Study of an ammonia-based wet scrubbing process in a continuous flow system

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HIGHLIGHTS

► A continuous gas and liquid flow, regenerative scrubbing process for CO_2 capture was demonstrated at the bench-scale level using an aqueous ammonia-based solution.
► Ammonia emissions from the absorber and regenerator must be accounted for in the overall process.
► Testing was conducted at near steady-state conditions.
► A spray chamber within the regeneration step proved extremely effective in capturing a significant amount of the ammonia that would typically be vented from the regenerator.

ARTICLE INFO

ABSTRACT

A continuous gas and liquid flow, regenerative scrubbing process for CO_2 capture was demonstrated at the bench-scale level. An aqueous ammonia-based solution captures CO_2 from simulated flue gas in an absorber and releases a nearly pure stream of CO_2 in the regenerator. After the regeneration, the solution of ammonium compounds is recycled to the absorber. The design of a continuous flow unit was based on earlier exploratory results from a semi-batch reactor, where a CO_2 and N_2 simulated flue gas mixture flowed through a well-mixed batch of ammonia-based solution. During the semi-batch tests, the solution was cycled between absorption and regeneration steps to measure the carrying capacity of the solution at various initial ammonia concentrations and temperatures. Consequentially, a series of tests were conducted on the continuous unit to observe the effect of various parameters on CO_2 removal efficiency and regenerator effectiveness within the flow system. The parameters that were studied included absorber temperature, regenerator temperature, initial NH_3 concentration, simulated flue gas flow rate, liquid solvent inventory in the flow system, and height of the packed-bed absorber. From this testing and subsequent testing, ammonia losses from both the absorption and regeneration steps were quantified, and attempts were made to maintain steady state during operations. Implications of experimental results with respect to process design are discussed.

1. Introduction

Currently, the primary commercial process available for large-scale carbon dioxide (CO_2) capture in post-combustion applications is the monoethanolamine (MEA) process. MEA scrubbing produces valuable CO_2 for industrial usage. The cost of CO_2 separation from flue gas produced at power generation point sources by using the MEA process would be high if it is used to capture CO_2 for subsequent carbon sequestration purposes [1,2].

Similar to the MEA process, the ammonia-based wet scrubbing process is an aqueous liquid solution that chemically reacts with CO_2 to remove it from flue gas. The ammonia-based process offers the potential for a reduced parasitic load [3–8]. The National Energy Technology Laboratory (NETL) has tested the ammonia-based wet scrubbing process in a continuous flow system, where absorption and regeneration of CO_2 is performed [9]. The ammonia-based absorbent is regenerated by a temperature swing. A high purity CO_2 gas is evolved in the regenerator and can be sequestered.

Laboratory-scale tests indicate that the absorption/desorption process may be controlled so that the liquid is primarily cycling between ammonium bicarbonate and ammonium carbonate, reducing the heat of reaction for CO_2 absorption to 6.4 kcal/mol CO_2 compared to 20.2 kcal/mol CO_2 for MEA [5,7]. Because of the temperature of regeneration, the thermal desorption chemistry of

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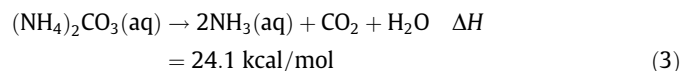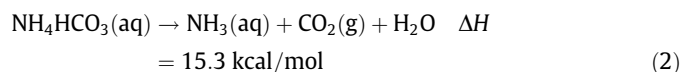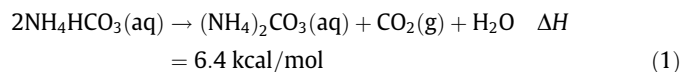[1] Tel.: +412 386 6013.

regenerating the rich bicarbonate solution will not require stripping steam to be formed, only heat to drive the desorption reaction, reducing latent heat requirements. Additionally, semi-batch tests had demonstrated that the aqueous ammonia-based system can carry a high amount of CO_2 per weight of solution. Subsequently, less solution needs to be circulated, resulting in a reduction in sensible heat and in the size of equipment.

Another advantage of the ammonia-based process is the potential control of SO_2, NO_x, and mercury emissions in addition to CO_2. The use of aqueous ammonia for NO_x and SO_2 and mercury control has been performed at a 50-MW$_e$ demonstration by Powerspan Corp. at FirstEnergy's R.E. Burger coal-fired power plant in Ohio, US [10]. SO_2 and NO_x capture with aqueous ammonia results in ammonium sulfate and ammonium nitrate generation, both salable by-products. Fertilizer byproducts could be sold world-wide. The melding of the two types of control processes could aid in the overall economics of ammonia scrubbing [11].

With respect to CO_2 capture, the regeneration chemistry can be summarized by three potential reactions,

$$2NH_4HCO_3(aq) \rightarrow (NH_4)_2CO_3(aq) + CO_2(g) + H_2O \quad \Delta H$$
$$= 6.4 \text{ kcal/mol} \quad (1)$$

$$NH_4HCO_3(aq) \rightarrow NH_3(aq) + CO_2(g) + H_2O \quad \Delta H$$
$$= 15.3 \text{ kcal/mol} \quad (2)$$

$$(NH_4)_2CO_3(aq) \rightarrow 2NH_3(aq) + CO_2 + H_2O \quad \Delta H$$
$$= 24.1 \text{ kcal/mol} \quad (3)$$

where ΔH is enthalpy of dissociation. In the absorber, the reverse of these reactions can occur. Obviously, dissociating CO_2 from ammonium bicarbonate (Eq. (1)) requires the least amount of thermal energy.

1.1. Previous semi-batch test results

Testing in a semi-batch reactor had been conducted on the aqueous ammonia system to determine the feasibility of the process [5]. This system passed a continuous flow of carbon dioxide through a batch of aqueous ammonia to determine equilibrium carbon dioxide capture capacities. In a separate step, the solution was then heated to regenerate the solution for multiple cycle testing. Titrimetric analysis of the solution determined the degree of carbonation. The results of the semi-batch testing are summarized below:

- With an initial solution of ammonia in water, most of the ammonia loss is in the first cycle. This finding suggests a preliminary carbonation step within a process application.
- Cycling tests demonstrated a CO_2 carrying capacity of 0.068, 0.053, and 0.040 g CO_2/g solution for initial solutions of 14%, 10.5%, and 7% ammonia, respectively.
- An ammonia-based solution that has absorbed CO_2 can be regenerated by heating the solution in a temperature swing. The amount of CO_2 evolved as a function of temperature was quantified. A saturated solution begins to regenerate at temperatures as low as 49 °C.
- Control of the regeneration temperature is demonstrated to be an effective means of controlling the degree of regeneration. At ambient regeneration pressure, the temperature at which ammonium hydroxide production is initiated is between 77 °C and 82 °C. It is expected that at higher regeneration pressures, this temperature will increase. Significant regeneration energy savings can be realized when the degree of regeneration is controlled, as described in Eqs. (1)–(3). Additionally, ammonia

loss is expected to be controlled by limiting the amount of ammonium hydroxide (aqueous ammonia) in the regenerated solution. Limiting the formation of ammonia (Eqs. (2) and (3)) minimizes the heat of reaction and the regenerator ammonia loss and improves the regenerative heat duty.

1.2. Previous continuous test results

Based on the semi-batch test results, a unit was constructed to continuously cycle the solution through the absorption and regeneration steps. The unit provided for no make-up ammonia or water, but was nonetheless useful to investigate the effect of various parameters on system performance [9]. The pertinent results of the continuous unit testing are summarized below:

- Increasing the regenerator residence time improved the system performance. This effect was presumably due to the improved heat transfer within the regenerator of the experimental apparatus. This effect leveled off at approximately 4000 g of system solution.
- Increasing the initial ammonia concentration improved system performance, but at the expense of higher fugitive ammonia emissions in both the regenerator and the absorber.
- Increasing the regenerator temperature from 71 °C to 82 °C improves solution performance. No further improvement was seen above 82 °C. The ammonia emissions increased linearly with regenerator temperature.
- Increasing the absorber temperature degrades system performance. The ammonia emissions increased linearly with absorber temperature.
- Four sections of structured packing were used in the absorber. The majority of the CO_2 absorption takes place in the bottom (gas inlet) two sections of packing. Minimal gains were seen by increasing the packing height above this level.
- No discernible effect of the simulated flue gas oxygen concentration on the CO_2 capture or ammonia emissions was observed.

Based on these results, the unit was further modified to allow for continuous operation with ammonia and water make-up, and the regenerator vent was modified to allow the regenerator vent composition to be quantified.

2. Experimental

The aqua ammonia continuous unit was designed to provide data regarding the carbon dioxide removal capability of aqueous ammonia solutions on a continuous basis, utilizing an absorber to capture CO_2 from a simulated flue gas, and a regenerator to liberate a concentrated CO_2 stream. The absorber and regenerator and ancillary components, very similar to an MEA scrubbing system, are contained in a walk-in hood. A schematic of the details of the system can be found in Fig. 1.

The unit utilizes a countercurrent flow, packed-bed absorber with structured packing (Koch-Glitsch BX gauge, 7.6 cm diameter, 4-sections, by 68.6 cm height total) to remove carbon dioxide from a simulated flue gas. The column is jacketed with water; the water temperature is controlled by a circulating heater/chiller. The simulated flue gas is generated by combining nitrogen and CO_2 (15% by volume), metered by mass flow controllers and heated to temperatures as high as 54 °C by a heater before introduction into the bottom of the absorber. For the tests described below, oxygen, sulfur dioxide and nitric oxide gases were not included in the feed gas. The absorber gauge pressure is maintained at approximately 6.9 kPa. The absorbent is initially a solution of aqueous ammonia (0–28 weight%). This absorbent flows countercurrently to the flue