analysis the iso-capacity of 4 molal is selected as the most promising for a carbon capture application. For this case the overall mass transfer coefficient of the CO₂ K_{ov} is measured experimentally with the Wetted Wall Column apparatus. The overall mass transfer coefficient K_{ov} [mol/(Pa m² s)] is defined as

$$\varphi_{CO_2} = K_{ov}(P_{CO_2}^{gas} - P_{CO_2}^{liq}) \quad (1)$$

where φ_{CO_2} [mol/(m² s)] is the surface flux of CO₂ absorbed by the solvent, $P_{CO_2}^{gas}$ [Pa] is the partial pressure of CO₂ in the gas phase and is the pressure of CO₂ in the liquid phase.

The aim is the comparison of the rate of the absorption for different composition of the solvent with the same CO₂ capacity at different temperatures and two different CO₂ loadings, a RICH and a LEAN case, which are the solvent conditions at the top and at the bottom of the absorber column. The results in Figure 3 (Left) shows that the kinetic of absorption decrease when the K₂CO₃ concentration increase with respect of the ammonia. Indeed, as demonstrated by Lillia *et al.* [6], the faster reaction is between ammonia and CO₂. Rising the K₂CO₃ concentration, the free ammonia concentration decreases and consequently decreases also the rate of absorption. This correlation is highlighted in Figure 3 (Right) where the chart overlay the values of the K_{ov} (left y-axis) with the concentration of the free ammonia in the bulk phase calculated with the Extended UNIQUAC model (right y-axis).

Finally, comparing the overall mass transfer coefficient of the analysed cases with data in literature measured for the solvent with pure K₂CO₃, NH₃ enhance the overall mass transfer coefficient almost 3 times [7].

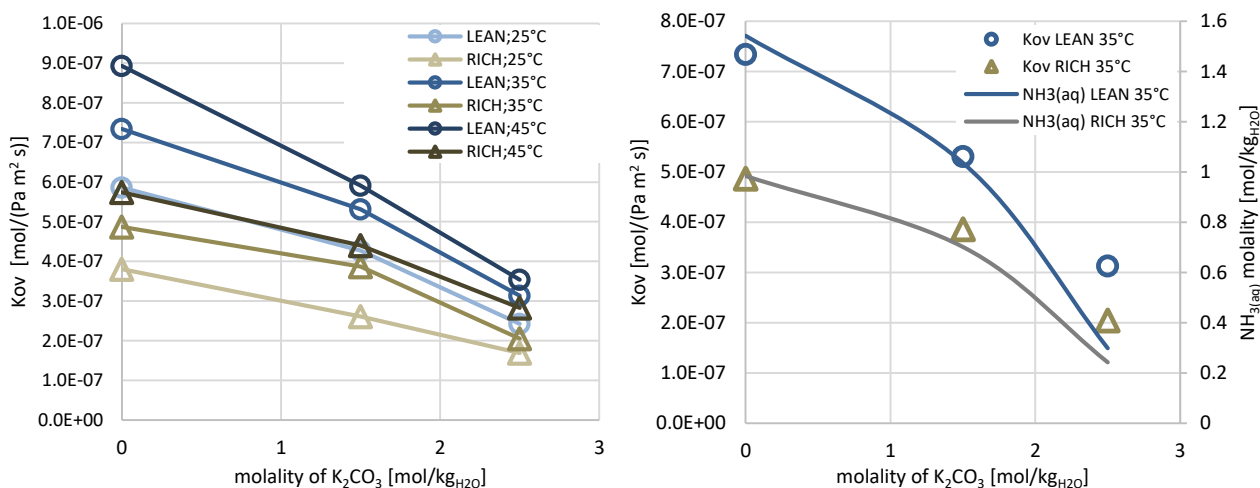


Figure 3. Left: overall mass transfer coefficient as a function of the K_2CO_3 initial molality for the iso-capacity of 4 molal at three different temperatures (25°C, 35°C and 45°C) and for two different CO_2 loadings (RICH loading and LEAN loading). Right: on the left y-axis the overall mass transfer coefficient is represented as a function of the K_2CO_3 initial molality for the iso-capacity of 4 molal at 35°C and for two different CO_2 loadings (RICH loading and LEAN loading), while on the right y-axis the free ammonia molality of the bulk solution calculated with the Extended UNIQUAC is represented as a function of the K_2CO_3 initial molality for the iso-capacity of 4 molal at 35°C and for two different CO_2 loadings (RICH loading and LEAN loading).

Concluding, the K_2CO_3 reduces the ammonia slip with reduction of the CO_2 heat of desorption of the CO_2 during the regeneration of the solvent. Comparing to K_2CO_3 solvent the ammonia enhances the rate of absorption of the solvent reducing the surface needed for the CO_2 capture.

Bibliography

- [1] G. Valenti, D. Bonalumi, and E. Macchi, "Modeling of ultra super critical power plants integrated with the chilled ammonia process," *Energy Procedia*, vol. 4, pp. 1721–1728, 2011.
- [2] H. Jilvero, F. Normann, K. Andersson, and F. Johnsson, "The rate of CO_2 absorption in ammonia-implications on absorber design," *Ind. Eng. Chem. Res.*, vol. 53, no. 16, pp. 6750–6758, Apr. 2014.
- [3] K. A. Mumford *et al.*, "Post-combustion capture of CO_2 : Results from the solvent absorption capture plant at hazelwood power station using potassium carbonate solvent," *Energy and Fuels*, vol. 26, no. 1, pp. 138–146, 2012.
- [4] I. Jayaweera, P. Jayaweera, R. Elmore, J. Bao, and S. Bhamidi, "Update on mixed-salt technology development for CO_2 capture from post-combustion power stations," *Energy Procedia*, vol. 63, pp. 640–650, 2014.
- [5] K. Thomsen and P. Rasmussen, "Modeling of vapor–liquid–solid equilibrium in gas–aqueous electrolyte systems," *Chem. Eng. Sci.*, vol. 54, no. 12, pp. 1787–1802, Jun. 1999.
- [6] S. Lillia, D. Bonalumi, P. L. Fosbøl, K. Thomsen, and G. Valenti, "Experimental study of the aqueous CO_2 - NH_3 rate of reaction for temperatures from 15 °C to 35 °C, NH_3 concentrations from 5% to 15% and CO_2 loadings from 0.2 to 0.6," *Int. J. Greenh. Gas Control*, vol. 70, no. July 2017, pp. 117–127, 2018.
- [7] A. Gladis, M. T. Gundersen, P. L. Fosbøl, J. M. Woodley, and N. von Solms, "Influence of temperature and solvent concentration on the kinetics of the enzyme carbonic anhydrase in carbon capture technology," *Chem. Eng. J.*, vol. 309, pp. 772–786, 2017.