Thermodynamic and kinetic properties of $\text{NH}_3\text{-K}_2\text{CO}_3\text{-CO}_2\text{-H}_2\text{O}$ system for carbon capture applications

Lillia, Stefano; Bonalumi, Davide; Fosbøl, Philip L.; Thomsen, Kaj; Jayaweera, Indira; Valenti, Gianluca

Published in:
International Journal of Greenhouse Gas Control

Link to article, DOI:
[10.1016/j.ijggc.2019.03.019](https://doi.org/10.1016/j.ijggc.2019.03.019)

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Lillia, S., Bonalumi, D., Fosbøl, P. L., Thomsen, K., Jayaweera, I., & Valenti, G. (2019). Thermodynamic and kinetic properties of $\text{NH}_3\text{-K}_2\text{CO}_3\text{-CO}_2\text{-H}_2\text{O}$ system for carbon capture applications. *International Journal of Greenhouse Gas Control*, 85, 121-134. <https://doi.org/10.1016/j.ijggc.2019.03.019>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Thermodynamic and kinetic properties of $\text{NH}_3\text{-K}_2\text{CO}_3\text{-CO}_2\text{-H}_2\text{O}$ system for carbon capture applications

Stefano Lillia^a, Davide Bonalumi^{a1}, Philip L. Fosbøl^b, Kaj Thomsen^b, Indira Jayaweera^c and Gianluca Valenti^a

^aPolitecnico di Milano – Dipartimento di Energia, Via R. Lambruschini 4, Milano, Italy

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

^cSRI International, 333 Ravenswood Avenue, Menlo Park, CA 94025, USA

Keywords:

- CO_2 capture
- Kinetics
- Rate of absorption
- Ammonia
- Mixed-Salt Technology
- Experimental measurements

Highlights:

- K_2CO_3 addition reduced the heat of CO_2 desorption with respect to aqueous NH_3 solvent
- Higher desorption temperature reduced the heat of desorption
- Upon addition of K_2CO_3 , the NH_3 partial pressure of the solvent decreased
- K_2CO_3 addition reduced the rate of CO_2 absorption compared to that in aqueous NH_3
- Free NH_3 molality was correlated with the CO_2 absorption rate

Abstract

An innovative solvent based on the quaternary system $\text{CO}_2\text{-NH}_3\text{-K}_2\text{CO}_3\text{-H}_2\text{O}$ is reported and characterized in terms of its thermodynamic properties and rate of CO_2 absorption. Thermodynamic properties of the solvent such as vapor-liquid equilibrium, solid-liquid equilibrium, and the heat of desorption were modelled with the Extended UNIQUAC thermodynamic model. The kinetics of CO_2 absorption in the solvent were studied experimentally with a wetted wall column set-up. The absorption

rate was investigated with respect to temperature, ammonia concentration, potassium carbonate concentration, and CO₂ loading, under the typical operating conditions of a capture plant. Globally, the solvent has a number of interesting properties for CO₂ capture applications. Indeed, adding K₂CO₃ to the ammonia solvent reduced both the ammonia slip and the heat of desorption. Experimental analysis showed that the kinetics of absorption were mainly influenced by the reaction between free ammonia and CO₂. Hence, the overall mass transfer coefficient decreased when increasing the K₂CO₃ content of the solvent.

1. Introduction

The correlation between anthropogenic carbon dioxide emissions in the atmosphere and the greenhouse effect is considered by many institutions to be a primary cause of the phenomenon of global warming. One of the most mature technologies for CO₂ capture at the emission source is the solvent-based chemical absorption/desorption process (Rochelle et al., 2011)(Rochelle, 2011). Widely known chemical sorbents for CO₂ capture include aqueous solutions of amines such as monoethanolamine (MEA), *N*-methyldiethanolamine (MDEA), and piperazine.

Currently, mature alternatives to amine-based technologies that have been developed beyond pilot and/or validation stages include ammonia- and potassium-carbonate-based aqueous solvents. Both the ammonia and the potassium carbonate solvents have low toxicity and do not suffer from the problem of degradation, unlike the amine-based solvents. Moreover, from the perspective of life cycle analysis (LCA) (Petrescu et al., 2017)(Grant et al., 2014), CO₂ capture technologies using inorganic solvents, such as NH₃ or K₂CO₃, have a lower environmental impact with respect to the amine-based counterparts, due mainly to the production chain of the solvent itself.

Solvents based on ammonia are capable of capturing CO₂ at higher loadings compared to amine-based solvent technology (Bai and Yeh, 1997). In addition, the ammonia-based technology can strip CO₂ at

high pressure, reducing the CO₂ compression costs (Bonalumi et al., 2016). However, such technology requires cooling of the flue gas and the solvent, as well as washing of the treated gas to reduce ammonia emissions (Kong et al., 2011). In comparison to the ammonia-based solvent technology, the potassium-carbonate-based technology does not involve any issues with emissions. However, it suffers from low CO₂ absorption efficiency, very low loading capacity, and the solvent cannot be regenerated at high pressure. As such, new approaches for improved potassium-carbonate-based CO₂ capture technology have been in development for decades (Williamson and Matheus, 1924)(Mumford et al., 2012)(Gladis et al., 2017).

The aim of this work was to study the thermodynamic properties and kinetics of CO₂ absorption of mixtures of NH₃ and K₂CO₃ in the same solvent with new data. This mixture was expected to be characterized by a low heat duty of regeneration, a reduced ammonia slip in comparison to the aqueous ammonia solvent, and a high regeneration pressure, combining the best properties of the two individual solvents. The studied solvent has been termed the ‘mixed-salt technology solvent’ in a patent by SRI International, and part of its characterization has already been published (Jayaweera et al., 2014)(Jayaweera et al., 2016)(Jayaweera et al., 2017). In these previous investigations, the background of the process was studied, and the results confirmed some of the promising properties of the solvent such as the reduced ammonia slip and heat of CO₂ desorption, both of which will be described in further detail in the present work. Moreover, the cited works reported some performance features that can be expected from the use of this solvent in a carbon capture process.

Modelling of the thermodynamic properties of the solvent was performed with the Extended UNIQUAC thermodynamic model (Thomsen and Rasmussen, 1999). The model parameters were determined on the basis of experimental data for the ternary systems NH₃-CO₂-H₂O, K₂CO₃-CO₂-H₂O, and K₂CO₃-NH₃-H₂O, which was updated in a 2018 report by SRI International (Jayaweera and Jayaweera, 2018).

75 The kinetics of CO₂ absorption in the solvent were investigated through an experimental study of the
76 absorption reaction of CO₂ in the K₂CO₃-NH₃-H₂O system. This study was conducted with a wetted wall
77 column set-up (Darde et al. 2011). Experiments were designed in order to determine the absorption rate
78 with respect to temperature, ammonia concentration, potassium carbonate concentration, and CO₂
79 loading, under typical operating conditions of a capture plant. Next, the overall mass transfer coefficient
80 was analyzed, and the kinetics of CO₂ absorption were described with the support of the thermodynamic
81 model used for calculating the speciation in the bulk liquid. The result is the description of the solvent
82 and the evidence of the advantages and disadvantages for its utilization for carbon capture applications.
83 The following sections describe: (i) the thermodynamic model and its validation with data from the
84 literature; (ii) the experimental set-up used for the measurement of the rate of absorption; (iii) and finally
85 the thermodynamic properties and the kinetic characteristics of absorption of the mixed-salt technology
86 solvent.

87 **2. Extended UNIQUAC thermodynamic model**

88 The thermodynamic properties of the solvent were assessed with the Extended UNIQUAC
89 thermodynamic model (Thomsen and Rasmussen, 1999). The current model used contains a further
90 recalibration of the parameters of the original version of 1999 (Jayaweera and Jayaweera, 2018). The
91 model parameters were determined on the basis of experimental data taken over the temperature range
92 from the freezing point of the solutions up to 200 °C. The parameters for the NH₃-CO₂-H₂O system, the
93 K₂CO₃-CO₂-H₂O system, and the K₂CO₃-NH₃-H₂O system were determined based on more than 8000
94 experimental data points recorded at pressures of up to 100 bar.

95 The reactions considered for the equilibrium and implemented in the thermodynamic model in order to
96 determine the speciation and ion concentration in the liquid phase are shown as reactions R1–R5.

97

98 In addition, the solubilities of the salts KOH, KOH·H₂O, KOH·2H₂O, K₂CO₃, 2K₂CO₃·3H₂O,
 99 K₂CO₃·6H₂O, KHCO₃, 2K₂CO₃·4KHCO₃·3H₂O, (NH₄)₂CO₃·K₂CO₃, (NH₄)₂CO₃, (NH₄)₂CO₃·H₂O,
 100 NH₄HCO₃, (NH₄)₂CO₃·2(NH₄HCO₃), NH₂COONH₄, and that of ice were considered. For the gas phase,
 101 the Soave-Redlich-Kwong equation of state was used as the model, without any additional parameters.
 102 Figure 1 to Figure 3 depict the agreement between the thermodynamic model and experimental data.
 103 Other comparisons between the model and experimental data used for model validation have been
 104 reported in previous works (Darde et al., 2012)(Jayaweera and Jayaweera, 2018).

105

106 Figure 1. (Left) CO₂ partial pressure over aqueous solutions of 1.8 molal K₂CO₃ loaded with CO₂. Model
 107 calculations are in good agreement with experimental data from Tosh et al. (1959); (right) total pressure
 108 over aqueous solutions of 0.43 molal K₂CO₃ with high loadings of CO₂. Model calculations are in good
 109 agreement with experimental data from Kamps et al. (2007).

Figure 2. Bubble pressure above KOH solutions with different amounts of ammonia as a function of temperature (Cacciola et al., 1995)(Sorina et al., 1967).

Figure 3. (Left) Solubility in the ternary $\text{KHCO}_3\text{-NH}_4\text{HCO}_3\text{-H}_2\text{O}$ system at 30 °C (Trypuć and Kiełkowska, 1996); (right) solubility in the $\text{K}_2\text{CO}_3\text{-KHCO}_3\text{-H}_2\text{O}$ system at 50 °C (Luzhnaya and Kosyachkova, 1955)(Hill, 1930).

3. Measurement of the absorption rate with the wetted wall column.

In this study, the wetted wall column set-up (WWC) was applied for the measurement of the CO_2 absorption rate (Darde et al., 2011). The WWC reproduces the mass transfer conditions of a packed column on a smaller scale. The experimental analysis allows comprehension of the overall phenomenon,

121 and thereby recognition of which of the operational parameters influence the CO₂ absorption to a greater
122 degree. The methodology applied for the measurement of the overall mass transfer coefficient is
123 explained in the work by Lillia et al. (2018a). The following section first reports a brief description of
124 the experimental set-up, followed by a description of the approach used for the measurement of the
125 overall mass transfer coefficient.

126 3.1. *Experimental set-up description*

127 Figure 4 shows a sketch of the WWC experimental set-up. The system was equipped with the necessary
128 mass flow controllers, valves, temperature controllers, and detectors for measuring the CO₂ composition
129 of the inlet gas mixture in the chamber. A bypass valve in the gas line before the reaction chamber
130 allowed the measurement of CO₂ concentration before and after the absorption reactions, sending the
131 flow straight to the CO₂ probe or to the reaction chamber.

132 The thermostatic bath controlled the temperature of the reaction by heating the gas, the solvent, and the
133 reaction chamber to predetermined temperatures. The solvent was prepared with a known composition
134 of NH₃, K₂CO₃, and CO₂ loading, and pumped into the reaction chamber which was comprised of a glass
135 cylinder with a stainless steel tube inside. During the measurement, the solvent flows from inside the
136 stainless steel tube and falls down around its external surface in a thin film, which permits simple
137 measurement of the contact area between the liquid and the gas phase.

138 The aim of the experiment was to assess the relation between the CO₂ flux absorbed by the solvent and
139 the CO₂ concentration in the gas mixture at a given temperature, by measuring the contact area between
140 the gas and the liquid and the amount of CO₂ absorbed in the chamber. The methodology used for solvent
141 preparation and the experimental procedure were reported previously (Lillia et al., 2018b), while the
142 description of the overall mass transfer coefficient measurement is presented in the following section.

143

144 Figure 4. Wetted wall column (WWC) layout: the solid blue line represents the solvent; the dashed red
 145 line represents the gas mixture; and the dotted black line represents the cooling water from the
 146 thermostatic bath (Gladis et al., 2017).

147 3.2. Overall mass transfer constant measurement

148 The gas flow fed to the reactor was composed of N_2 , CO_2 , and H_2O . The WWC set-up measured the CO_2
 149 concentration at the inlet and the outlet of the reactor. Moreover, the gas flow passed through two
 150 saturators at a set temperature, so the water concentration and consequently the nitrogen concentration
 151 were also known. Together, this data allowed the calculation of the flow of absorbed CO_2 (in moles),
 152 ΔN_{CO_2} [mol/s], according to:

$$\Delta N_{CO_2} = \frac{(N_{N_2} + N_{H_2O})(y_{CO_2}^{bypass} - y_{CO_2}^{WWC})}{(1 - y_{CO_2}^{bypass})(1 - y_{CO_2}^{WWC})} \quad (1)$$

153 where N_{N_2} [mol/s] is the flow of N_2 in moles, N_{H_2O} [mol/s] the flow of H_2O in moles, $y_{CO_2}^{bypass}$ [-] is the
 154 mole fraction in the bypass, and $y_{CO_2}^{WWC}$ [-] is the mole fraction after the reactor. The CO_2 probe measured
 155 the volumetric concentration of CO_2 , and consequently the mole fraction of CO_2 could be determined.
 156 The gas-liquid interface is the surface where the CO_2 passes from the gas to the liquid phase, and allows
 157 for calculation of the surface flow of CO_2 . This area was computed by measuring the contact area between
 158 the stainless steel cylinder wetted by the solvent and the gas phase. The total area was calculated as the
 159 area of the cylinder wetted by the liquid film, while the flow (in moles) specific to the gas-liquid interface,
 160 φ_{CO_2} [mol/(m² s)], was computed as:

$$\varphi_{CO_2} = \frac{\Delta N_{CO_2}}{A_{int}} \quad (2)$$

161 where A_{int} [m²] is the surface of the gas-liquid interface and ΔN_{CO_2} [mol/s] is the carbon dioxide flow
 162 absorbed (in moles).

163 Considering the gas flow of an ideal mixture of ideal gases, the CO_2 partial pressure, $P_{CO_2}^{WWC}$ [Pa], in the
 164 reactor is given by:

$$P_{CO_2}^{WWC} = y_{CO_2}^{WWC} P_{TOT}^{WWC} \quad (3)$$

165 where P_{TOT}^{WWC} [Pa] is the total pressure inside the reactor. Since the molar fraction of CO_2 in the gas phase
 166 is not constant along the reactor, the partial pressure in the reactor, $P_{CO_2}^{gas}$ [Pa], is evaluated using the
 167 logarithmic mean:

$$P_{CO_2}^{gas} = \frac{P_{CO_2}^{in} - P_{CO_2}^{out}}{\ln\left(\frac{P_{CO_2}^{in}}{P_{CO_2}^{out}}\right)} \quad (4)$$

168 where $P_{CO_2}^{in}$ [Pa] is the partial pressure of CO_2 in the reactor inlet and $P_{CO_2}^{out}$ [Pa] is the partial pressure of
 169 CO_2 in the reactor outlet.

170 According to Fick's law, the linear proportionality between the flux of carbon and the carbon dioxide
 171 concentration gradient in the direction of diffusion can be described by the diffusion coefficient.
 172 The two-film theory is a model used to describe the absorption of CO₂ from a gas bulk with a partial
 173 pressure $P_{CO_2}^{gas}$ [Pa] by a liquid with CO₂ concentration $C_{CO_2}^{liq}$ [mol/m³] (Figure 5).

174 Figure 5. Left: the solid line represents the CO₂ partial pressure profile in the vapor bulk and the
 175 diffusion layer, whereas it represents the CO₂ concentration profile in the diffusion and reaction layer
 176 and the liquid bulk, according to the two-film theory (Lewis and Whitman, 1924). Right: the solid line
 177 in both the gas and liquid phases represent the CO₂ partial pressure profile according to the two-film
 178 theory (Lewis and Whitman, 1924).

179 In order to make the mass transfer phenomenon dependent on the partial pressure of CO₂ also in the
 180 liquid phase, the partial pressure of CO₂ in liquid phase is calculated as:

$$P_{CO_2} = H_{CO_2} C_{CO_2} \quad (5)$$

181 where H_{CO_2} [(Pa m³)/mol] is the partition coefficient and C_{CO_2} [mol/m³] is the CO₂ concentration in the
 182 liquid phase. In this work, the partition coefficient was taken as the Henry constant of CO₂ in the solvent.

183 The two-film theory (Lewis and Whitman, 1924) describes the flux of CO₂ as the product of a mass
 184 transfer coefficient and the corresponding driving force which is expressed as the difference in CO₂
 185 partial pressure or CO₂ concentration. Within this approach, the following expressions hold true:

$$\varphi_{CO_2}^G = k_G (P_{CO_2}^{gas} - P_{CO_2}^{int}) \quad (6)$$

$$\varphi_{CO_2}^L = k_{liq} (C_{CO_2}^{int} - C_{CO_2}^{liq}) = \frac{k_{liq}}{H_{CO_2}} (P_{CO_2}^{int} - P_{CO_2}^{liq}) = k'_{liq} (P_{CO_2}^{int} - P_{CO_2}^{liq}) \quad (7)$$

$$\varphi_{CO_2} = K_{ov} (P_{CO_2}^{gas} - P_{CO_2}^{liq}) \quad (8)$$

$$\varphi_{CO_2} = \varphi_{CO_2}^L = \varphi_{CO_2}^G \rightarrow \frac{1}{K_{ov}} = \frac{1}{k_G} + \frac{1}{k'_{liq}} \quad (9)$$

186 where $\varphi_{CO_2}^G$ [mol/(s m²)] is the CO₂ flux in the gas phase, k_G [mol/(m² s Pa)] is the gas-side mass transfer
 187 coefficient, $P_{CO_2}^{gas}$ [Pa] is the partial pressure of CO₂ in the gas bulk, $P_{CO_2}^{int}$ [Pa] is the partial pressure of
 188 CO₂ at the interface, $\varphi_{CO_2}^L$ [mol/(s m²)] the CO₂ flux in the liquid phase, k_{liq} [m/s] is the liquid-side mass
 189 transfer coefficient based on the liquid concentrations, $C_{CO_2}^{int}$ [mol/m³] is the CO₂ concentration in the
 190 liquid phase at the interface, $C_{CO_2}^{liq}$ [mol/m³] is the concentration in the liquid bulk, k'_{liq} [mol/(m² s Pa)] is
 191 the liquid-side mass transfer coefficient based on partial pressures, $P_{CO_2}^{liq}$ [Pa] is the partial pressure of
 192 carbon dioxide in the liquid bulk, φ_{CO_2} [mol/(s m²)] is the CO₂ flux, and K_{ov} [mol/(m² s Pa)] is the overall
 193 mass transfer coefficient.

194 The K_{ov} was measured for different solvent compositions and temperatures by changing the reaction
 195 temperature, the concentration of ammonia in the solvent, the concentration of K₂CO₃ in the solvent, and
 196 the CO₂ loading. Once the operation point was determined by setting these parameters, the CO₂
 197 absorption was measured at five different CO₂ partial pressures in the reactor by changing the CO₂
 198 composition in the gas phase. Matching the values of φ_{CO_2} and $P_{CO_2}^{gas}$ gives a chart like that shown in
 199 Figure 6, where the slope is represented by the K_{ov} and the intercept with the x axis is the $P_{CO_2}^{liq}$. The

approach used herein to measure the overall mass transfer coefficient neglects the ammonia slip in the reaction chamber. This assumption is supported by a simulation of the reaction chamber that was previously carried out with a rate-based approach in Aspen Plus with the Extended UNIQUAC thermodynamic model (Jayaweera and Jayaweera, 2018), the results of which estimated an ammonia loss of less than 3% of the total ammonia present in the solvent during the course of the experiment.

Figure 6. Flux of CO₂ absorbed as a function of CO₂ partial pressure in the reactor for the case with NH₃ molality of 2.5, K₂CO₃ molality of 1.5, CO₂ loading 0.35, and temperature of 25 °C. The overall mass transfer coefficient, K_{ov} , is the slope of the trend line, the intercept indicates the partial pressure of CO₂ in the liquid, and the R^2 is the correlation coefficient which determines the degree of agreement between the fitted line and the experimental data.

4. Results and discussion

The influences of K₂CO₃, NH₃, and temperature on the heat of desorption are discussed in the following sections. Variations in these parameters were very important for the heat duty during regeneration of the solvent. The impact of K₂CO₃ on the ammonia slip is also discussed. Ammonia slip is one of the main drawbacks associated with the use of ammonia-based solvents. Finally, the WWC results are presented and explained with the support of the Extended UNIQUAC thermodynamic model.

217 4.1. *CO₂ absorption and CO₂ desorption properties of the Mixed-Salt Technology solvent*

218 The capture of CO₂ by chemical absorption is based on the ability of the solvent to absorb CO₂ at low
219 temperature and desorb CO₂ at high temperature. The absorption is exothermic, so the temperature of the
220 solvent rises while absorbing CO₂. In the regeneration process, the solvent is heated to a temperature of
221 around 120 °C. This causes the desorption of CO₂, an endothermic reaction. Solvent regeneration is the
222 part of the process requiring the largest amount of energy, so the heat of CO₂ desorption is a key
223 thermodynamic property for reducing the heat duty of this process.

224 The graphs in Figure 7 represent the heat duty for different mixes of NH₃ and K₂CO₃. The curves shown
225 are iso-capacity curves. Iso-capacity is the sum of the molality of NH₃ and the molality of K₂CO₃, and is
226 defined as:

$$iso-capacity = \frac{n_{NH_3} + n_{K_2CO_3}}{m_{H_2O}} \quad (10)$$

227 where n_{NH_3} is the amount of ammonia in the solvent [mol], $n_{K_2CO_3}$ is the amount of K₂CO₃ in the solvent
228 [mol], and m_{H_2O} is the mass of water (the solvent) [kg_{H2O}]. The result is the sum of the molality of
229 ammonia and the molality of potassium carbonate. The approach and the equations used for the
230 computation of the heat of CO₂ desorption are described in the work by Darde et al. (2012).

231 The x -axis in the graphs indicates the molality of K₂CO₃ in the solvent. The molality of NH₃ can then be
232 calculated using the iso-capacity of the specific curve. The y -axis represents the heat of CO₂ desorption,
233 calculated considering a carbon capture of 90% from exhaust containing 13% CO₂ at 1 bar of pressure
234 (which are the typical conditions for a coal power plant). Hence, the heat of desorption is calculated at a
235 determined temperature for a solvent CO₂ loading corresponding to a partial pressure of CO₂ under lean
236 conditions at 0.013 bar and 20 °C (the inlet temperature in the absorber).

237 The curves in the graphs are interrupted at the points where salt deposition takes place at the rich loading
 238 (a CO₂ partial pressure of 0.13 bar at 40 °C). Both graphs show data recorded at a constant regeneration
 239 temperature; the left-hand graph in Figure 7 at 120 °C and the right-hand graph at 130 °C.

240

241 Figure 7. Heat of CO₂ desorption at 120 °C (left) and 130 °C (right) as a function of solvent composition
 242 at different iso-capacity values expressed as the definition given in (Eq. (10)) in [mol/kg_{H2O}]. The curves
 243 extend until the points at which salt deposition occurs.

244 The results indicate a benefit in terms of heat of desorption upon increasing the fraction of K₂CO₃ in the
 245 solvent, which agrees with the results of a previous study (Jayaweera et al., 2016). This impact was
 246 greater at increased regeneration temperatures, and reduced the iso-capacity of the solvent. Indeed, upon
 247 increasing the temperature, the molality of carbonate ions increased relative to that of bicarbonate ions,
 248 reducing the heat of desorption. Thus, increasing the amount of K₂CO₃ in the solvent amplified this
 249 effect. Moreover, at the same molality of potassium carbonate, the ratio of potassium ions to ammonium
 250 ions increased as the iso-capacity decreased, so the impact of the K₂CO₃ concentration on the heat of
 251 desorption was larger at lower iso-capacity. On the other hand, when the molality of K₂CO₃ was more
 252 than 2.5 mol/kg_{H2O}, the solution became supersaturated and salt deposition took place. The analysis
 253 identified the most desirable properties for the solvent with an iso-capacity of 4 mol/kg_{H2O}. In detail, the

254 heat of desorption increased until approximately 1 molal K_2CO_3 and then decreased upon increasing the
 255 K_2CO_3 molality further, as already mentioned. This phenomenon is explained by the speciation reported
 256 in Figure 8 for the cases of iso-capacity 4 and 8. Indeed, when the concentration of aqueous CO_2 in the
 257 solvent was low, the heat of desorption was mainly affected by the ion concentrations. On the other hand,
 258 when the concentration of aqueous CO_2 was high enough (above approximately 1 molal K_2CO_3), the
 259 heat of desorption was not strictly dependent on the concentrations of ions in the solution, and the heat
 260 of desorption was lower.

261
 262 Figure 8. (Left) The molality of each species in liquid phase as a function of the molality of K_2CO_3 , for
 263 the case with iso-capacity of 4. The solid lines correspond to the left y-axis, while the dashed grey line
 264 corresponds to the right y-axis. (Right) The molality of each species in liquid phase as a function of the
 265 molality of K_2CO_3 , for the case with iso-capacity of 8. The solid lines correspond to the left y-axis, while
 266 the dashed grey line corresponds to the right y-axis.

267 Figure 9 highlights the impact of regeneration temperature on the heat of desorption in different mixtures
 268 of NH_3 and K_2CO_3 for an iso-capacity of 4 mol/kg H_2O . The results show that temperature exerts a weak
 269 influence on the heat of desorption of CO_2 from an aqueous ammonia solvent. When the K_2CO_3 fraction
 270 was increased, an increased regeneration temperature reduced the heat of desorption. This effect is due
 271 to the higher concentration of CO_3^{2-} due to dissociation of K_2CO_3 . Increased CO_3^{2-} levels shifted the

272 equilibrium toward a higher concentration of $\text{CO}_{2(\text{aq})}$, so the impact of CO_2 solubility, which decreases
 273 as the temperature increases, thereby reduces the heat of CO_2 desorption.

274

275 Figure 9. Temperature dependence of the heat of CO_2 desorption for different mixtures of H_2O - NH_3 -
 276 K_2CO_3 .

277 4.2. Ammonia slip of the Mixed-Salt Technology solvent

278 Ammonia slip is one of the main drawbacks of ammonia-based solvent technology. The addition of
 279 potassium carbonate to the solvent mixture changes the solubility of ammonia in the solvent and,
 280 consequently, its volatility. The parameter considered to best describe the ammonia slip is the partial
 281 pressure of ammonia. Indeed, at higher partial pressures of ammonia, the ammonia is more volatile and
 282 thus the slip in the absorption column is greater.

283 Figure 10 depicts the partial pressure of ammonia for different constant-capacity lines of the solvent. The
 284 points presented correspond to a constant CO_2 partial pressure (0.013 bar) and a temperature of 25 °C.
 285 The solid lines change to dashed lines at the points where salt precipitation begins. Figure 10 shows that
 286 the partial pressure of ammonia initially increased, but then decreased with increasing K_2CO_3 in the
 287 solvent. In consideration of the salt precipitation, the constant-capacity line with the greatest benefits in

288 terms of the range of its values is the line corresponding to 4 mol/kg_{H2O}. Similar behavior in this mixture
 289 was reported previously (Jayaweera et al., 2016), wherein a decreasing partial pressure of ammonia upon
 290 increasing the K₂CO₃ content in the Mixed-Salt solvent was reported.

292

293 Figure 10. Partial pressure of ammonia as a function of initial K₂CO₃ molality for different iso-capacities
 294 of the solvent. The partial pressure of CO₂ was constant at 0.013 bar, and the temperature was 25 °C.
 295 The solid lines are the conditions prior to salt precipitation, while the dashed line represent the points
 296 where salt precipitation occurs.

297 Figure 11 (left) shows the partial pressure of ammonia at constant CO₂ partial pressure (0.013) and at
 298 varying initial ammonia concentration at 25 °C as a function of the K₂CO₃ content. Figure 11 (right)
 299 depicts the concentration of species for the solvent with an initial concentration of 4 molal ammonia as
 300 a function of the K₂CO₃ content in the solvent.

301

302 Figure 11. (Left) Ammonia partial pressure as a function of the K_2CO_3 concentration for different
 303 ammonia initial concentration. The partial pressure of CO_2 is constant, 0.013 bar, and the temperature is
 304 25 °C. (Right) Molality of every species in the solvent for a solvent with an initial ammonia molality of
 305 4. In both charts the lines are interrupted when salt precipitation starts.

306 The results do not indicate any significant variation in the partial pressure of ammonia with increasing
 307 fraction of K_2CO_3 in the solvent. Since K_2CO_3 is a weak base, at the beginning it shifts the reaction (R2)
 308 equilibrium toward an increased $\text{NH}_3(\text{aq})$ concentration and reduced concentration of NH_4^+ , with the effect
 309 of a weak increase in the ammonia slip. However, upon increasing the K_2CO_3 concentration further, the
 310 equilibrium of the reactions (R2) and (R5) maintain the $\text{NH}_3(\text{aq})$ concentration stable, and the NH_4^+ reacts
 311 to form NH_2COO^- . This is a beneficial property of the solvent, since the ammonia slip remains constant
 312 while the higher concentration of K_2CO_3 increases the capacity of the solvent.

313 4.3. Overall mass transfer coefficient and kinetics of absorption

314 The property measured with the WWC is the overall mass transfer coefficient (K_{ov}), according to the
 315 definition in equation (8).

316 During the absorption of CO₂ by the aqueous ammonia and potassium carbonate solvent, three main
 317 reactions occur in the liquid film and drive the kinetics of absorption. These reactions are the formation
 318 of carbonic acid (R6), the formation of bicarbonate (R7), and the formation of carbamate (R8):

319 According to Blauwhoff (1983), reaction (R6) has a negligible contribution to the overall rate of
 320 absorption because this reaction is very slow compared to the others involved.

321 The rate of reaction (R7), $r_{CO_2-OH^-}$ [mol/(m³ s)], was described previously in an experimental study by
 322 Pinsent et al. (1956), which indicated second-order reaction kinetics in an Arrhenius expression of the
 323 kinetic constant:

$$r_{CO_2-OH^-} = k_{OH^-} C_{CO_2} C_{OH^-} \quad \text{with} \quad k_{OH^-} = 4.2 * 10^{13} \exp\left(\frac{-24069 \left[\frac{J}{mol}\right]}{RT}\right) \quad (11)$$

324 where k_i [1/s] is the kinetic constant for the component i and C_i [mol/m³] is the concentration of
 325 component i .

326 The rate of reaction (R8) was described in an experimental study by Lillia et al. (2018a):

$$r_{CO_2-NH_3} = k_{NH_3} C_{CO_2} C_{NH_3}^\gamma \quad \text{with} \quad k_{NH_3} = 1.41 * 10^8 \exp\left(-\frac{60680 \left[\frac{J}{mol}\right]}{RT}\right) \quad \text{and} \quad \gamma = 1.89 \quad (12)$$

327 where 60680 J/mol is the activation energy, 1.41×10^8 [m³/(mol s)] is a pre-exponential factor of the
 328 Arrhenius constant, and γ is an experimentally fitted coefficient.

329 Figure 12 reports the overall mass transfer coefficient (K_{ov}) of the solvent under 18 different conditions.

330 The x -axis represents the initial molality of K₂CO₃ in the solvent, while the y -axis represents the K_{ov} .

331 The solvent was analyzed for both lean and rich loadings at three different temperatures (25 °C, 35 °C,
332 and 45 °C).

333 The CO₂ loading of the solvent is defined as:

$$CO_2 \text{ load.} = \frac{n_{app,CO_2} - n_{K_2CO_3}}{n_{NH_3} + n_{K_2CO_3}} \quad (13)$$

334 where n_{NH_3} is the initial amount of NH₃ in the solvent in moles, $n_{K_2CO_3}$ is the initial amount of K₂CO₃
335 in the solvent in moles, and n_{app,CO_2} is the apparent amount of CO₂ in moles. The numerator is
336 determined by the difference between the apparent amount of CO₂ and amount of K₂CO₃ because it
337 considers only the additional CO₂ absorbed without considering the CO₂ available in K₂CO₃.

338 The experimental analysis focused on the iso-capacity of 4 mol/kgH₂O since it was the most promising
339 with respect to its thermodynamic properties and salt deposition behavior. Moreover, the iso-capacity of
340 4 mol/kgH₂O maintains a high regeneration pressure in every solvent composition since the bubble pressure
341 of CO₂ at 120 °C is always higher than 10 bar at a lean CO₂ loading, which allows a CO₂ capture of 90%
342 in a typical coal plant. The three solvent compositions analyzed were 4 molal NH₃ without K₂CO₃, 2.5
343 molal NH₃ with 1.5 molal K₂CO₃, and 1.5 molal NH₃ with 2.5 molal K₂CO₃.

344 The lean loading was 0.35 for the case of 4 molal NH₃ and 0.25 for the other two cases containing K₂CO₃.
345 These values were chosen in consideration of a partial pressure of CO₂ of less than 0.013 bar (specifically,
346 0.003 bar) which comprises a driving force to achieve capture of 90% of CO₂ from the flue gas of a coal-
347 fired power plant. The same logic was adopted to estimate the rich loadings of 0.45 for the case of 4
348 molal NH₃ and of 0.35 for the other two solvent mixtures. In this way, a comparison between the kinetic
349 conditions possible at the top and bottom of an absorption column with different solvent mixtures could
350 be assessed. These loading values were not taken from a pilot plant, so they are not an index of the cyclic
351 capacity of the solvent since they are not correlated. The lean and rich loading values were taken in order

352 to highlight the effect of the loading on the overall mass transfer coefficient, based on two different
 353 loadings that could be used in a capture plant.

354

355 Figure 12. Overall mass transfer coefficient, K_{ov} , as a function of K_2CO_3 molality for solvents with iso-
 356 capacity of 4 mol/kgH₂O. The data were measured at 3 different temperatures (25 °C, 35 °C, and 45 °C)
 357 and 2 different CO₂ loadings (lean and rich).

358 The first trend analyzed from the results shown in Figure 12 was the dependence of K_{ov} on the CO₂
 359 loading. The results show that K_{ov} decreased with increased CO₂ loading of the solvent. Indeed, the
 360 solvents with rich loadings were more saturated by CO₂, and consequently the reactant concentrations in
 361 the liquid phase were lower since they had already reacted with the CO₂. As shown by equations (6) and
 362 (12), the rates of reactions (R7) and (R8) are dependent on the reactant concentrations, which were
 363 reduced in this case due to reactions with the loaded CO₂.

364 The second trend analyzed was the temperature dependence; the results confirm the Arrhenius expression
 365 of the kinetic constant shown in equation (11). As indicated in equation (12), there is an exponential
 366 dependence of K_{ov} on temperature following the Maxwell-Boltzmann distribution of the kinetic energy
 367 of the molecules, where increasing the temperature of the reaction increases the rate of reaction.

368 The third trend analyzed was the effect of different proportions of NH_3 and K_2CO_3 at constant iso-
 369 capacity on the K_{ov} . The results indicated a reduction in the K_{ov} with increasing fraction of K_2CO_3 in the
 370 solvent. Indeed, as demonstrated in Figure 13, with increasing K_2CO_3 content, the free ammonia, $\text{NH}_{3(aq)}$,
 371 in the liquid decreased. As demonstrated by Darde et al.(2011) and Lillia et al. (2018a), among the
 372 reactions (R6) to (R8), reaction (R8) contributes most significantly to the overall kinetics of absorption.
 373 This explains why the K_{ov} decreased with decreasing free ammonia concentration in the liquid, where
 374 reaction (R8) involves high concentrations of reagents and contributes significantly to the rate of
 375 absorption. On the other hand, the impact of free ammonia concentration becomes less significant as the
 376 K_2CO_3 concentration increases, at which point the influence of reaction (R8) on the rate of absorption
 377 decreases and the contribution by reaction (R6) increases.

378

379 Figure 13. The overall mass transfer coefficient is represented as a function of the initial molality of
 380 K_2CO_3 (left y-axis); the blue circles represent the values at 35 °C and lean loadings while the grey
 381 triangles represent the values at 35 °C and rich loadings. The molality of free ammonia ($\text{NH}_{3(aq)}$) in the
 382 solvent is represented as a function of the initial molality of K_2CO_3 (right y-axis); the blue solid line
 383 represents the values at 35 °C and lean loadings while the grey solid line represents the values at 35 °C
 384 and rich loadings.

385 For the sake of completeness, Figure 14 reports the speciation as a function of the CO₂ loading at 35 °C
386 for three different mixtures of NH₃ and K₂CO₃. Since there is a correlation between reactant
387 concentration in the liquid and the reaction kinetics, the speciation, especially the concentration of
388 NH_{3(aq)}, can be used to predict trends in K_{ov} and consequently in the kinetics of absorption.

389 As shown in all three graphs of Figure 14, the NH_{3(aq)} concentration decreased with increasing CO₂
390 loading. It follows that the K_{ov} would decrease with increased CO₂ loading, which was confirmed by the
391 experiment and explained previously. When the CO₂ loading increased, the concentration of NH_2COO^-
392 also increased, up to a CO₂ loading of about 0.5, and thus carbamate is the main species formed by CO₂.
393 Beyond this loading, the concentration of HCO_3^- increased, finally exceeding the concentration of
394 NH_2COO^- . At the same time, free ammonia forms NH_4^+ as pH decreases due to CO₂ absorption. The
395 ammonium cation then combines with bicarbonate to form ammonium bicarbonate (NH₄HCO₃), which
396 is the main ammonium salt formed in the carbon capture process.

397 Comparing the results of the three graphs of Figure 14 corresponding to the different mixtures of NH₃
398 and K₂CO₃, it can be concluded that reducing the NH₃ concentration resulted in a decrease in the
399 concentration of free ammonia. Consequently, the rate of absorption decreased, as supported by the
400 results shown in Figure 13. Further, increasing the K₂CO₃ concentration in the solvent resulted in a higher
401 concentration carbonate ions (CO_3^{2-}). The presence of carbonate ions and potassium ions (K^+) changes
402 the equilibrium of the bicarbonate ions when the CO₂ loading increases. Indeed, as shown by Figure 14,
403 in the presence of K₂CO₃, the concentration of bicarbonate ions was higher in the solvents with higher
404 CO₂ loadings. The same influence was also seen for the carbamate ion (NH_2COO^-), the concentration
405 of which increased in the presence of K₂CO₃ in the solvent.

406 A further observation about the properties of the three different mixtures presented in Figure 14 concerns
407 the carrying capacity of the solvent. The carrying capacity is defined as:

$$CC = \frac{m_{CO_2,app}}{V_{H_2O}} \left[\frac{g_{CO_2}}{L_{H_2O}} \right] \quad (14)$$

where CC is the carrying capacity [g_{CO_2}/L_{H_2O}], $m_{CO_2,app}$ is the apparent mass of CO_2 in the solvent [g_{CO_2}], and V_{H_2O} is the volume of water in the solvent [L_{H_2O}]. The carrying capacity indicates the capacity of one liter of solvent to dissolve and carry CO_2 in the liquid phase. Its value, calculated at 35 °C for the maximum loading before the saturation point, is 158.44 [g_{CO_2}/L_{H_2O}] for the solvent with 4 molal NH_3 , 224.45 [g_{CO_2}/L_{H_2O}] for the solvents with 2.5 molal NH_3 and 1.5 molal K_2CO_3 , and 233.25 [g_{CO_2}/L_{H_2O}] for the solvent with 1.5 molal NH_3 and 2.5 molal K_2CO_3 . Thus, increasing the fraction of K_2CO_3 in the solvent resulted in increased carrying capacity.

Finally, Figure 15 shows the K_{ov} for the aqueous ammonia solvent and MEA solvent at different concentrations, different CO_2 loadings, and different temperatures, in order to allow for qualitative comparisons with the Mixed-Salt solvent. The order of magnitude of the values of K_{ov} for the Mixed-Salt solvent compositions analyzed herein is the same as that of the values reported for the NH_3 and MEA solvents, as shown in Figure 15. Considering the temperature range and the loading of the Mixed-Salt solvent analyzed, the values of K_{ov} for the ammonia and MEA shown in Figure 15 are on average 1.5-2 times larger ($4e-7 \div 1.4e-6$ mol/(Pa m² s)) than those of the Mixed-salt solvent (ranging from $2e-7 \div 8e-7$ mol/(Pa m² s)), and by extension the size of the absorber required would be expected to be 1.5-2 times larger. However, the K_{ov} depends on the concentration of the reagent in the solvent, and the iso-capacity 4 was selected based on thermodynamic properties. Increasing the iso-capacity also increased the K_{ov} , reducing the size of the absorber needed but hurting the performance of the process in terms of energy efficiency. Moreover, the reduction in the ammonia slip in the Mixed-Salt solvent might allow higher temperatures to be used in the absorber, increasing the K_{ov} process.

Figure 14. The graphs represent the molality of the different species in the liquid phase as a function of CO₂ loading at 35 °C for (i) the solvent with NH₃ molality of 4, (ii) the solvent with NH₃ molality of 2.5 and K₂CO₃ molality of 1.5, and (iii) the solvent with NH₃ molality of 1.5 and K₂CO₃ molality of 2.5.

Figure 15. Overall mass transfer coefficient, K_{ov} , as a function of the CO₂ loading at different solvent concentrations and different temperatures. The experimental data for the MEA solvent was taken from the work by Darde et al. (2011), while the data for the NH₃ solvent was taken from the work by Lillia et al. (2018a).

5. Conclusions

This work presented the thermodynamic and kinetic properties of CO₂ absorption in the NH₃-K₂CO₃-CO₂-H₂O solvent system. The thermodynamic properties and the speciation of the solvent were calculated with the Extended UNIQUAC thermodynamic model, while the kinetics of absorption were measured experimentally using a WWC setup.

The heat of desorption decreased with increased regeneration temperature. For instance, heat of desorption of the solvent comprised of 2 molal NH₃ and 2 molal K₂CO₃ decreased from 58 kJ/mol_{CO2} at 120 °C to 40 kJ/mol_{CO2} at 130 °C. The heat of desorption also decreased when the fraction of K₂CO₃ in the solvent was increased, and this effect overshadowed the effect of increasing the regeneration temperature. For instance, at 120 °C, the heat of desorption decreased from 70 kJ/mol_{CO2} (for a mixture

450 of 3 molal NH_3 and 1 molal K_2CO_3) to 55 kJ/mol CO_2 (for a mixture of 2 molal NH_3 and 2 molal K_2CO_3).

451 The ammonia slip decreased with increasing fraction of K_2CO_3 in the solvent due to the decrease of free
452 ammonia in the liquid phase. Increasing the concentration of K_2CO_3 in the solvent resulted in reduced
453 solubility. Consequently, salt precipitation occurred at a lower CO_2 loading. The overall mass transfer
454 coefficient increased with increasing temperature and decreased with increasing CO_2 loading, following
455 the kinetic description of the Arrhenius equation.

456 The overall mass transfer coefficient decreased with increased fraction of K_2CO_3 in the solvent due to
457 the reduction in the amount of free ammonia in the reactive layer. For instance, between the solution of
458 4 molal NH_3 and the solution of 1.5 molal NH_3 and 2.5 molal K_2CO_3 (both at 35 °C), the overall mass
459 transfer coefficient decreased from 7.34×10^{-7} [mol/(Pa m² s)] to 3.14×10^{-7} [mol/(Pa m² s)].

460 The kinetics of absorption were mainly influenced by the reaction between free ammonia and CO_2 . The
461 overall mass transfer coefficient decreased with increasing K_2CO_3 fraction in the solvent.

462 The carrying capacity increased with increasing fraction of K_2CO_3 in the solvent, from 158.44
463 [g CO_2 /L H_2O] for the solvent with 4 molal NH_3 to 224.45 [g CO_2 /L H_2O] for the solvent with 1.5 molal NH_3
464 and 2.5 molal K_2CO_3 .

465 The Mixed-Salt solvent had an overall mass transfer coefficient 1.5-2 times smaller than that of MEA.

466 Globally, the solvent has interesting properties for CO_2 capture applications. As a first analysis, the
467 solvent compositions considered in this evaluation have good thermodynamic properties (low ammonia
468 slip and low heat of desorption), with the drawback of slower absorption kinetics compared to those in
469 an aqueous ammonia solvent.

474 **Nomenclature:**

475 *Acronyms*

476	Bulk	Bulk layer
477	LCA	Life cycle assessment
478	WWC	Wetted wall column
479	WWC, in	Wetted wall column inlet
480	WWC, out	Wetted wall column outlet

481 *Symbols*

482	A	pre-exponential factor of the Arrhenius constant [$\text{m}^3/(\text{mol s})$]
483	A_{int}	interfacial area in the wetted wall column [m^2]
484	C_i^j	concentration of component i at position j [mol/m^3]
485	CC	carrying capacity [$\text{g}_{\text{CO}_2}/\text{L}_{\text{H}_2\text{O}}$]
486	H_{CO_2}	partition coefficient of CO_2 [$(\text{Pa m}^3)/\text{mol}$]
487	K_{ov}	overall mass transfer coefficient for the CO_2 transport [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
488	k_i	kinetic constant for component i [$\text{m}^3/(\text{mol s})$]
489	k_G	gas-side mass transfer coefficient [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
490	k_{liq}	liquid-side mass transfer coefficient related to the difference in concentrations [m/s]
491	k'_{liq}	liquid-side mass transfer coefficient of the difference in partial pressure [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
492	$m_{\text{CO}_2,app}$	apparent mass of CO_2 in the solvent [g_{CO_2}]
493	N_i^j	molar flow of component i at position j [mol/s]
494	P_i^j	partial pressure of component i at position j [mol/s]
495	r_{i-j}	rate of reaction between components i and j [$\text{mol}/(\text{m}^3 \text{ s})$]
496	$V_{\text{H}_2\text{O}}$	volume of H_2O in the solvent [$\text{L}_{\text{H}_2\text{O}}$]
497	y_i^j	mole fraction of component i at position j in the gas phase [-]
498	<i>Greek symbols</i>	
499	Δx	difference between the inlet and the outlet of the x variable
500	γ	experimental parameter [-]
501	φ_i^j	molar surface flow of species i in media j [$\text{mol}/(\text{m}^2 \text{ s})$]

502

503

504

505

506 **Bibliography**

- 507 Bai, H., Yeh, A.C., 1997. Removal of CO₂ Greenhouse Gas by Ammonia Scrubbing. Ind. Eng. Chem.
508 Res. 36, 2490–2493. <https://doi.org/10.1021/ie960748j>
- 509 Blauwhoff, P.M.M., 1983. a Study on the Reaction Between CO₂ and Alkalonamines in aqueous
510 solutions. Chem. Eng. Sci. 38, 1411–1429. [https://doi.org/10.1016/0009-2509\(83\)80077-3](https://doi.org/10.1016/0009-2509(83)80077-3)
- 511 Bonalumi, D., Valenti, G., Lillia, S., Fosbøl, P.L., Thomsen, K., 2016. A Layout for the Carbon
512 Capture with Aqueous Ammonia without Salt Precipitation. Energy Procedia 86, 134–143.
513 <https://doi.org/10.1016/j.egypro.2016.01.014>
- 514 Cacciola, G., Restuccia, G., Aristov, Y., 1995. Vapor Pressure of (Potassium Hydroxide + Ammonia +
515 Water) Solutions. J. Chem. Eng. Data 40, 267–270. <https://doi.org/10.1021/je00017a058>
- 516 Darde, V., Thomsen, K., van Well, W.J.M., Bonalumi, D., Valenti, G., Macchi, E., 2012. Comparison
517 of two electrolyte models for the carbon capture with aqueous ammonia. Int. J. Greenh. Gas
518 Control 8, 61–72. <https://doi.org/10.1016/j.ijggc.2012.02.002>
- 519 Darde, V., van Well, W.J.M., Fosboel, P.L., Stenby, E.H., Thomsen, K., 2011. Experimental
520 measurement and modeling of the rate of absorption of carbon dioxide by aqueous ammonia. Int.
521 J. Greenh. Gas Control 5, 1149–1162. <https://doi.org/10.1016/j.ijggc.2011.07.008>
- 522 Gladis, A., Gundersen, M.T., Fosbøl, P.L., Woodley, J.M., von Solms, N., 2017. Influence of
523 temperature and solvent concentration on the kinetics of the enzyme carbonic anhydrase in carbon
524 capture technology. Chem. Eng. J. 309, 772–786. <https://doi.org/10.1016/j.cej.2016.10.056>
- 525 Grant, T., Anderson, C., Hooper, B., 2014. Comparative life cycle assessment of potassium carbonate
526 and monoethanolamine solvents for CO₂ capture from post combustion flue gases. Int. J. Greenh.
527 Gas Control 28, 35–44. <https://doi.org/10.1016/j.ijggc.2014.06.020>
- 528 Hill, A.E., 1930. Hydrated Potassium Sesquicarbonate K₂CO₃·2KHCO₃·3/2H₂O. J. Am. Chem. Soc.
529 52, 3817–2825.
- 530 Jayaweera, I., Jayaweera, P., 2018. Development of Mixed-Salt Technology for Carbon Dioxide
531 Capture from Coal Power Plants. <https://doi.org/10.2172/1441205>
- 532 Jayaweera, I., Jayaweera, P., Elmore, R., Bao, J., Bhamidi, S., 2014. Update on mixed-salt technology
533 development for CO₂ capture from post-combustion power stations. Energy Procedia 63, 640–650.
534 <https://doi.org/10.1016/j.egypro.2014.11.070>
- 535 Jayaweera, I., Jayaweera, P., Kundu, P., Anderko, A., Thomsen, K., Valenti, G., Bonalumi, D., Lillia,
536 S., 2017. Results from Process Modeling of the Mixed-salt Technology for CO₂Capture from
537 Post-combustion-related Applications, in: Energy Procedia.

538 <https://doi.org/10.1016/j.egypro.2017.03.1220>
 539 Jayaweera, I., Jayaweera, P., Yamasaki, Y., Elmore, R., 2016. Mixed salt solutions for CO₂ capture,
 540 Absorption-Based Post-Combustion Capture of Carbon Dioxide. [https://doi.org/10.1016/B978-0-](https://doi.org/10.1016/B978-0-08-100514-9.00008-1)
 541 08-100514-9.00008-1
 542 Kamps, A.P.S., Meyer, E., Rumpf, B., Maurer, G., 2007. Solubility of CO₂ in aqueous solutions of
 543 KCl and in aqueous solutions of K₂CO₃. J. Chem. Eng. Data 52, 817–832.
 544 <https://doi.org/10.1021/je060430q>
 545 Kong, S., Application, F., Data, P., 2011. (12) United States Patent 2, 12–15.
 546 [https://doi.org/10.1016/j.\(73\)](https://doi.org/10.1016/j.(73))
 547 Lewis, W.K., Whitman, W.G., 1924. Absorption symposium. Ind. Eng. Chemnistry 16, 1215–1220.
 548 <https://doi.org/10.1021/ie50180a002>
 549 Lillia, S., Bonalumi, D., Fosbøl, P.L., Thomsen, K., Valenti, G., 2018. Experimental study of the
 550 aqueous CO₂-NH₃ rate of reaction for temperatures from 15 °C to 35 °C, NH₃ concentrations from
 551 5% to 15% and CO₂ loadings from 0.2 to 0.6. Int. J. Greenh. Gas Control 70, 117–127.
 552 <https://doi.org/10.1016/j.ijggc.2018.01.009>
 553 Lillia, S., Bonalumi, D., Fosbøl, P.L., Thomsen, K., Valenti, G., 2018. Experimental data of the
 554 aqueous NH₃ and CO₂ absorption at temperatures from 15 °C to 35 °C, NH₃ concentrations from
 555 5% to 15% and CO₂ loadings from 0.2 to 0.6 measured with the Wetted Wall Column. Data Br.
 556 17. <https://doi.org/10.1016/j.dib.2018.02.047>
 557 Luzhnaya, N.P., Kosyachkova, S.N., 1955. Solubility isotherm at 50° of the quaternary system
 558 K₂CO₃-K₂SO₄-KHCO₃-H₂O.
 559 Mumford, K.A., Smith, K.H., Anderson, C.J., Shen, S., Tao, W., Suryaputradinata, Y.A., Quyn, D.M.,
 560 Qader, A., Hooper, B., Innocenzi, R.A., Kentish, S.E., Stevens, G.W., 2012. Erratum: Post-
 561 combustion capture of CO₂: Results from the Solvent absorption capture plant at hazelwood
 562 power station using potassium carbonate solvent (Energy and Fuels (2012) 26:1 (138-146) DOI:
 563 10.1021/ef201192n). Energy and Fuels 26, 6449. <https://doi.org/10.1021/ef3015519>
 564 Petrescu, L., Bonalumi, D., Valenti, G., Cormos, A.M., Cormos, C.C., 2017. Life Cycle Assessment for
 565 supercritical pulverized coal power plants with post-combustion carbon capture and storage. J.
 566 Clean. Prod. 157, 10–21. <https://doi.org/10.1016/j.jclepro.2017.03.225>
 567 Pinsent, B.R.W., Pearson, L., Roughton, F.J.W., 1956. The kinetics of combination of carbon dioxide
 568 with hydroxide ions. Trans. Faraday Soc. 52, 1512. <https://doi.org/10.1039/tf9565201512>
 569 Rochelle, G., Chen, E., Freeman, S., Van Wagener, D., Xu, Q., Voice, A., 2011. Aqueous piperazine as

570 the new standard for CO₂ capture technology. Chem. Eng. J. 171, 725–733.
571 <https://doi.org/10.1016/j.cej.2011.02.011>

572 Rochelle, G.T., 2011. Amine Scrubbing for CO₂ Capture. Science (80-.). 325, 19–22.
573 <https://doi.org/10.1126/science.1176731>

574 Sorina, G.A., Miniovich, V.M., Efremova, G.D., 1967. Solubility of ammonia in aqueous solutions of
575 KOH. Zhurnal Obs. Khimii 37, 2150–2154.

576 Thomsen, K., Rasmussen, P., 1999. Modeling of vapor–liquid–solid equilibrium in gas–aqueous
577 electrolyte systems. Chem. Eng. Sci. 54, 1787–1802. [https://doi.org/10.1016/S0009-](https://doi.org/10.1016/S0009-2509(99)00019-6)
578 [2509\(99\)00019-6](https://doi.org/10.1016/S0009-2509(99)00019-6)

579 Tosh, J.S., Field, J.H., Benson, H.E., Haynes, W.P., 1959. Equilibrium study of the system potassium
580 carbonate, potassium bicarbonate, carbon dioxide, and water.

581 Trypuć, M., Kiełkowska, U., 1996. Solubility in the NH₄HCO₃ + NH₄VO₃ + H₂O System. J. Chem.
582 Eng. Data 41, 1005–1007. <https://doi.org/10.1021/je950290c>

583 Williamson, R. V., Matheus, J.H., 1924. Endowment Fund. Ind. Eng. Chem. 16, 1102–1104.
584 <https://doi.org/10.1021/ie50179a001>
585