

WOJCIECH M. BUDZIANOWSKI*

CO₂ REACTIVE ABSORPTION FROM FLUE GASES INTO AQUEOUS AMMONIA SOLUTIONS: THE NH₃ SLIPPAGE EFFECT

Future deployment of NH₃-based CO₂ capture technology into coal-fired power plants will shift unwanted emissions from those currently comprising SO₂, NO_x and particulate matter towards those comprising NH₃. This is due to volatility of ammonia. Therefore, the current paper aims at understanding of NH₃ slippage to flue gases from the NH₃-based CO₂ capture process and at identifying the opportunities to limit this unwanted slippage. The paper presents experimental and 2D modelling-based analysis of CO₂ reactive absorption from flue gases into aqueous ammonia solutions in a falling film reactor. The results enable one to characterise hydrodynamics of the falling film reactor, to analyse the effect of pH, pressure and temperature on CO₂ absorption and NH₃ slippage and to explain the role of migrative transport of ionic species in total mass transport. It was found that NH₃ slippage to the gaseous phase can be limited by alleviated operating temperatures, optimised pH, increased pressure and large CO₂ absorption fluxes which force negative enhancement of NH₃ mass transfer [16]. The NH₃ slippage under CO₂ capture conditions and under air stripping conditions is illustrated by experimental and simulation data. Finally, main approaches used for the integration of CCS systems into power plants are expounded.

1. INTRODUCTION

Recent atmospheric observations confirm that the concentration of CO₂ in the atmosphere has increased by nearly 30% for the last 150 years, with an accelerating trend in last years. The global mean concentration of CO₂ in 2005 was 379 ppm, leading to a radiative forcing of 1.66 W·mol⁻². For the 1995–2005 decade, the growth rate of CO₂ in the atmosphere was 1.9 ppm·yr⁻¹ and the CO₂ radiative forcing increased by 20%: this is the largest increase observed for any decade in at least the last 200 years. From 1999 to 2005, global CO₂ anthropogenic emissions from fossil fuel and cement production increased at the rate of roughly 3% by year [1].

*Faculty of Chemistry, Division of Chemical and Biochemical Processes, Wrocław University of Technology, Wybrzeże Wyspiańskiego 27, Wrocław, Poland, e-mail: wojciech.budzianowski@pwr.wroc.pl

There are two major carbon reservoirs which comprise 99.90% of the total Earth's carbon, i.e. carbon rocks (limestone, chalk, dolomite) and organic-rich rocks (coal, oil, natural gas) [2]. Both those reservoirs are intensively exploited, e.g. in cement and energy production, respectively; leading to large anthropogenic emissions of CO₂ into the atmosphere. At the same time, Earth's plant-covered areas are severely limited due to the civilisation development and thus the remaining plants are unable to recycle all the emitted carbon back to organic-rich rocks or at least into the soil. Also, it must be noted that carbon rocks formation in deep oceans is a very slow process which requires absorption of atmospheric CO₂ into oceans. When Earth's temperature rises, the CO₂ solubility in water alleviates, which limits the role of oceanic CO₂ sink and can even the release of some CO₂ dissolved in oceans amplifying the initial global warming.

Therefore, it can be concluded that recent human activities such as uncontrolled exploitation of natural carbon reservoirs and reduction in atmospheric CO₂ recycle potentials by plants and oceans can contribute to net anthropogenic CO₂ emissions as it is clearly evidenced by recent atmospheric measurements [1]. CO₂ is the final product of numerous human activities which in large quantities accumulates in the atmosphere causing dangerous climate changes.

Consequently, urgent deployment of renewable and nuclear energy technologies is needed, while CO₂-intensive power plants must be integrated with carbon capture and sequestration (CCS). Therefore, the current paper provides modelling analysis of CO₂ separation from flue gases by using aqueous ammonia solutions in a falling film reactor. The study investigates complex phenomena of mass transfer, chemical reactions, electrochemistry and hydrodynamics in very simple but offering realistic operating conditions reactor geometry. Results of the simulation and experiments illustrate the problem of NH₃ slippage to the gaseous phase and discuss opportunities to limit this unwanted slippage.

2. MODELLING OF CO₂ ABSORPTION INTO AQUEOUS AMMONIA SOLUTIONS

Absorption of CO₂ into aqueous ammonia solutions has attracted attention as a potential CCS method for power plants relatively recently [3].

2.1. REACTION KINETICS AND THERMODYNAMICS

The most important liquid phase elementary chemical reactions in the CO₂-NH₃-H₂O system are presented in Table 1.

Table 1

Elementary chemical reactions in the CO₂-NH₃-H₂O system

Equation	Process	No.
$\text{CO}_2 + \text{NH}_3 \longleftrightarrow \text{NH}_2\text{COO}^- + \text{H}^+$	formation of ammonia carbamate	(1)
$\text{CO}_2 + \text{OH}^- \longleftrightarrow \text{HCO}_3^-$	formation of bicarbonate by combination of CO ₂ with hydroxyl ions	(2)
$\text{HCO}_3^- \longleftrightarrow \text{CO}_3^{2-} + \text{H}^+$	formation of carbonate	(3)
$\text{NH}_3 + \text{H}_2\text{O} \longleftrightarrow \text{NH}_4^+ + \text{OH}^-$	hydrolysis of ammonia	(4)
$\text{H}_2\text{O} \longleftrightarrow \text{OH}^- + \text{H}^+$	dissociation of water	(5)

Equations for reaction rates are summarised in Table 2.

Table 2

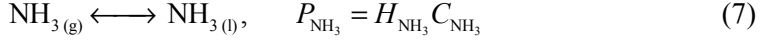
Rates of elementary reactions from Eqs. (1)–(5)

No.	Kinetics	Source
(1)	$R_{(1)} = 1.66 \cdot 10^{11} \exp\left(\frac{-61000}{R^G T}\right) C_{\text{CO}_2} C_{\text{NH}_3}$	[4]
(2)	$R_{(2)} = 4.32 \cdot 10^{10} \exp\left(\frac{-55420}{R^G T}\right) C_{\text{CO}_2} C_{\text{OH}^-}$	[5, 6]
(3)–(5)	instantaneous reactions	[7]

CO₂ absorbed in ammonia solutions forms ammonia carbamate being a dominant species at low CO₂ loadings and in presence of excess NH₃. For higher CO₂ concentrations and hence for lower free ammonia concentrations, the equilibria of ammonia carbamate are shifted to favour bicarbonate formation. This shift allows higher CO₂ loadings to be achieved in NH₃-based systems compared with MEA-based systems where CO₂ remains predominantly as a carbamate. Such observations have been confirmed by Mani et al. [8] based on ¹³C NMR spectroscopy. However, the equilibria shifting towards bicarbonate requires higher pH in order to have higher concentrations of hydroxyl ions which promote bicarbonate formation (Eq. (2)). Carbamate formation is accompanied by H⁺ generation which lowers pH and favouring hydrolysis of free ammonia. When free ammonia is completely hydrolysed pH decreases and bicarbonate formation may stop due to relevant equilibria shifting.

Modelling of reversibility of reactions (1)–(5) is based on reaction equilibrium constants [7]. The rate of physical dissolution of gaseous CO₂, NH₃, and H₂O in aqueous solutions is relatively high. Therefore, equilibrium at the interface can be assumed. For CO₂ and NH₃ the Henry's law may be introduced:

$$\text{CO}_{2(g)} \longleftrightarrow \text{CO}_{2(l)}, \quad P_{\text{CO}_2} = H_{\text{CO}_2} C_{\text{CO}_2} \quad (6)$$



2.2. GOVERNING EQUATIONS

CO₂ reactive absorption into a NH₃-H₂O electrolyte solution in a falling film reactor is described by using 2D modelling. A simplified 2D model includes reaction kinetics, chemical reaction equilibria, interphase equilibria, diffusion of species and convection, following modern process modelling directions outlined in [9]. The governing equations of the model in a liquid phase are:

$$D_i \frac{\partial^2 C_i(x, z)}{\partial x^2} - w_z(z) \frac{\partial C_i(x, z)}{\partial z} = - \sum_{r=1}^{r=NR} R_r(C_i) \quad (8)$$

- boundary conditions:

$$C_i(x, 0) = C_i^{IN} \quad (9)$$

$$-D_i \frac{\partial C_i(\delta, z)}{\partial x} = 0 \quad (10)$$

- volatile species:

$$-D_i \frac{\partial C_i(0, z)}{\partial x} = k_i^{GP} (P_i - H_i C_i) \quad (11)$$

- non-volatile species:

$$-D_i \frac{\partial C_i(0, z)}{\partial x} = 0 \quad (12)$$

Further, in order to enable an in-depth analysis of electrochemical engineering aspects a more detailed 2D axis-symmetric model is formulated. This model can describe migration of ionic species in a liquid phase. It also includes mass and momentum balance for the gaseous phase domain and hence it does not require mass transfer coefficients at the gas side. Main electrochemical aspects in the liquid phase arise from the mass and charge balance:

$$\nabla \cdot (D_i \nabla C_i - w C_i + v_i F m_i C_i \nabla \phi) = - \sum_{r=1}^{r=NR} R_r(C_i) \quad (13)$$

$$\nabla \cdot (\lambda^E \nabla \phi) = 0 \quad (14)$$

2.3. A FALLING FILM REACTOR

Falling-film reactors offer very simple geometries and well defined hydrodynamics which makes them to be well-suited for detailed kinetic studies. Besides, falling film reactors offer adjustable empty spaces and thus any crystallisation problems under highly concentrated and low temperature operating conditions can be limited. Furthermore, CO₂ separation processes under industrially relevant short contact times conditions usually do not approach equilibrium conditions due to limited reaction and mass transport rates. Hence reaction and mass transfer kinetics-oriented studies are of primary importance for detailed design of such gas–liquid reactors [10]. Figure 1 illustrates a falling film reactor utilised here for CO₂ separation from flue gases by aqueous ammonia solutions. The falling film reactor is well suited for aforementioned kinetic studies and can be operated in practical hydrodynamic conditions.

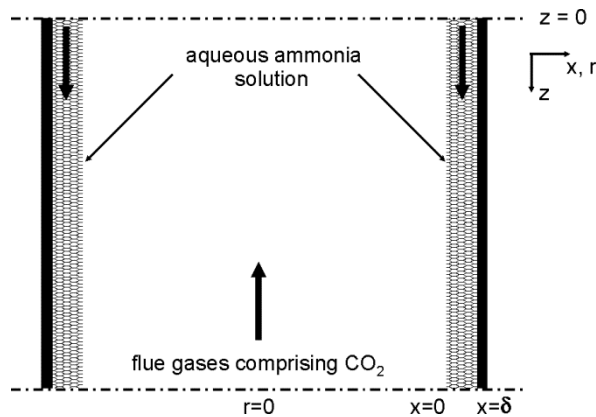


Fig. 1. Scheme of the falling film reactor

3. ANALYSIS OF THE NH₃ PROCESS

Among conventional CO₂ reactive processes, a monoethanolamine (MEA) process has been comprehensively studied and successfully used in chemical plants for CO₂ recovery. Although the MEA process is a promising method for the control of CO₂ emissions from massive discharging plants [11], it is a relatively expensive option. In addition, it has several major disadvantages including slow absorption rate, low solvent capacity, amine degradation by SO₂, NO₂, HCl, HF and O₂ from flue gases, high equipment corrosion rates, and high energy consumption during solvent regeneration (i.e. high heat of reaction compared with the CO₂-NH₃ system) [12].

In the MEA process SO₂ and NO_x must be removed prior to CO₂ absorption. This preliminary costly removal might not be necessary when an aqueous ammonia solu-

tion is used which can capture all those acidic gases simultaneously with CO_2 . The products of absorption of CO_2 , SO_2 and NO_x into aqueous ammonia solutions are ammonium bicarbonate, ammonium sulphate and ammonium nitrate, respectively, which are well known fertilizers for certain crops. Unfortunately, ammonia salts have high solubility in water. Their removal by, e.g. crystallisation followed by filtration or sedimentation, can be enhanced under the chilled NH_3 operating conditions (2–10 °C [13]) or by the addition of ethanol to aqueous ammonia solution which decreases solubility of salts [14]. Fertilisers from the NH_3 process offer great unexplored potential for cultivation of energy crops, i.e. biomass, which can tolerate fertilisers having lower quality and comprising some flue gas-derived impurities.

Further, an aqueous ammonia solvent is characterised in increased CO_2 absorption capacity of 1.2 kg CO_2 /kg NH_3 , while for MEA it is only 0.4 kg CO_2 /kg MEA. There is little effect of oxidative degradation of ammonia as it comprises no carbon chains and thus it can offer improved solvent absorption/regeneration cycling. It has been shown [15] that CO_2 absorption fluxes into ammonia can be 3 times higher than those into MEA under similar conditions. Also in [14] it has been shown that aqueous ammonia solvent has very high CO_2 removal efficiency as compared with MEA or DGA solvents under similar operating conditions. Among major drawbacks of the NH_3 process one can indicate ammonia volatility which leads to the contamination of flue gases. All available methods directed at NH_3 removal [16] from diluted gases are costly. Therefore, to avoid ammonia slippage from the NH_3 process careful attention must be paid to all process design and operation aspects.

It should be emphasised that future deployment of NH_3 -based CO_2 capture into power plants can change the composition of unwanted emissions from the energy-generating sector. Namely, CO_2 capture technologies using alkali aqueous solvents can offer simultaneous removal of SO_2 , NO_x and particulate matter (PM) thus those emissions will be reduced. However, NH_3 -based CO_2 capture technologies can lead to large increase of NH_3 emissions [17] due to ammonia volatility. Therefore, the present study focuses on the opportunities for the reduction of NH_3 emissions in NH_3 -based CO_2 capture systems. In this context, effects of ammonia volatility, falling film reactor hydrodynamics, pH, migration in electrolyte solutions, elevated pressure and temperature on the NH_3 process are analysed and discussed.

3.1. EFFECT OF AMMONIA VOLATILITY

Field tests of CO_2 capture into aqueous ammonia solutions indicate that a considerable ammonia slip to flue gases is frequently experienced under standard operating conditions. For instance Kozak et al. [18] have reported NH_3 contents in flue gases up to 2000 ppmv due to desorber instabilities, and for more stable operation the NH_3 slip has amounted up to 500 ppmv. Mathias et al. [19] have reported a smaller NH_3 slip from their absorber, i.e. 242 ppmv in flue gases. Current permissible limits in several countries allow release of flue gases comprising less than 10 ppmv NH_3 . Therefore,

when utilising the NH₃ process, one must guarantee limited ammonia vaporisation to the gaseous phase.

NH₃ slippage to the gaseous phase can be reduced to meet the required level by controlling pH of the liquid, by making use of a negative enhancement of NH₃ transfer effect and by thorough process and reactor designs. pH of the liquid can be conveniently controlled by adjusting NH₃ content in water. Further, NH₃ transfer to the gaseous phase can be negatively enhanced in situations when CO₂ absorption flux is large enough to be able to substantially lower pH at the gas–liquid interface. Under the conditions of interfacial pH shift, NH₃ slippage can be limited even under total driving forces promoting NH₃ desorption [16].

Figure 2 shows NH₃ slippage under air stripping [20] experimental conditions. It can be observed that the NH₃ removal from the liquid is proportional to the stripping air flow rate. Such dependence is associated with gas–liquid phase equilibrium attained in the investigated conditions. Therefore, it can be concluded that the air-stripping process attains gas–liquid equilibrium at the investigated operating and geometrical ranges of parameters.

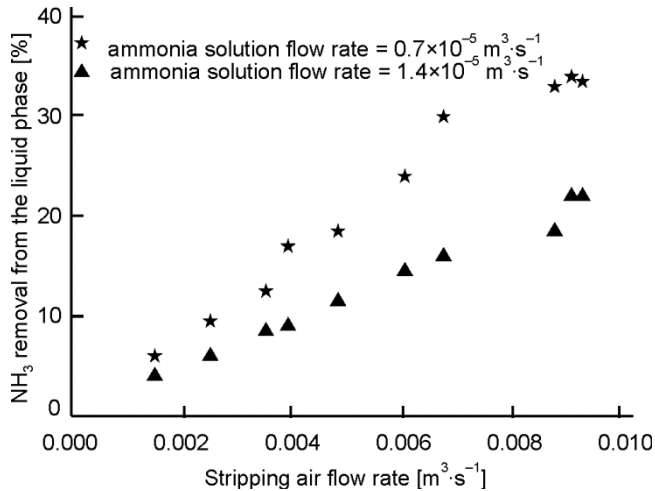


Fig. 2. NH₃ slippage under air stripping experimental conditions, the effect of air flow rate on NH₃ removal at 295 K, $P_{\text{CO}_2}^{\text{IN}} = 0$, $P_{\text{NH}_3}^{\text{IN}} = 0$, $C_{\text{CO}_2}^{\text{IN}} = 20 \text{ mol}\cdot\text{m}^{-3}$, $C_{\text{NH}_3}^{\text{IN}} = 93 \text{ mol}\cdot\text{m}^{-3}$.

Experimental data for the packed-bed counter-current stripper
with packing height of 1 m and packing diameter of
0.1 m, 15 mm ceramic Raschig rings

Under CO₂ absorption conditions the phenomenon of NH₃ slippage is more complex. Figure 3 illustrates that the liquid concentration of free (i.e. undissociated) NH₃ decreases along the falling film reactor by means of two main mechanisms, i.e. by the reaction of NH₃ with CO₂ (Eq. (1)) and by NH₃ desorption to the gas. As it is seen,

under operating conditions utilising large CO_2 absorption flux, free NH_3 is completely reacted or desorbed within around 15 cm of the falling film reactor length. For comparison, when the desorption flux is switched off in the model and thus NH_3 is consumed solely by the aforementioned reactive mechanism, the required length is considerably prolonged to around 30 cm. The contribution of the two competing NH_3 consuming mechanisms strictly depends on process operating conditions [21]. It is expected that the contribution of NH_3 slippage can be substantially reduced by using process design approaches.

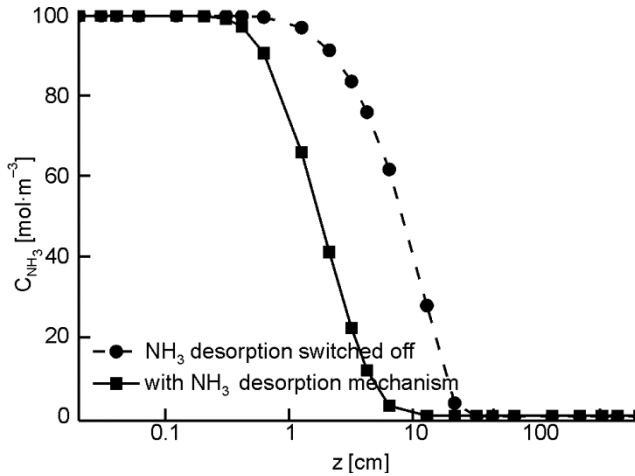


Fig. 3. NH_3 slippage under CO_2 absorption conditions, the effect of NH_3 desorption and reaction on NH_3 content in the liquid phase along the absorber at 288 K.

$$P_{\text{CO}_2}^{\text{IN}} = 10^4 \text{ Pa}, P_{\text{NH}_3}^{\text{IN}} = 0/1 \text{ Pa (without/with desorption)}, C_{\text{CO}_2}^{\text{IN}} = 0, C_{\text{NH}_3}^{\text{IN}} = 100 \text{ mol}\cdot\text{m}^{-3}.$$

Simulations data from the simplified 2D model of the falling film reactor

The Henry's constant of ammonia is much lower than that of CO_2 . H_{NH_3} is typically of the order of $1 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$ while H_{CO_2} typically amounts to the order of $2000 \text{ Pa}\cdot\text{m}^3\cdot\text{mol}^{-1}$. For instance, at $T = 288 \text{ K}$ and $C_{\text{NH}_3} = 100 \text{ mol}\cdot\text{m}^{-3}$ (free ammonia), the gaseous phase equilibrium partial pressure is 100 Pa NH_3 , i.e. 1000 ppmv in flue gases (under atmospheric pressure) which means that free NH_3 can easily desorb to the gas since its desorption driving force is relatively large and shown in Fig. 2 gas-liquid equilibrium is likely. Further, H_{NH_3} is a rising function of temperature; therefore lower temperatures should disfavour ammonia volatility. However, the dependence of H_{NH_3} on T is a relatively weak function, i.e. by decreasing temperature from 303 to 273 K, only a 5-fold drop in H_{NH_3} is achieved. For instance, NH_3 partial pressure equilibrated with $100 \text{ mol}\cdot\text{m}^{-3}$ of free NH_3 solution under 273 K is still around 40 Pa NH_3 , i.e. 400 ppmv in flue gases (under atmospheric pressure). Consequently, new processes such as a chilled ammonia process [13] do not offer a complete solution to a NH_3

volatility problem and thus some additional NH₃ slippage limiting techniques are still necessary.

3.2. EFFECT OF PH ON MASS TRANSFER AND ON NH₃ SLIPPAGE

In practice, in CO₂ absorbers and solvent regenerators pH oscillates from 8,8 to 9,6 [12]. Ammonia slippage increases under high pH due to increased concentration of free NH₃ in the liquid. On the other hand, under lower pH CO₂ absorption is not enhanced by chemical reactions and thus CO₂ fluxes are degraded. Consequently, an optimum pH value should be found from economic evaluations of the whole CO₂ capture system. An optimum NH₃ content in water depends on CO₂ loading, CO₂ content in flue gases, temperature and pressure; however reasonable values can oscillate around 5%.

3.3. EFFECT OF HYDRODYNAMICS

In a falling film reactor, the liquid flow is solely driven by gravity while the gas flow is mainly driven by application of an external pressure, whereas gravity does virtually play no role. From present hydrodynamic analysis of the falling film reactor it can be deduced that liquid can be entrained by gas, especially for thin liquid films and large gas to liquid velocity ratios.

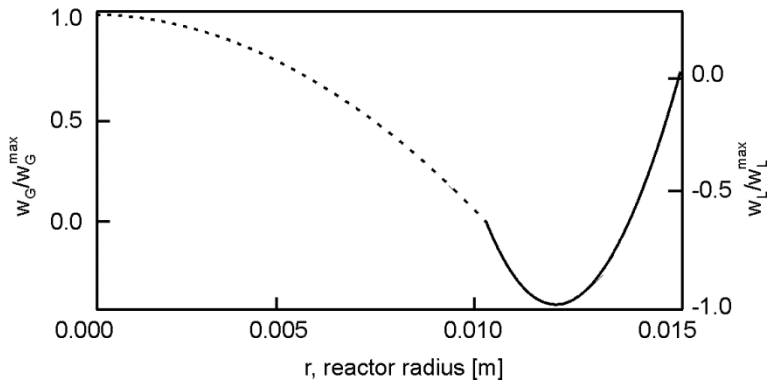


Fig. 4. Gas and liquid axial velocity profiles in a falling film reactor: dashed line – gaseous phase, solid line – liquid phase; w_L – liquid velocity, w_G – gas velocity, w^{\max} – maximum velocity in a relevant film. Simulation data from the detailed 2D axis-symmetric model of the falling film reactor

Figure 4 illustrates results of simulation for a vertical falling film reactor (cf. Fig. 1). The gas flows in an upward direction and its velocity at the gas–liquid interface is substantially decreased compared with the bulk gas velocity. The liquid phase velocity profile is more complex. Under the operating conditions shown in Fig. 4 liquid en-

trainment is exhibited, at least close to the gas–liquid interface. At the gas–liquid interface velocity discontinuity is observed (note that the scales are different in Fig. 4). At the wall, liquid velocity approaches 0 due to the domination of friction forces. Consequently, maximum liquid velocity is attained somewhere in between the interface and the wall. This hydrodynamic effect is very disadvantageous for CO₂ absorption fluxes since the velocity of saturated interfacial liquid is alleviated and hence its exposure time to the gas is prolonged. In contrast, this hydrodynamic effect can be beneficial for limiting NH₃ slippage, especially under the conditions of simultaneous large CO₂ absorption fluxes which can shift the equilibria at the gas–liquid interface towards complete consumption of free volatile ammonia.

It is expected that reactors with larger gas channels and of simpler geometry such as falling film reactors with thin liquid films can provide conditions for high CO₂ removal, low NH₃ slippage, ability to operation under high-pressure and to cope with salts crystallisation.

3.4. EFFECT OF MIGRATIVE SPECIES TRANSPORT

A NH₃–CO₂–H₂O solution is a weak electrolyte and thus comprises numerous ionic species. Simulations conducted with the detailed 2D axis-symmetric model provide some interesting insights into the NH₃ process in this regard. Accordingly, apart from diffusive and convective motions involved, ionic species can also undergo migrative motion. According to the Nernst–Planck equation, migrative fluxes tend to reduce electrical potential gradients which arose here from diffusion of species (Eqs. (13), (14)). Such gradients of electrical potential can be formed when species substantially differ in diffusivities and when mass transfer fluxes are large. For instance, from the products of reaction in Eq. (1), H⁺ cations have 3-fold higher diffusivity than carbamate anions. Hence, under a large CO₂ absorption flux, faster diffusion of H⁺ from the gas–liquid interface creates small gradient of the electrical potential. In this electric field, carbamate anions formed diffuse and migrate in the same direction but H⁺ cations migrate and diffuse in the opposite one. This effect arises from the same direction of diffusion for all species produced in the liquid film due to CO₂ absorption and the opposite directions of migration of ions with negative and positive valences, i.e. anions and cations, within the electric field. Consequently, the transport of a carbamate anion (which carries CO₂ and bounded NH₃) is enhanced by its migrative motion and thus CO₂ transport is favoured by a migrative mechanism from the interface to the liquid bulk. In a similar way, the migrative mechanism favours the transport of NH₄⁺ from the liquid bulk to the gas–liquid interface beneficially facilitating ammonia transport. The above conclusions can also be deduced from Eq. (13) taking into account relevant valences of anions and cations as well as concentration and potential gradients formed in CO₂ absorption into aqueous NH₃. The migrative transport can only have indirect effect on NH₃ slippage since NH₃ is not an ionic species.

3.5. EFFECT OF ELEVATED PRESSURE

Elevated pressure affects vapour–liquid equilibria. It increases absorption fluxes and it alleviates desorption fluxes of both CO₂ and NH₃. Namely, under elevated pressure conditions partial pressures of CO₂ and NH₃ are increased by a factor comparable with a compression ratio applied. Increased partial pressures enhance CO₂ absorption and beneficially degrade NH₃ slippage. High pressures can be attained by e.g. the integration of an absorber with a gas turbine. High pressures are necessary in a desorber unit (ca. 15 MPa) also with the aim to limit ammonia vaporisation from the hot regenerated liquid. Thus the NH₃ process is well suited for all pressurised combustion or IGCC power systems.

3.6. EFFECT OF TEMPERATURE

Experimental data on the effect of temperature on NH₃ slippage under air stripping operating conditions is shown in Fig. 5. Increase in temperature facilitates NH₃ slippage due to decreased NH₃ solubility in water, i.e. H_{NH_3} increases with temperature.

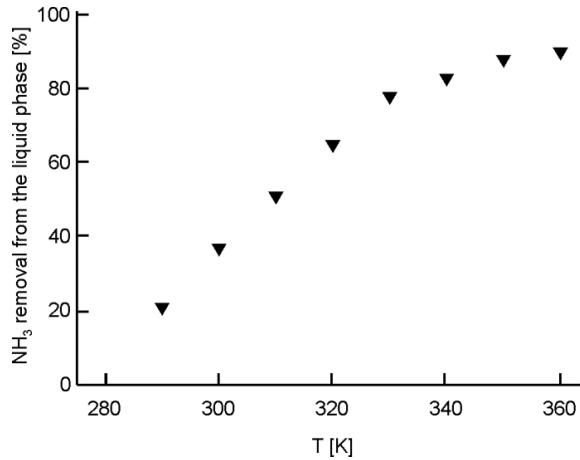


Fig. 5. Effect of temperature on NH₃ slippage under air stripping experimental conditions; $T = 296$ K, $P_{\text{CO}_2}^{\text{IN}} = 0$, $P_{\text{NH}_3}^{\text{IN}} = 0$, $C_{\text{CO}_2}^{\text{IN}} = 20$ mol·m⁻³, $C_{\text{NH}_3}^{\text{IN}} = 93$ mol·m⁻³, aqueous ammonia solution flow rate = 1.4×10^{-5} m³·s⁻¹, stripping air flow rate = 6.7×10^{-3} m³·s⁻¹. Experimental data from the packed-bed counter-current stripper with the packing height of 1 m and packing diameter of 0.1 m utilising 15 mm ceramic Raschig rings

Again, the thermal behaviour of NH₃ slippage under CO₂ capture conditions is a bit more complex than under air stripping conditions. Semi-batch CO₂ absorption experiments [12] indicate that the net amount of CO₂ absorbed decreases upon increasing temperature. This result arises from the decreased solubility of CO₂ at higher temperatures since H_{CO_2} increases upon increasing T . On the other hand, higher tem-

peratures tend to increase diffusivities of species and reaction rates. Besides, under CO₂ capture conditions pH can strongly vary along the reactor due to CO₂ absorption.

A thermal process control is a powerful tool in combating NH₃ slippage [22–24]. However, a process utilising chilled NH₃ [13] seems to be relatively expensive. Namely, the chilled NH₃ process requires chilling of flue gases including the condensation of water, chilling of regenerated ammonia from a desorber and chilling of an absorber itself. The costs of chilling can be reduced in power plants having unlimited access to large cold water resources such as rivers or lakes.

3.7. EFFECT OF INTEGRATION INTO POWER PLANTS

Integration of CO₂ capture systems into power plants necessitates advanced management of energy and mass flows in order to reduce the CCS-induced power plant efficiency drop penalty. Besides, for the NH₃ process the aspect of limited NH₃ slippage must be considered. Integration can benefit from the following measures:

- recirculation of flue gases back to combustion chambers which improves cycle efficiency and beneficially enriches CO₂ in flue gases [25],
- thermal integration of processes [26–30],
- utilisation of processes and apparatuses which enable one to reduce exergy losses (large losses are typically linked with heaters, fans, compressors and reactors),
- high-pressure CO₂ separation,
- optimising pressure and other parameters of steam supplied to a desorber,
- optimising stripper operation and its configuration,
- integration of CCS with more sophisticated energy technologies such as fuel cells [31, 32] or bioenergies [33, 34].

More specifically, the NH₃ process can benefit from highly reactive solvents such as NH₃, simultaneous removal of acidic gases (SO₂ and NO_x) and PM and direct integration of a desorber with a heat recovery steam generator unit (HRSG). The NH₃ process offers a reduction in regeneration energy requirements due to the higher loading capacity of an aqueous ammonia solution, the lower heat of reaction, and the lower heat of vaporisation when compared with standard MEA solutions.

4. CONCLUSIONS

Deployment of NH₃-based CO₂ capture into coal-fired power plants would shift unwanted emissions from those currently comprising SO₂, NO_x and particulate matter towards those comprising NH₃ which necessitates research efforts directed at limiting NH₃ slippage from NH₃-based CO₂ capture power systems. The presented experimental and 2D simulation data of the NH₃ process characterised the hydrodynamics of the

falling film reactor, determined the effect of pH, pressure and temperature on CO₂ absorption and explained the role of migrative transport of ionic species in total mass transport. It was found that NH₃ slippage could be limited by alleviated operating temperatures, optimised pH, increased pressure and large CO₂ absorption fluxes, which forced negative enhancement of NH₃ mass transfer to the gaseous phase. NH₃ slippage under CO₂ capture conditions and under air stripping conditions were illustrated by simulation and experimental data. Approaches used in the integration of CCS systems into power plants were expounded.

SYMBOLS

CCS	– carbon capture and sequestration
E	– activation energy, J·mol ⁻¹
HRSG	– heat recovery steam generator
K	– chemical equilibrium constant, mol·m ⁻³ or, m ³ ·mol ⁻¹ or, mol ² ·m ⁻⁶
k^{GP}	– mass transfer coefficient in the gaseous phase, mol·m ⁻² ·s ⁻¹ ·Pa ⁻¹
M	– molecular mass of species, kg·mol ⁻¹
MEA	– monoethanolamine
PM	– particulate matter
R	– reaction rate, mol·m ⁻³ ·s ⁻¹
C	– molar concentration in liquid phase, mol·m ⁻³
D	– molecular diffusivity, m ² ·s ⁻¹
F	– Faraday's constant, A·s·mol ⁻¹
H	– Henry's constant, Pa·m ³ ·mol ⁻¹
m	– mobility of ion, s·mol·kg ⁻¹
P	– pressure or partial pressure, Pa
r	– radial coordinate, m
R^G	– universal gas constant, J·mol ⁻¹ ·K ⁻¹
T	– temperature, K
v	– valence of ion
w	– velocity, m·s ⁻¹
w_z	– z component of velocity vector \mathbf{w} , m·s ⁻¹
x	– space coordinate, m
δ	– film thickness, m
λ	– thermal conductivity, J·mol ⁻¹ ·s ⁻¹ ·K ⁻¹
λ^E	– electrical conductivity, S·mol ⁻¹
φ	– electric potential in the electrolyte, V
G	– gaseous phase
i, j	– compound
L	– liquid phase
r	– reaction
z	– space or axial coordinate, m

GREEK SYMBOLS

δ	film thickness, m
λ	thermal conductivity, $\text{J}\cdot\text{mol}^{-1}\cdot\text{s}^{-1}\cdot\text{K}^{-1}$
λ^E	electrical conductivity, $\text{S}\cdot\text{mol}^{-1}$
φ	electric potential in the electrolyte, V

SUBSCRIPTS AND SUPERSSCRIPTS

G	gaseous phase
i, j	compound
L	liquid phase
r	reaction

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