

*Original Research*

# Laboratory Studies of Ammonia Emissions from the CO<sub>2</sub> Capture Process Using Aqueous Ammonia from the Solvay Process

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## Abstract

The aqueous solutions of various amines are used as chemical absorbents in gas treating processes. It is considered that aqueous ammonia can be used as a promising solvent for CO<sub>2</sub> capture. Apart from the many advantages of ammonia as a CO<sub>2</sub> capture solvent, its major drawback is high volatility. As a consequence, a large amount of ammonia can be released into the atmosphere. In this paper we investigated the effects of process parameters on ammonia emissions from the absorber used for CO<sub>2</sub> capture. Ammonia solution withdrawn from the ammonia recovery tower of the Solvay Process was used as solvent. During the research, the absorber pressure, liquid to gas flow ratio (L/G) and concentration of ammonia have been varied. In addition, a novel simple method for quantitative analysis of absorbed CO<sub>2</sub> in the ammonia solvent was described. We found that increasing the L/G ratio and ammonia concentration in the solvent resulted in a growth of ammonia emissions. The amount of released ammonia from the absorber was in the range 14-46 mg/dm<sup>3</sup>. However, it is important to note that no emission reduction devices were applied. The test of CO<sub>2</sub> capture using aqueous ammonia was satisfactory, with more than 90% of the inlet CO<sub>2</sub> stream being removed.

**Keywords:** aqueous ammonia; ammonia emissions; carbon capture; carbon dioxide; Solvay Process

## Introduction

Amine solutions are used to remove CO<sub>2</sub> in various areas ranging from natural gas production to the food and beverage industry [1]. Monoethanolamine (MEA), diethanolamine (DEA), and N-methyldiethanolamine (MDEA) are well-known chemical solvents used for

removing sour gases from process gas streams [2, 3]. As the reduction of greenhouse gases gains importance, the use of amines and alternative solvents for CO<sub>2</sub> post combustion carbon capture (PCCC) is a significant area of research and development. Among the various approaches to separate CO<sub>2</sub> from flue gas, the absorption-based CO<sub>2</sub> capture technology is known to be the most practical method due to its technical maturity and large capacity for treating large gas volumes [4-6]. The ability to retrofit to existing power plants is also a strength of liquid absorbent-based PCC technologies.

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Amines have numerous advantages, such as high reaction rates with CO<sub>2</sub>, satisfactory absorption capacity and a reasonable price [7, 8]. Nonetheless, the high regeneration energy, corrosiveness and degradation resulting in the loss of amine and potential to form harmful chemicals are major drawbacks of amine solvents [3, 6, 9, 10]. Owing to the degradation process, SO<sub>2</sub> and NO<sub>x</sub> must be removed from feed gas prior to CO<sub>2</sub> absorption. Furthermore, the amine-based installations may pose environmental risks due to nitrosamine formation [6, 11, 12].

Aqueous ammonia is an alternative CO<sub>2</sub> capture solvent that has many advantages. Aqueous ammonia features low regeneration temperature (and thus low regeneration energy), low corrosion rates of the plant equipment, higher absorption capacity than MEA, low cost and resistance to degradation in the presence of oxygen and sulfur oxides [13-15]. Additionally, ammonia can also be used to produce value-added products such as ammonium sulfate and ammonium nitrate, which can be used as fertiliser [16]. However, slower kinetics than amine solutions and high volatility are the two main demerits of ammonia solvent [17].

In the past few years, researchers have investigated ammonia as a promising solvent for CO<sub>2</sub> capture, from bench to pilot plant scale. Alstom in 2006 developed a chilled ammonia process (CAP) in which CO<sub>2</sub> is absorbed in a highly concentrated ammonia solution (25-28 wt%) at low temperatures (0-10°C) [18] as well as a wide variety of industrial applications. Initial tests conducted at the We Energies Pleasant Prairie Power Plant indicate that CAP can absorb CO<sub>2</sub> using regenerated ionic solution on a continuous basis. The We Energies facility is designed to capture over 35 tonnes/day of CO<sub>2</sub> at design rates. The facility was engineered, installed, and is being operated as a co-operative effort between Alstom (the process supplier). The CAP technology was tested at field pilots that were designed and installed at the We Energies Power Plant in Pleasant Prairie (USA) and the E.ON Karlshamn power plant in Sweden. The first product validation facility was installed at the AEP Mountaineer Power Plant in New Haven, USA (capacity 0.1 Mt CO<sub>2</sub>/year) [19]. In addition, the largest facility for testing the CAP was commissioned in 2012 at the Technology Centre Mongstad (TCM) in Norway [20].

Australia's Commonwealth Scientific and Industrial Research Organisation (CSIRO) with Delta Electricity have tested the PCCC process in a pilot plant at the Munmorah Black Coal-Fired Power Station [13], [21]. They used 2-6 wt% NH<sub>3</sub> as a solvent and regeneration took place at 90-150°C and pressure 300-850 kPa<sub>a</sub>.

Powerspan has been developing a CO<sub>2</sub> capture process using ammonia liquor, known as the ECO<sub>2</sub> process. It can be combined with a desulfurization process – ECO-SO<sub>2</sub>, by utilizing the reaction of ammonia with sulfur oxides to produce ammonium sulfate. Pilot tests were carried out at First Energy's R.E. Burger Plant in USA [16]. Scientists from RIST (Research Institute

of Industrial Science and Technology) demonstrated an ammonia-based carbon dioxide capture process to remove CO<sub>2</sub> from blast furnace gas (about 20% CO<sub>2</sub>). They conducted experimental tests at a pilot plant facility with a gas-treating capacity of 1000 m<sup>3</sup>/h at the POSCO-Pohang Works, South Korea [22]. They found that aqueous ammonia (5-7 wt%) can be used for CO<sub>2</sub> capture and successfully regenerated using waste heat.

Absorption using ammonia has been recognized as a mature technology in the gas industry for treating acid gases such as CO<sub>2</sub>, SO<sub>x</sub>, etc. However, one of the major remaining issues of aqueous ammonia-based CO<sub>2</sub> capture technology is ammonia slip. This phenomenon poses serious environmental risks. Moreover, excessive loss of ammonia would also impart a significant cost on the PCC process. For the amine-based carbon dioxide capture process, typical NH<sub>3</sub> emissions are in the range of 5-500 mg/m<sup>3</sup> [23, 24]. In the ammonia-based plant, ammonia slip in the absorber overhead can be higher than 1500 mg/m<sup>3</sup> [25]. Therefore, water and acid wash towers are required to remove ammonia from the vent gas of the absorber. Moreover, additives limiting ammonia evaporation (by reducing ammonia vapour pressure) are receiving increasing attention. Organic additives containing hydroxyl groups have been found to be effective candidates for the suppression of ammonia loss by intermolecular interactions between the additive and ammonia via hydrogen bonding [26, 27]. Although the complexation of ammonia by metal ions (Cu, Zn, Ni) has been reported for the effective suppression of ammonia loss, it also reduced reactivity toward CO<sub>2</sub> [28].

Ammonia is used in the Solvay Process for brine ammoniation, which consists of bubbling gaseous ammonia through concentrated brine. In the next step in the Solvay process, CO<sub>2</sub> from the lime kiln bubbles up through the ammoniated brine and as a result sodium bicarbonate precipitates out of the solution. Ammonia causes a pH change of the solution to basic and facilitates the formation of sodium bicarbonate, which is filtered out from the solution. Then the solution (mainly containing NH<sub>4</sub>Cl) is heated with calcium hydroxide (slaked lime) in ammonia recovery towers to form ammonia and calcium chloride (byproduct). Thus ammonia is recycled back to the process.

It was considered that reclaimed ammonia could be used to capture CO<sub>2</sub> from residual gas streams of the Solvay Process [29]. Nevertheless, the high volatility of ammonia causes operating issues. Ammonia vapor can be present in the CO<sub>2</sub> product stream and may form a precipitate (mainly ammonium bicarbonate) in the condenser and reflux line, causing flow resistance or even shutting down the entire plant [13]. Therefore, the results of experimental research on ammonia emission and CO<sub>2</sub> capture efficiency is so significant.

This paper presents the CO<sub>2</sub> capture efficiency of an aqueous ammonia solution. Ammonia solution (hereafter: ammonia solvent or aqueous ammonia) was

withdrawn from the ammonia recovery tower of the Solvay process. The effect of process parameters on ammonia emission from the absorption column were studied using a laboratory unit for CO<sub>2</sub> capture. During the research, the following parameters have been investigated: ammonia concentration, absorber pressure and both solvent and gas flow rates (expressed as L/G ratio). Additionally, a simple volumetric method for CO<sub>2</sub> determination in ammonia samples was described. The presented research was carried out in Poland in the Institute for Chemical Processing of Coal.

## Experimental Procedures

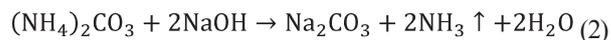
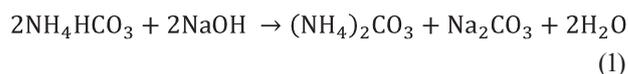
### Materials and Methods

Aqueous ammonia was supplied by CIECH Soda Polska S.A. This solution contained ammonia and ammonia-CO<sub>2</sub> salts (mainly ammonium carbamate and bicarbonate) dissolved in water. The total ammonia concentration in the supplied solution was 11.25 wt% and was determined by acid-base titration. To prepare various concentration of the solvent (6.5%, 8.0 and 10%), the 11.25% aqueous ammonia solution was diluted with distilled water in proper proportion. The CO<sub>2</sub> content in the solution was 0.296-301 mole of CO<sub>2</sub> per mole of ammonia and was determined by the volumetric method described in the chemical analysis section. The carbon dioxide (purity 4.0) was delivered by Linde Gaz Polska Sp. z o.o.

The concentrated sulfuric acid, hydrochloric acid, sodium hydroxide and barium chloride dihydrate (all pure for analysis) were supplied by Avantor Performance Materials Poland S.A. The solutions of these chemicals were prepared by dilution with distilled water. Additionally, the solutions used in chemical analysis (i.e., NaOH, HCl, BaCl<sub>2</sub>) were prepared just before the experiment, and additionally distilled water was degassed by boiling.

### Chemical Analysis

To determine the CO<sub>2</sub> content in the liquid sample (in other words, CO<sub>2</sub> loading), a novel volumetric analysis was employed (hereinafter: sodium carbonate method). It consists in the reaction of CO<sub>2</sub>-ammonia salts with strong base (i.e., sodium hydroxide) used in excess. As a result, a gaseous ammonia is released and sodium carbonate is formed, according to the reactions (1)-(3). Thereafter, sodium carbonate in the presence of sodium hydroxide is analyzed by titration with standard strong acid. Determining sodium hydroxide and carbonate in a mixed solution is known as Warder's method [30, 31]. To the best of our knowledge, an approach of converting the CO<sub>2</sub>-ammonia salts to sodium carbonate in aqueous ammonia samples in order to determine CO<sub>2</sub> loading has not been previously described.



The procedure of analysis was as follows: 1 cm<sup>3</sup> of analyzed sample was placed in a conical flask and 20 cm<sup>3</sup> of 0.15M NaOH and 50 cm<sup>3</sup> of distilled water were added immediately. Then the solution was boiled for approx. 10 minutes in order to remove all ammonia from the sample (this can be indicated using Nessler's reagent or indicator paper). Thereafter, the solution was cooled down in an ice bath and 50 cm<sup>3</sup> of distilled water and phenolphthalein as an indicator were added. In the next step, the solution was titrated against standardized HCl until the solution lost its pink color, which corresponds to the first end point of titration, i.e., about 8.3 pH (reactions (4)-(5)). During titration, the solution was mixed gently to avoid a local excess of hydrochloric acid.



Afterward, orange methyl was added to the solution, which was subsequently titrated with HCl until color change, in consonance with the second end point of titration (reaction (6)). The pH-meter WTW 3310 was used in addition to the indicators in order to precisely detect the end points of titration. The pH meter was calibrated before measurements according to the manufacturer's guidelines. The total amount of CO<sub>2</sub> (mole of CO<sub>2</sub>/dm<sup>3</sup> of solution) was calculated using the following equation (7):

$$\text{CO}_2 = \frac{C_t(V_2 - V_1)}{V_{pr}} \quad (7)$$

where  $V_{pr}$  is volume of sample (cm<sup>3</sup>),  $C_t$  is concentration of titrant (mol/dm<sup>3</sup>), and  $V_1$  and  $V_2$  are titrant volume at the first and second end points of titration, respectively.

In addition, for each analysis the blank probe result was taken into consideration. For comparison, the CO<sub>2</sub> content in the solvent was verified by the "BaCl<sub>2</sub> method" [32], which is based on a reaction of CO<sub>2</sub> with barium chloride in alkaline solution, which leads to barium carbonate precipitation. Then, barium carbonate is filtered out of the solution and determined by gravimetric analysis or back titration. The amount of barium carbonate corresponds to CO<sub>2</sub> dissolved in the solvent. For verification purposes,

Table 1. Verification of the sodium-carbonate method used for CO<sub>2</sub> loading analysis.

| CO <sub>2</sub> loading, mole of CO <sub>2</sub> /mole of NH <sub>3</sub> |                            |                         |
|---|----------------------------|-------------------------|
| Standard solution   | BaCl <sub>2</sub> analysis | Sodium carbonate method |
| 0.412   | 0.382                      | 0.382                   |
|   | 0.392                      | 0.382                   |
|   | 0.396                      | 0.389                   |
|   | 0.394                      | 0.383                   |
|   | 0.393                      | 0.382                   |
| Mean  | 0.391                      | 0.384                   |
| RSD %   | 1.395                      | 0.795                   |
| Stand. dev.   | 0.005                      | 0.003                   |

analysis was performed five times. Additionally, to estimate an accuracy of the sodium carbonate method, the CO<sub>2</sub> content of a standard sample (i.e., containing a known quantity of CO<sub>2</sub>) was determined. The standard solution was prepared by saturation ammonia liquor (of known NH<sub>3</sub> concentration) with pure CO<sub>2</sub> in a special glass reactor used to study the absorption capacity of amine solvents [8, 33]. The results are summarized in Table 1.

It can be seen that the sodium carbonate method seems to be more precise than the BaCl<sub>2</sub> method, although the former is not as accurate as the latter. The presented discrepancies between the standard CO<sub>2</sub> loading and the measured values could result from CO<sub>2</sub> losses during titration [30-31]. Errors occurring in the BaCl<sub>2</sub> method could be related to the low solubility of barium carbonate in ammonium chloride solution (formed during displacement reaction between barium chloride and ammonium carbonate). Nonetheless, in contrast to the BaCl<sub>2</sub> method, the proposed analysis technique is simple and comparatively quite fast (two titrations in one flask without filtering out the precipitate). Furthermore, toxic barium salts are not employed. As a part of these studies, other volumetric analyses also have been carried out [34-35]. These analyses included titration of the sample with standard HCl in the presence of two indicators as well as with an addition of barium chloride. Nevertheless, the results of these analyses were not satisfactory (approx. 16% relative errors). Moreover, authors of the paper [35] stated that the solution color change during titration is feeble when determining ammonium bicarbonate and ammonium carbonate. The reason for this could be the presence of mixed salts (carbamate and bicarbamate) in connection to low solubility of barium carbonate in ammonium chloride solution and a high concentration of free ammonia. Additionally, the high volatility of the solvent resulting in pH fluctuation could also be a cause of the errors.

## Laboratory Unit and Ammonia Emission Measurement

To study ammonia emissions from the CO<sub>2</sub> capture process we utilized a special laboratory unit. The primary element of the unit was an absorber containing a packed bed of 700CY packing (height 1.5 m, diameter 0.1 m, material: stainless steel 316 grade, surface area: 700 m<sup>2</sup>/m<sup>3</sup>, void fraction 85%). Furthermore, auxiliary equipment such as a blower, solvent pump, tanks and flowmeters were used. Nevertheless, it should be noted that neither demister nor other devices for reducing emission from the column have been applied. Additionally, the laboratory unit has been equipped with approximately 15 measuring points and controlled by a supervisory control and data acquisition system (SCADA). The gas and solvent flow rate were monitored by Intergaz and Tecfluid M21 flowmeters, respectively. The temperature and the pressure system were controlled by Limatherm PT-100 sensors and pressure transducers from Wika, respectively. The CO<sub>2</sub> volume fraction both at the gas inlet and outlet was measured by a Siemens Ultramat 23 gas analyzer (with NDIR technology; the absorber used in this laboratory unit was used in previous research and more technical details can be found in [36]).

Since ammonia is volatile, it evaporates and is carried over by the gas stream that flows upward through the absorber and thus is present in vent gas (purified gas). To estimate the ammonia emission from the absorber, the vent gas was collected using an impinger sampling technique (Fig. 1). The first impinger was filled with glass Raschig rings in order to separate entrained droplets. Two further impingers contained 10% sulfuric acid and the last one was filled with desiccant to protect the downstream rotameter from moisture. All impingers were immersed in a cold bath during the experiments. The impinger train was located upstream of the back pressure regulator. The inlet gas flow rate was maintained at approx. 140 dm<sup>3</sup>/h by means of a rotameter. Furthermore, it is important to note that the small diameter of gas pipelines precluded an isokinetic sampling.

The collection efficiency of the impingers was tested before the first measurement and the result showed more than 95% capture efficiency (meaning that more than

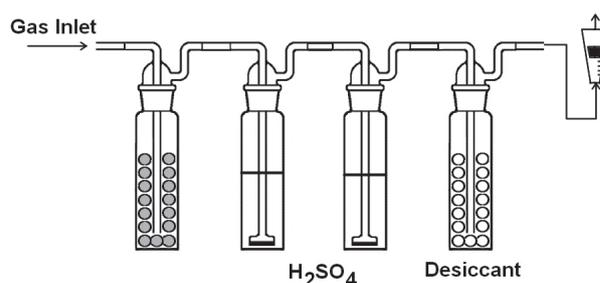


Fig. 1. Impingers used in ammonia emission measurement.

95% of ammonia from the gas stream was absorbed in the impingers). To determine the amount of absorbed ammonia, sulfuric acid withdrawn from the impingers was titrated against a standard NaOH solution [31]. Since the volume of gas that passed through the impingers was known, the ammonia content in the vent gas was calculated as follows:

$$E_A = \frac{M_A n_A}{V_r \cdot t} \tag{8}$$

where  $E_A$  is ammonia emission ( $\text{g}/\text{m}^3$ ); at STP (standard temperature and pressure, 273.15 K and 100 kPa)  $M_A$  is molar mass of ammonia (17,01 g/mol),  $n_A$  is moles of ammonia absorbed in sulfuric acid (considering that 2 moles of NaOH titrant reacts with 1 mole of sulfuric acid),  $V_r$  is volume flow rate of gas at STP ( $\text{m}^3/\text{s}$ ), and  $t$  is time of gas flow through impinger(s).

The volume flow rate of a gas at STP was calculated using following formula:

$$V_r = V_g + \frac{273.15K}{T_g} \cdot \frac{p_g}{100kPa} \tag{9}$$

where  $V_g$ ,  $T_g$  and  $p_g$  are volume flow rate, temperature and pressure of the gas passed through impingers, respectively. The emission for each changed parameter was measured three times and the mean value was calculated.

### Process Flow Description

The feed gas was directed to the absorber by a blower. The inlet gas mixture was prepared from ambient air and carbon dioxide. During all the tests, carbon dioxide content in a feed gas was maintained at 10.30 vol% ( $\pm 0.2$  vol%) using a Bronkhorst EL-FLOW gas mass flow controller. To simplify the experiment, ambient air instead of nitrogen was used. The gas flowed up through the absorber and reacted with aqueous ammonia trickling downward in the column. The aqueous ammonia was pumped to the absorber from an ammonia lean solvent tank by a gear pump. As a result of chemical reaction, carbon dioxide was removed from the feed gas and the treated gas left from the absorber top. Column pressure was maintained via a pressure control loop that regulated a control valve on the treated gas stream. Solvent with the absorbed  $\text{CO}_2$  (rich ammonia) was pumped to the ammonia-rich solvent tank.

Solvent directed to the absorber was defined as a lean solvent, because it contained a small amount of  $\text{CO}_2$  and corresponds to the solution withdrawn from the desorber in a typical ammonia gas treating process. The process schematic of the laboratory unit used in this research is shown in Fig. 2. The most important process parameters are given in Table 2.

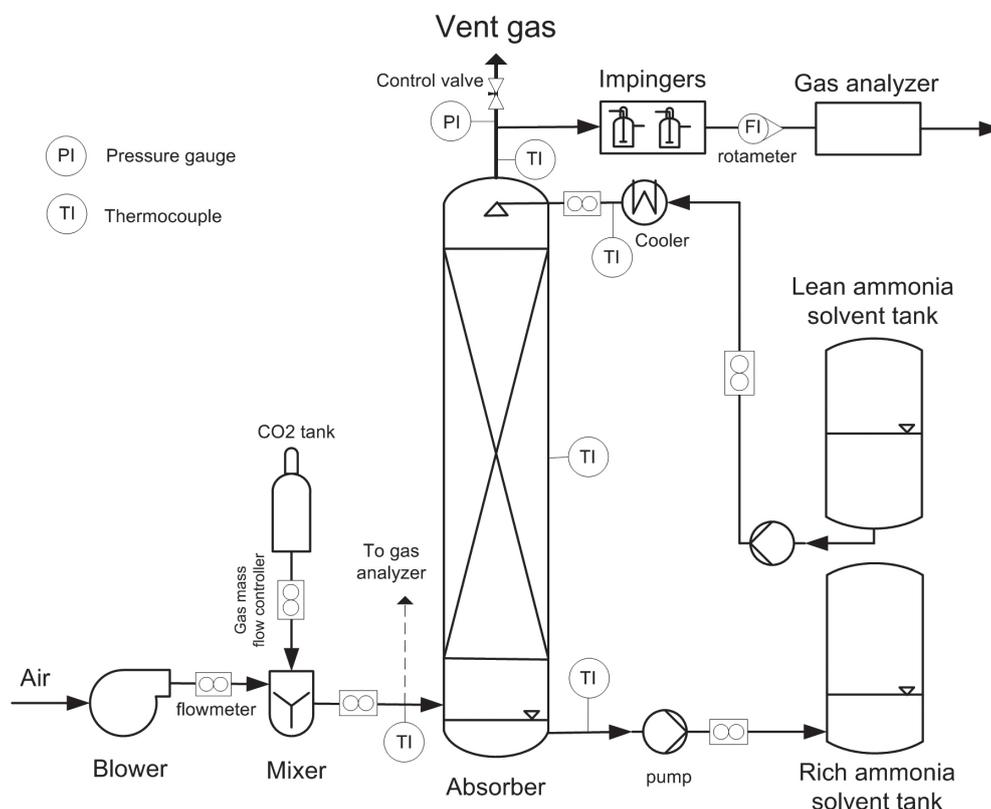


Fig. 2. Overall schematic of the laboratory unit used in investigated studies.

Table 2. Process parameters of laboratory unit used for CO<sub>2</sub> capture in the studies.

| Parameter                                     | Value  |
|---|--|
| CO <sub>2</sub> flow rate                     | 0.2-0.3 m <sup>3</sup> /h                              |
| Feed gas (inlet gas) flow rate                | 1.5-2.5 m <sup>3</sup> /h                              |
| CO <sub>2</sub> concentration in the feed gas | 10.20-10.58 vol%.                                      |
| Temperature of the feed gas                   | 17-22°C  |
| Pressure in the absorber                      | 1.2 - 1.3 bar <sub>a</sub>                             |
| Solvent flow rate                             | 10-40 dm <sup>3</sup> /h                               |
| Temperature of the ammonia lean solvent       | 20-23°C  |
| Temperature in the absorber                   | 21-27°C  |
| Temperature of the treated gas                | 22-24°C  |
| Concentration of ammonia                      | 6.5-11.25 wt%  |
| The CO <sub>2</sub> loading of lean solvent   | 0.296-0.301 mole CO <sub>2</sub> /mole NH <sub>3</sub> |
| The CO <sub>2</sub> loading of rich solvent   | 0.349-0.442 mole CO <sub>2</sub> /mole NH <sub>3</sub> |

## Results and Discussion

This chapter presents the results of conducted studies. In further description, the term “CO<sub>2</sub> removal efficiency” or “CO<sub>2</sub> recovery” signifies the amount of CO<sub>2</sub> captured from the inlet gas (calculated as removed CO<sub>2</sub> divided by inlet CO<sub>2</sub> and multiplied by 100%).

The effect of the L/G ratio on ammonia emission and CO<sub>2</sub> recovery is shown in Fig. 3. During the tests, the solvent flow rate was changed from 10 to 40 dm<sup>3</sup>/h while the feed gas flow rate was maintained in the range of 2.1-2.3 m<sup>3</sup>/h (hereafter, the base flow). However, in three cases (indicated as triangle points in Fig. 3), the inlet gas flow rate was changed at constant solvent flow rate (30dm<sup>3</sup>/h). In those tests, the gas flow rates were 2.716, 2.589, and 1.747 m<sup>3</sup>/h respectively. As aforementioned (in section 2.4), in all cases, the volume percent of CO<sub>2</sub> in a feed gas was kept at constant level. The concentration of ammonia in the solvent was 8.0%.

The effect of L/G ratio on ammonia emissions is shown in Fig. 3. As can be seen, with increasing L/G ratio the ammonia emission varies from 14 to 27 mg/dm<sup>3</sup>. However, above an L/G ratio of 10 kg/kg the emission seems to level off. At the same time, the CO<sub>2</sub> recovery rises significantly at an increase in L/G ratio from 3 to 6 kg/kg, and then rises slightly at higher L/G ratio. Finally, the CO<sub>2</sub> removal efficiency levels off due to absorption equilibrium and approx. 95% of CO<sub>2</sub> is captured.

An increase in ammonia emission with L/G ratio is related to liquid holdup. A growth in L/G ratio causes a rise in liquid holdup, when there is more liquid retained in the packing. Thereby, the surface of liquid

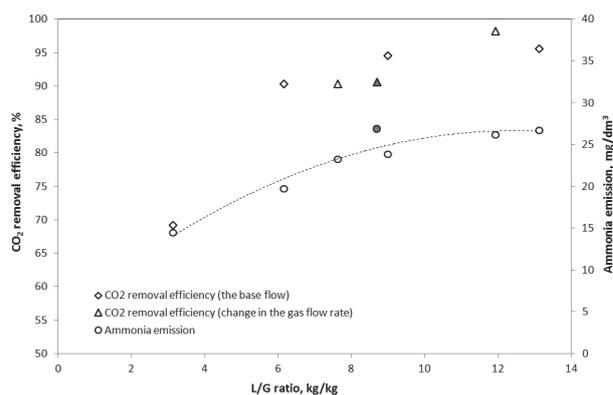


Fig. 3. The CO<sub>2</sub> removal efficiency and ammonia emission as a function of L/G ratio. Dotted line (polynomial regression of ammonia emission) is for the clarity of the plot. Filled figures stand for a decrease in the absorber pressure.

is greater and ammonia evaporates faster. However, this increasing surface approaches the maximum level and thus the measured emission levels off. Additionally, the gas passing through the packing intensifies the ammonia evaporation and liquid entrainment process. It can be observed in Fig. 3, when the gas flow rate was increased at a given solvent flow rate (two triangle points at L/G ratio of 7.6 and 11.9 kg/kg). At higher gas flow rate (2.716 m<sup>3</sup>/h) the ammonia emission was 23.2 mg/dm<sup>3</sup> and at a lower gas flow rate (1.747 m<sup>3</sup>/h) the emission was 26.2 mg/dm<sup>3</sup>. Although it seems that increasing gas flow rate decreases NH<sub>3</sub> emissions, in point of fact the effect is reversed. It must be emphasized that in this paper emission is defined as the amount of ammonia emitted per volume of the cleaned gas. Therefore, a higher feed gas flow rate results in higher total NH<sub>3</sub> emissions (i.e., the amount of released ammonia per hour).

A growth in CO<sub>2</sub> capture with increasing L/G (at constant feed gas flow) results from a greater amount of solvent entering the absorber in proportion to the CO<sub>2</sub> stream. The higher the amount of solvent entering the absorber, the more CO<sub>2</sub> from the inlet gas stream that can be removed, up to CO<sub>2</sub> absorption equilibrium. In other words, an increase in the L/G ratio means that more solvent is available for CO<sub>2</sub> capture.

In the investigated studies, at base gas flow, the maximum CO<sub>2</sub> capture was 95.6% (L/G = 13.1 kg/kg). Nonetheless, in order to investigate ammonia emission, the base gas flow was varied. When the feed gas flow rate was changed, whereas the solvent flow rate remained constant, the obtained results slightly deviate from the observed CO<sub>2</sub> recovery trend, as seen in Fig. 3. As a consequence, a lower gas flow rate (1.747 m<sup>3</sup>/h) results in 98% CO<sub>2</sub> capture at L/G 11.9 kg/kg. The CO<sub>2</sub> capture was more efficient than predicted by the trend, because a lower amount of CO<sub>2</sub> entered the absorber. In turn, for greater gas flow rate (2.716 m<sup>3</sup>/h) the response is reverse (90.3% CO<sub>2</sub> capture).

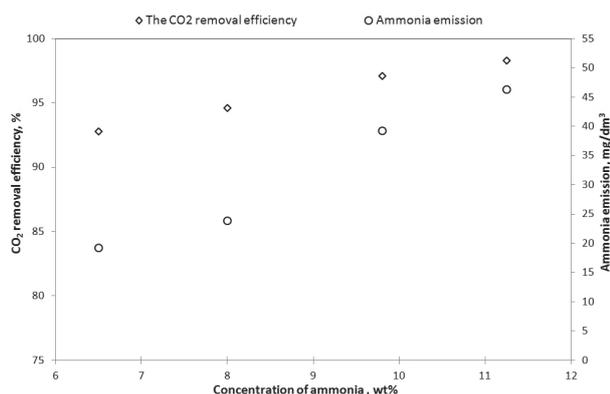


Fig. 4. The CO<sub>2</sub> removal efficiency and ammonia emission depending on ammonia concentration.

In one case, in order to investigate the effect of absorber pressure on ammonia emission, the former was decreased to 120 kPa (absolute). The results of this experiment are indicated as a grey circle and a grey triangle in Fig. 3. As can be seen from the plot, a drop in the absorber pressure causes a slight increase in ammonia emission (from 23.8 to 26.9 mg/dm<sup>3</sup>). A lower pressure facilitates the evaporation of ammonia from the solvent. For this reason, ammonia emission is higher.

The effect of ammonia concentration on NH<sub>3</sub> escape and CO<sub>2</sub> capture is presented in Fig. 4. The NH<sub>3</sub> concentration in the solvent was varied from 6.5 to 11.25%. The maximum concentration corresponds to undiluted aqueous ammonia drawn from the Solvay Process.

As expected, the ammonia emission grows with NH<sub>3</sub> concentration. Increasing the solvent concentration from 6.5 to 11.25% causes NH<sub>3</sub> emissions to increase from 19 to 46 mg/dm<sup>3</sup>. The more ammonia in the solution, the higher the ammonia partial pressure. Thus, the vapor of the solvent contains more ammonia which, in turn, is carried over by the gas passing through the absorber. In consequence, ammonia escapes into the atmosphere along with cleaned gas. What can also be observed, CO<sub>2</sub> removal increases from 92.8% to 98.3% with the ammonia concentration. Due to a higher concentration of ammonia, the solvent can absorb more CO<sub>2</sub>. Additionally, increasing ammonia concentration increases reaction rate with CO<sub>2</sub>.

## Conclusions

During the research, laboratory studies on ammonia emissions and CO<sub>2</sub> recovery using aqueous ammonia from the Solvay Process were carried out. It was demonstrated that increasing solvent and gas flow rates results in a growth in ammonia emissions from the absorber. The ammonia emission depends on L/G ratio and was in the range 14-27 mg/dm<sup>3</sup>. Furthermore, an increase in ammonia emissions from 19 mg/dm<sup>3</sup> to

46 mg/dm<sup>3</sup> was caused by increasing the concentration of ammonia in the solvent from 6.5% to 11.25%, respectively. An increase in feed gas flow rate intensifies the liquid entrainment process. Additionally, the gas passing through the column is saturated by ammonia vapor and thus a growth in the gas flow rate enhances the ammonia escape. Furthermore, the liquid flow rate is related to the amount of solvent retained in the packing of the column. The liquid distribution provides a large surface area for chemical reaction to occur in the absorber. It was examined that increasing liquid flow rate causes a growth of NH<sub>3</sub> concentration in the vent gas of the absorber.

Although obtained results show that ammonia emission is high, it is important to note that no devices for reducing vapor and droplets in the exhaust gas were utilized. Furthermore, gas sampling was not isokinetic. It is assumed that at the pilot scale the emissions will be comparatively lower (than at lab scale) because of the use of ammonia emission abatement systems. Therefore, the outcomes of the pilot plant research are desirable.

Appropriate liquid-to-gas flow ratio could contribute to reduced NH<sub>3</sub> emissions, whereby CO<sub>2</sub> removal efficiency is kept at a high level. We also discovered that aqueous ammonia solution drawn from the Solvay Process is an effective solvent for CO<sub>2</sub> capture. Research conducted using a laboratory-scale absorber to investigate the CO<sub>2</sub> capture process (capacity 5m<sup>3</sup>/h of feed gas) has shown that more than 95% of the inlet CO<sub>2</sub> was captured.

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## Conflict of Interest

The authors declare no conflict of interest.

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