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Heat requirement of CO_2 absorption by aqueous ammonia

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Aqueous ammonia has lately emerged as a promising absorbent of CO_2 in post-combustion capture applications, often referred to as the chilled ammonia process (CAP). The heat required for regeneration, i.e. the reboiler duty (kJ/kg CO_2), is a crucial parameter for all absorbents. For the CAP, the required reboiler duty presented in literature ranges from 1,500 to 4,200 kJ/kg CO_2 [1-6]. This is a wide range with crucial consequences for the feasibility of the process. The aim of this work is to review the different sources in order to explain the large difference in heat requirement.

Figure 1 presents the reboiler duty as a function of ammonia concentration (mole NH_3/kg H_2O) and CO_2-loading (mole NH_3/mole CO_2 in the lean solution) from six different investigations [1-6]. The investigations may be divided into three categories depending on method applied to decide the reboiler duty: 1) simulations assuming CO_2 to be absorbed solely by ammonium carbonate crystals (Reaction 1) [2], 2) equilibrium based process simulations [1,3-5], 3) pilot plant studies [6]. Group 1 shows on the lowest regeneration heat, around 1,500 kJ/kg CO_2 [1]. Group 2, range from 2,000 to 4,000 kJ/kg CO_2 highly dependent on the ammonia concentration [2-5]. So far, pilot plant data is only recorded at low ammonia concentrations (2 to 5wt%) and the lowest registered regeneration heat is around 4,000 kJ/kg CO_2 [6], which agrees with the equilibrium calculations under similar conditions.

The ammonia concentration mainly affects the thermal performance through the increase in mass flow when the ammonia concentration declines; hence the sensible heat requirements are increased. However, the ammonia concentration also affects the chemistry. The low sensitivity of the reboiler duty above 7 moles NH_3/kg H_2O (CO_2-loading of 0.25) shown by the equilibrium calculations is caused by the precipitation of ammonium bicarbonate at these ammonia concentrations. The reduced sensible heat requirements are counteracted by the heat of dissolution of the solid ammonium bicarbonate. At a CO_2-loading of 0.15, precipitation does not occur.

The regeneration heat is related to the heat of reaction. Carbon dioxide may be absorbed trough Reactions 1-4. Reaction 1 is the absorption by ammonium carbonate, which is slow and has a low heat of reaction. Reactions 2-4 include free ammonia, which makes them faster but with a significantly larger heat of formation. Thus, if the process is forced through Reaction 1 a considerably lower reboiler duty is achieved. The high reboiler duty of the pilot plant [6] is caused by the low ammonia concentration which promotes Reaction 3 and increases the sensible heat through a larger amount of water in the system.

The CO_2-loading has a large influence on the liquid species concentrations as seen in Figure 2. Due to the stoichiometric conditions of Reactions 1-4 a low CO_2-loading promotes Reactions 3 and 4, while a higher CO_2-loading promotes the formation of ammonium bicarbonate through Reaction 2 and eventually Reaction 1. The heat of reaction is, however, fairly constant until the free ammonia is consumed and Reaction 1 will dominate. Qin et al. [7] stressed that Reaction 1 is promoted by the elimination of free ammonia, and, thus, of a CO_2/NH_3-ratio that approaches unity. This is, however, not the case at the CO_2-loadings of Valenti et al. [2], and the absorption will not be determined solely by Reaction 1. The possibilities of utilizing Reaction 1 are, nevertheless, interesting and experiments with higher NH_3 concentrations and solid formation would be of high value.

There are large uncertainties in the heat of regeneration of the CAP. The largest remaining uncertainty is how the carbon dioxide is bound by the ammonia. There are not enough experimental data to verify the available vapour-liquid-solid equilibrium models for the relevant operating conditions. Furthermore, it is important to investigate the reaction rate of the competing absorption reactions which controls the overall heat of reaction.

$$2NH_4HCO_3\ (aq) \leftrightarrow (NH_4)_2CO_3\ (aq) + CO_2(g) + H_2O \qquad \Delta H = 26.88\ kJ/mol \qquad (1)$$
$$NH_4HCO_3\ (aq) \leftrightarrow NH_3\ (aq) + CO_2(g) + H_2O \qquad \Delta H = 64.26\ kJ/mol \qquad (2)$$
$$(NH_4)_2CO_3\ (aq) \leftrightarrow 2NH_3\ (aq) + CO_2(g) + H_2O \qquad \Delta H = 101.22\ kJ/mol \qquad (3)$$
$$NH_2COONH_4\ (aq) \leftrightarrow 2NH_3\ (aq) + CO_2(g) \qquad \Delta H = 72.32\ kJ/mol \qquad (4)$$

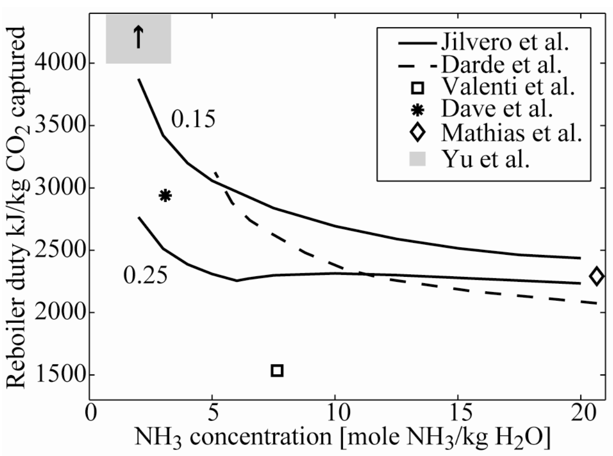

Figure 1. The specific reboiler duty when simulated with ammonia concentrations of 2-20 moles NH_3/kg H_2O and CO_2-loadings of 0.15 and 0.25. The CO_2-loading for the remaining sources: Darde et al. (0.33), Valenti et al. (0.25), Dave et al. (Unknown), Mathias et al. (0.36) and Yu et al. (0-0.6).

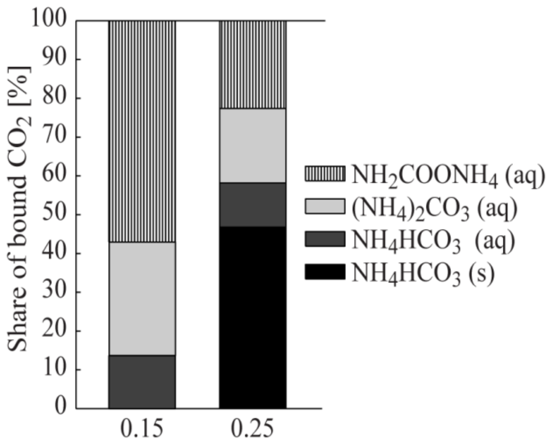

Figure 2. Distribution of how carbon dioxide is bound in the ammonia for CO2-loadings of 0.15 and 0.25. In these simulations an ammonia concentration of 15 moles NH_3/kg H_2O are applied. Simulations after Jilvero et al. [5].

1. Valenti, G., D. Bonalumi, and E. Macchi, 2009. **1**: p. 1059-1066.
2. Darde, V., et al., International Journal of Greenhouse Gas Control, 2009.
3. Mathias, P.M., S. Reddy, and J.P. O'Connell, International Journal of Greenhouse Gas Control, 2009.
4. Dave, N., et al., Energy Procedia, 2009. **1**(1): p. 1235-1246.
5. Jilvero, H., et al., in *10th International Conference on Greenhouse Gas Control Technologies*. 2010.
6. Yu, H., et al., in *10th International Conference on Greenhouse Gas Control Technologies*. 2010.
7. Qin, F., et al., International Journal of Greenhouse Gas Control, 2010. **Article In Press**.