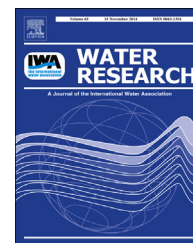


Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Biogas upgrading by chemical absorption using ammonia rich absorbents derived from wastewater

Andrew McLeod, Bruce Jefferson^{*}, Ewan J. McAdam

Cranfield Water Science Institute, Building 39, Cranfield University, Bedfordshire, MK43 0AL, UK

ARTICLE INFO

Article history:

Received 23 May 2014

Received in revised form

1 September 2014

Accepted 6 September 2014

Available online 18 September 2014

Keywords:

Carbon dioxide sequestration

Crystallisation

Gas/liquid contactor

Chemical scrubbing

ABSTRACT

The use of ammonia (NH₃) rich wastewaters as an ecological chemical absorption solvent for the selective extraction of carbon dioxide (CO₂) during biogas upgrading to 'biomethane' has been studied. Aqueous ammonia absorbents of up to 10,000 gNH₃ m⁻³ demonstrated CO₂ absorption rates higher than recorded in the literature for packed columns using 20,000–80,000 g NH₃ m⁻³ which can be ascribed to the process intensification provided by the hollow fibre membrane contactor used in this study to support absorption. Centrifuge return liquors (2325 g m⁻³ ionised ammonium, NH₄⁺) and a regenerant (477 gNH₄⁺ m⁻³) produced from a cationic ion exchanger used to harvest NH₄⁺ from crude wastewater were also tested. Carbon dioxide fluxes measured for both wastewaters compared reasonably with analogue ammonia absorption solvents of equivalent NH₃ concentration. Importantly, this demonstrates that ammonia rich wastewaters can facilitate chemically enhanced CO₂ separation which eliminates the need for costly exogenic chemicals or complex chemical handling which are critical barriers to implementation of chemical absorption. When testing NH₃ analogues, the potential to recover the reaction product ammonium bicarbonate (NH₄HCO₃) in crystalline form was also illustrated. This is significant as it suggests a new pathway for ammonia separation which avoids biological nitrification and produces ammonia stabilised into a commercially viable fertiliser (NH₄HCO₃). However, in real ammonia rich wastewaters, sodium bicarbonate and calcium carbonate were preferentially formed over NH₄HCO₃ although it is proposed that NH₄HCO₃ can be preferentially formed by manipulating both ion exchange and absorbent chemistry.

© 2014 Published by Elsevier Ltd.

1. Introduction

Biogas produced through the anaerobic digestion of sewage sludge can be exploited either through co-generation for electricity and heat production (CHP) or it can be upgraded to natural gas standards (biomethane). Due to recently introduced financial incentives the revenue from biomethane can be up to 70% higher than for electricity production (Read and Hofmann, 2011). Whilst trace biogas impurities, such as

hydrogen sulfide H₂S and particulates, are routinely removed (e.g. by activated carbon) prior to further biogas utilisation (Rautenbach and Welsch, 1994); upgrading to produce biomethane requires additional removal of the bulk CO₂ fraction to increase methane content to the equivalent of natural gas and is most commonly undertaken by absorption (Persson et al., 2007). This represents a new unit process operation to the water industry, although the same separation technology has seen extensive investigation for deployment into carbon capture and storage (CCS). In CCS, chemical absorption is

^{*} Corresponding author.

E-mail address: b.jefferson@cranfield.ac.uk (B. Jefferson).
<http://dx.doi.org/10.1016/j.watres.2014.09.010>
 0043-1354/© 2014 Published by Elsevier Ltd.

applied in a packed column which mediates contact between the CO₂ rich gas and a highly reactive chemical solvent such as monoethanolamine (MEA) that is selective for CO₂ and offers high absorption capacities of around 0.55 kg CO₂ kgMEA⁻¹ (Mani et al., 2006). However, a high specific energy demand for solvent regeneration, in addition to chemical losses due to persistent solvent degradation, and associated costs have largely hindered uptake of chemical absorption by water utilities implementing biogas upgrading. Instead, physical absorption using a water solvent is favoured, despite requiring larger absorption columns and higher liquid consumption due to a lower overall mass transfer coefficient (Patterson et al., 2011).

Aqueous free ammonia (NH₃) has been identified as an alternate chemical absorbent pathway to organic chemicals (e.g. MEA) for CCS as it does not degrade, it is not corrosive and it requires up to 75% less energy than MEA for regeneration due to weaker bonding of CO₂ to ammonia (Budzianowski, 2011a). Furthermore, aqueous ammonia provides an absorption capacity of 1.76 kgCO₂ kgNH₃⁻¹ which is around three times higher than the capacity (by mass) of MEA and is only one sixth of the cost (Mani et al., 2006; Makhloufi et al., 2014). Aqueous ammonia therefore presents analogous opportunities for biogas upgrading where the gas phase is characterised by a higher CO₂ mole fraction than in CCS. Budzianowski (2011b) suggested that ecological solvents rich in ammonium offered potential for exploitation in biogas upgrading. At wastewater treatment works, sludge liquors comprise ammonium concentrations ranging 500 to 2000 mg NH₄⁺ L⁻¹ (0.2% wt.) (Thornton et al., 2007) although ammonium concentrations up to 10,000 mgNH₄⁺ L⁻¹ (1% wt.) have been achieved using zeolites to harvest and concentrate ammonium from dilute wastewaters (Mackinnon et al., 2003). Whilst this is an attractive route to chemical cost reduction for water utilities undertaking biogas upgrading, this concentration range is below the 8–10% wt. range commonly applied to aqueous ammonia CO₂ absorption in packed columns (Puxty et al., 2010; Shuangchen et al., 2013; Budzianowski, 2011b) which suggests that ecological solvents may offer less favourable enhancement of absorption.

The key disadvantage of aqueous ammonia solvents is that the high saturated vapour pressure introduces NH₃ slip into the gas phase, where outlet flue gas concentrations of up to 2000 ppmv NH₃ have been reported (Kozak et al., 2009). This requires ammonia washing abatement equipment at the outlet of the absorption column which will influence both capital cost and energy demand (Shuangchen et al., 2013). Budzianowski (2011b) proposed that NH₃ slip could be diminished through the introduction of hollow fibre membrane contactor (HFMC) technology as an alternative absorption process to conventional packed columns. Rather than enabling direct contact between the gas and liquid phase as with conventional columns, the hydrophobic membrane in the HFMC supports non-dispersive contact between gas and liquid phase with gases free to diffuse through the micropores. Porous membranes are resilient to common biogas impurities (i.e. H₂S) and may even combine removal with upgrading if necessary since the acid gas does not permeate through the polymer (Rongwong et al., 2012). HFMC therefore present an opportunity to exploit the key advantages of

aqueous ammonia absorption for biogas upgrading whilst also diminishing NH₃ slip. The high specific surface area (around 3000 m² m⁻³) in HFMCs also provides greater process intensification when compared to packed columns (around 300 m² m⁻³) reducing both process scale and absorption solvent consumption (Makhloufi et al., 2014). For instance, Nii and Takeuchi (1992) compared HFMC technology with packed columns for chemical absorption and noted an order of magnitude reduction in absorbent solvent flow rate required to achieve analogous CO₂ separation from flue gas. It is therefore proposed that the enhanced absorbent utilisation afforded by HFMC technology could enable the practicable use of lower concentration ecological solvents for chemical cost reduction.

Absorption and reaction of CO₂ into aqueous ammonia is complex with both NH₃ and CO₂ undergoing multiple liquid phase reactions (Mani et al., 2006; Budzianowski, 2011a). However, several authors have cited the potential of this process for the production and recovery of the key reaction product ammonium bicarbonate (NH₄HCO₃) which has a commercial value of around €111 tonne⁻¹ (Budzianowski, 2011b; Hernandez and Torero, 2013). This is particularly attractive for biogas upgrading using ammonia rich wastewater as the chemical solvent since stabilisation of ammonium into the reaction product circumvents the need for direct biological treatment of ammonium in the wastewater. The following investigation therefore aims to establish the suitability of ammonia rich wastewater as a chemical solvent for biogas upgrading using HFMC technology as the underpinning absorption process. Specifically, this study seeks to: (i) quantify the chemical absorption potential of low concentration (environmentally relevant) aqueous ammonia solvents for CO₂ separation; (ii) determine the reactivity of real ammonia rich wastewaters compared to exogenic ammonia absorbents of equal concentration; (iii) measure the volatility of NH₃ into the gas phase within appropriate absorbent and process boundary conditions; and (iv) establish the feasibility of recovering the favoured reactant product NH₄HCO₃.

2. Materials and methods

2.1. Equipment setup and operation

Synthetic biogas was prepared using mass flow controllers (0.01–1.0 L min⁻¹, Roxspur Measurement and Control Ltd., Sheffield, UK) to mix methane (99.995%) and carbon dioxide (99.7%) (BOC gases, Ipswich, UK) in-line at a typical flow rate 750 mL min⁻¹ (2.5 s HFMC residence time) to provide a 60:40/CH₄:CO₂ gas which was supplied into the hollow fibre membrane lumen. The HFMC comprised 7400 polypropylene fibres each with an outer diameter and length of 300 μm and 0.113 m respectively (total surface area 0.79 m², Membrana GmbH, Wuppertal, Germany). The fibres comprised a 0.03 μm nominal pore size and 40% porosity with a packing density of 0.369 (Fig. 1a). Absorbent was stored in a 10 L PVC tank, maintained at 19–21 °C by a thermostatic water bath (GD120, Grant Instruments Cambridge Ltd., Shepreth, UK) and was passed through the HFMC shell, in counter-current mode using a centrifugal pump (max. 6 L min⁻¹, 50010 series, Jabsco GmbH,

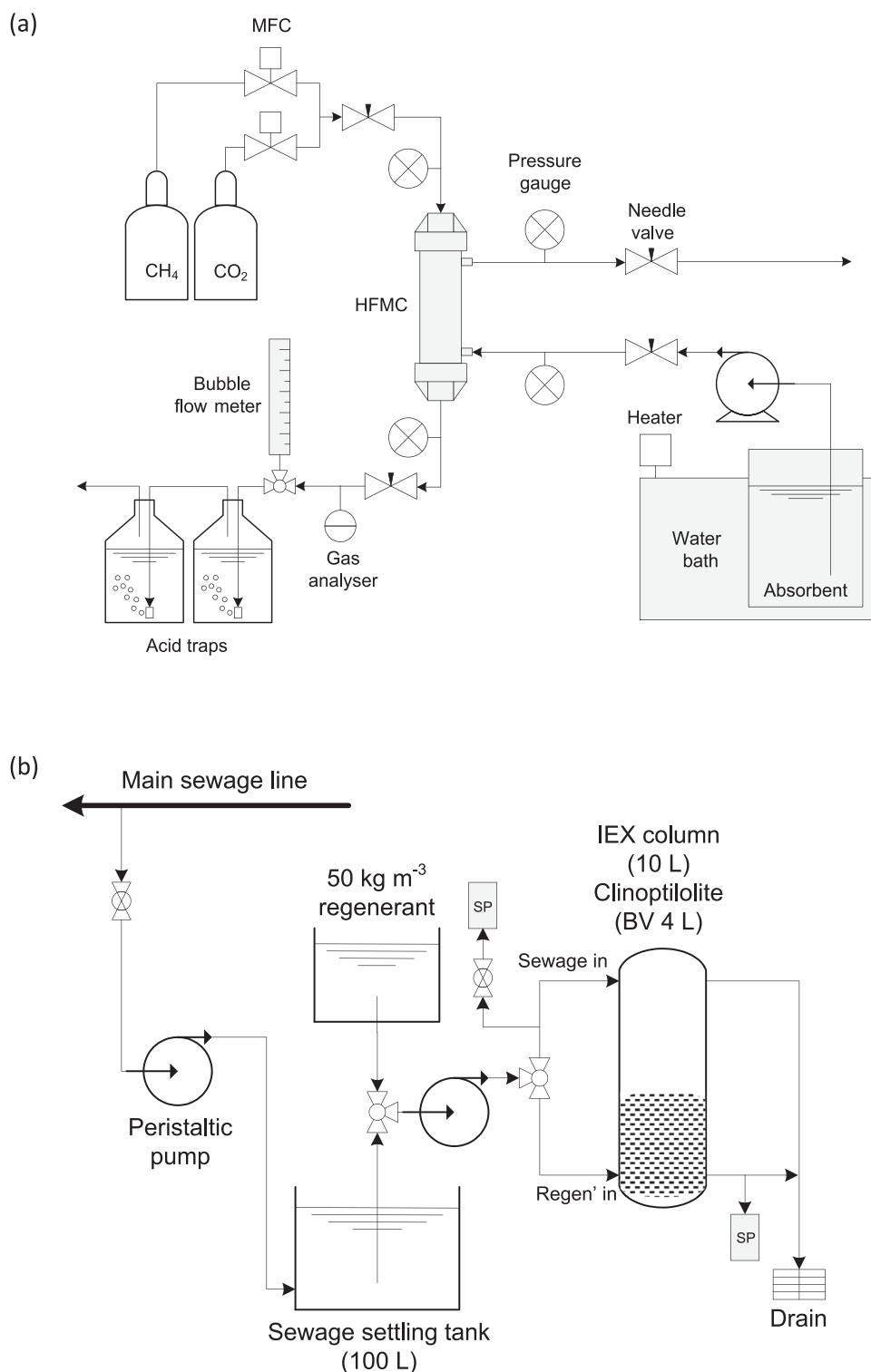


Fig. 1 – (a) Set-up used for gas absorption in a polypropylene micro-porous hollow fibre membrane contactor; (b) ion exchange (IEX) column for removal of ammoniacal nitrogen (NH₄-N) from raw sewage by clinoptilolite and subsequent production of NH₄-N rich IEX regenerant. SP indicates sampling point.

Norderstedt, Germany) at a typical flow rate of 100 mL min⁻¹ (60 s hydraulic residence time). Ammonia slip in to the gas phase was determined by the method described by Kuntke et al. (2012). The out-gas was bubbled through diffusers in two 1 L capacity gas tight aspirator bottles (Schott Duran,

VWR, The Netherlands) in series, containing 500 mL of 0.4 mol L⁻¹ sulphuric acid; the second bottle enabling verification of breakthrough from the first.

The ion exchanger comprised a 10 L column containing 4 l of clinoptilolite resin (RS Minerals, Guisborough, UK) and was

prepared by passing a 50 g_{NaCl} L⁻¹ (99%, Fisher Chemicals, Loughborough, UK) regenerant through the column at 5 bed volumes per hour (Bv h⁻¹) for 30 min followed by a DI rinse at 5 Bv h⁻¹ for 60 min (McAdam et al., 2010) (Fig. 1b). The column was operated in down-flow using crude sewage (10–20 gNH₄⁺ m⁻³) at 4.2 Bv h⁻¹ (Aiyuk et al., 2004) until breakthrough which was noted at 166 Bv. The column was regenerated using 20 L of 50 g_{NaCl} L⁻¹ at 1 BV h⁻¹. The IEX regenerant was filtered through a 1.2 μm filter (GF/C 15 mm, Fisher Scientific, Loughborough, UK) prior to use. Return liquor was collected from a digestate dewatering centrifuge at a local WWTW and was filtered through a 6–12 μm filter before centrifugation (Sorvall Legend RT+, Thermo Fisher Scientific, Hemel Hempstead, UK) at 5000 rpm for 10 min with the decant filtered through a 1.2 μm filter.

2.2. Chemical preparation, sampling and analysis

Analogue absorbents were freshly prepared by adding saturated aqueous ammonia solution (35%, 2.5 L, Fisher Chemicals) to DI water. Ammonia concentration was confirmed by ammonium cell test. The pH of real and synthetic absorbents was fixed at pH 11 (excluding variable pH experiments). Aqueous ammonia analysis was undertaken using cell tests (VWR International Ltd., Poole, UK) with photometric determination using a Spectroquant Nova 60 (Merck-Millipore, Darmstadt, Germany). Gas composition after the HFMC was determined using an infrared biogas analyser (Yieldmaster, accuracy <0.2% full-scale, Bluesens gas sensor GmbH, Herten, Germany). Gas flow rate was measured using a bubble flow meter (50 mL, Restek, Bellefonte, USA). Flux (*J*_{CO₂}, mol m⁻² s⁻¹) was calculated using:

$$J_{\text{CO}_2} = \frac{[(Q_{G,\text{in}} \times C_{G,\text{in}}) - (Q_{G,\text{out}} \times C_{G,\text{out}})] \times 273.15 \times 1000}{(22.4 \times A_m \times T_G)} \quad (1)$$

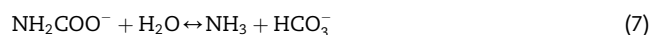
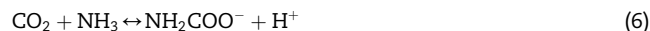
where *Q*_{G, in} and *Q*_{G, out} are gas flow rate before and after HFMC respectively (m³ s⁻¹), *c*_{G, in} and *c*_{G, out} are the CO₂ content before and after HFMC respectively (mol mol⁻¹), *A*_m refers to the membrane surface area for absorption (m²) and *T*_G is the gas temperature (K) (Atchariyawut et al., 2007). The enhancement in flux provided by the chemical reactivity of the absorbent was characterised using the ‘enhancement factor’ (*E*) which can be applied providing an identical driving force for mass transfer is assumed (Dindore et al., 2005):

$$E = \frac{\text{CO}_2 \text{ flux (chemical)}}{\text{CO}_2 \text{ flux (physical)}} \quad (2)$$

Microscopy of membrane fibres and crystals was performed by scanning electron microscope (SEM, XL30, FEI, Hillsboro, Oregon, USA), energy dispersive x-ray spectroscopy (EDX, Oxford Instruments NTS, Abingdon, UK) and X-ray diffraction (XRD, D5005, Siemens, Munich, Germany).

2.3. Liquid phase chemical reactions of CO₂ and aqueous ammonia

The following chemical reactions are known to take place during chemical absorption of CO₂ into aqueous ammonia (Puxty et al., 2010; Niu et al., 2012):



The ammonium–ammonia equilibrium can be driven toward free ammonia (NH₃, Equation (5)) by increasing absorbent pH (SM 1). Carbon dioxide reacts with either water to form bicarbonate (Equation (3)) or free ammonia to form carbamate (NH₂COO⁻) (Equation (6)).

3. Results

3.1. Assessment of CO₂ absorption using analogue ammonia absorbents

An increase in solvent pH under fixed hydrodynamic conditions notably increased *J*_{CO₂} at higher free ammonia concentrations (Fig. 2). For example, *J*_{CO₂} increased from 0.14 × 10⁻⁴ mol m⁻² s⁻¹ at pH 8 (20 °C) to 0.26 × 10⁻⁴ mol m⁻² s⁻¹ at pH 11 (20 °C). An increase in pH drives the ammoniacal nitrogen ([NH₄⁺] + [NH₃], NH₄-N) equilibrium toward free ammonia with around 15%, 90% and 99% present as free ammonia at pH 8, 10 and 11 respectively at 20 °C (SM 1, Equation (5)). Initial aqueous ammonia concentration also positively increased *J*_{CO₂} with a flux of 0.7 × 10⁻⁴ mol m⁻² s⁻¹ recorded in 10 g m⁻³ NH₃ solution compared to 0.38 × 10⁻⁴ mol m⁻² s⁻¹ in 10,000 g m⁻³ NH₃ solution operated under identical boundary conditions (pH 11, 20 °C). However, absorbent temperature did not markedly change *J*_{CO₂} except for the most concentrated solvent tested (10,000 gNH₃ m⁻³).

At a G/L of 0.075, the CH₄ composition of the outlet gas phase was between 98% and 99% for the 5000 gNH₃ m⁻³ and 10,000 gNH₃ m⁻³ absorbents (Fig. 3a). Upon increasing *Q*_G (with a fixed *Q*_L, 6.7 × 10⁻⁶ m³ s⁻¹), biogas CH₄ composition decreased which was more evident for the higher concentration ammonia absorbents. However, *J*_{CO₂} increased as *Q*_G and with higher fluxes noted when using the more concentrated NH₃ absorbents (Fig. 3b). At the maximum hydrodynamic conditions tested (G/L 4.2), *J*_{CO₂} were 0.94 × 10⁻⁴ mol m⁻² s⁻¹ for the 10 and 100 gNH₃ m⁻³ absorbents and 1.7 × 10⁻⁴ mol m⁻² s⁻¹ and 2.3 × 10⁻⁴ mol m⁻² s⁻¹ for the 5000 and 10,000 gNH₃ m⁻³ ammonia absorbents respectively.

3.2. Measurement of ammonia volatility within process boundary conditions

The loss of ammonia into the gas phase (or NH₃ slip) was ostensibly a function of initial aqueous ammonia concentration when *Q*_L and *Q*_G were fixed at 1.67 × 10⁻⁶ m³ s⁻¹ and

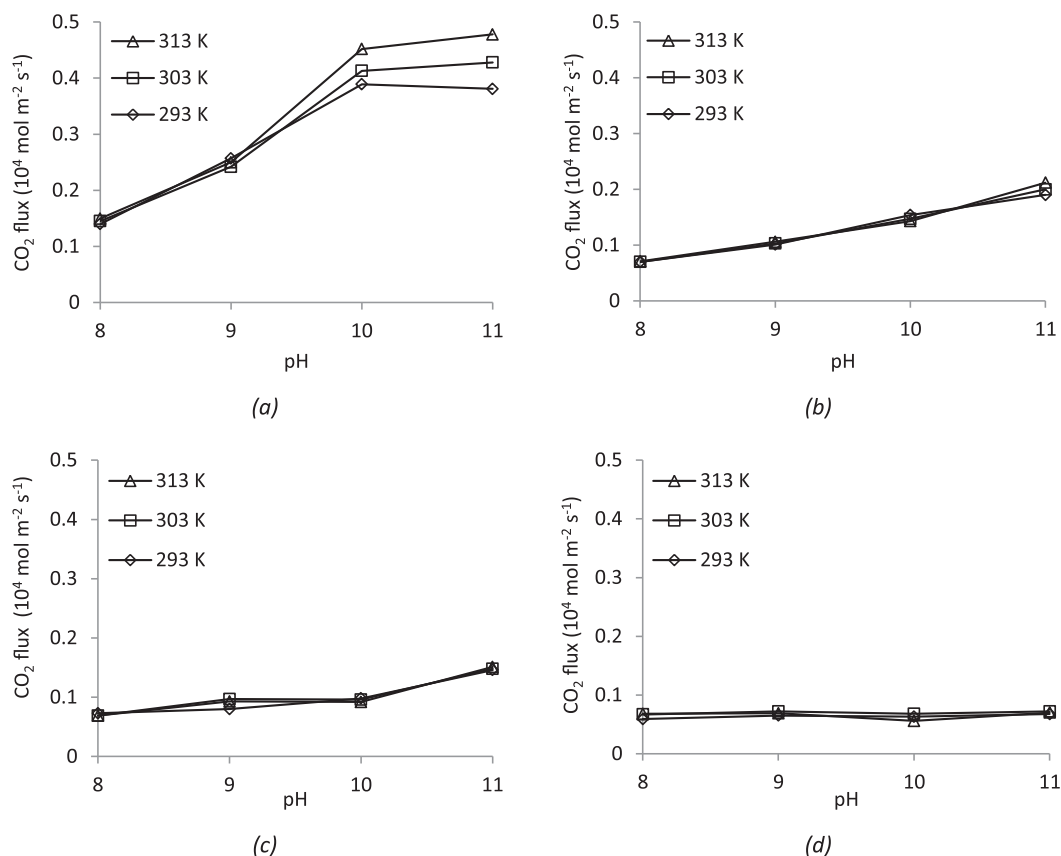


Fig. 2 – Influence of pH and temperature upon CO₂ flux (J_{CO_2}) in analogue NH₃ absorbents with concentrations of: (a) 10000 g_{NH3} m⁻³; (b) 1000 g_{NH3} m⁻³; (c) 100 g_{NH3} m⁻³; and (d) 10 g_{NH3} m⁻³ under fixed liquid and gas flow rates (1.67×10^{-6} m³ s⁻¹ and 1.25×10^{-5} m³ s⁻¹ respectively).

1.25×10^{-5} m³ s⁻¹ respectively at constant pH (11) and solvent temperature (20 °C) (Fig. 4). At an aqueous NH₃ absorbent concentration of 10,000 g m⁻³, which has been achieved in ecological absorbents through concentrating ammonia using ion exchange (Mackinnon et al., 2003), an NH₃ concentration of only 0.002 g_{NH3} m⁻³ was measured in the treated gas phase. This is below the proposed UK standard for gas phase ammonia in gas to grid applications (dashed line) (Environment Agency, 2013). Niu et al. (2012) also noted NH₃ slip was dependent on initial NH₃ concentration when testing ammonia absorbents within the same concentration range for CO₂ separation from a packed column. However, the observed losses were considerably higher than noted in this study.

3.3. Efficacy of real ammonia rich wastewaters to deliver enhanced CO₂ absorption

Return liquor and IEX regenerant were prepared and characterised (Table 2). For both of the real absorbents tested, chemical enhancement was maximised at the highest G/L ratio imposed (Fig. 5). A maximum E of 14.9 and 2.9 were determined for the return liquor (2325 g_{NH3} m⁻³) and IEX regenerant (447 g_{NH3} m⁻³) respectively at a G/L of 37.5. However, E reduced sharply following a decrease in G/L ratio toward an E of 1 which is comparable to the J_{CO_2} measured with

DI water as the physical absorption solvent. Enhancement factors produced from the real wastewaters were compared to those measured with analogue ammonia absorbents using the same boundary conditions (Fig. 6a and b). The enhancement factor for the return liquor was broadly in agreement with that determined for the analogue. The chemical enhancement of the IEX regenerant was characterised by a gradient similar to the parity line (where $E_{\text{real}}/E_{\text{syn}} = 1$) but was below that predicted based on the analogue.

3.4. Identifying the reaction products formed in real absorbents

In a preliminary assessment, synthetic biogas was bubbled through an 85,000 g_{NH3} m⁻³ analogue NH₃ solution and within a short time frame a solid NH₄HCO₃ product was produced in situ which displayed regularly shaped crystals when examined by SEM (Fig. 7). The crystals comprised only carbon (C), oxygen (O) and nitrogen (N) peaks (EDX spectra) with an O:N ratio of 3:1 which is indicative of the NH₄HCO₃ salt and was confirmed by XRD. In a subsequent assessment, an 85,000 g_{NH3} m⁻³ analogue absorbent was then run through a single fibre microporous HFMC (a PTFE fibre was used for easy potting) for approximately 5 min. Whilst no solid was visible within the absorbent reservoir, SEM analysis of the fibre

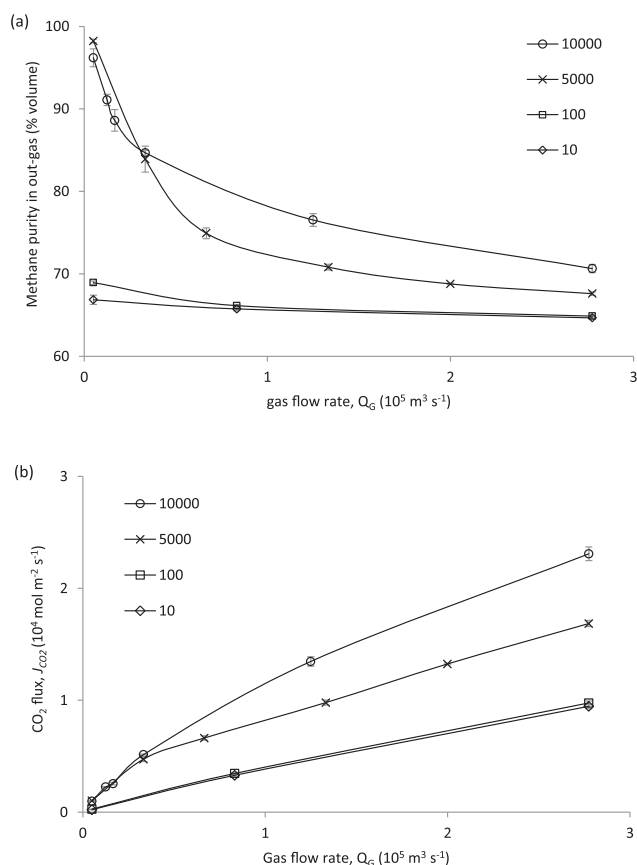


Fig. 3 – Effect of variable gas flow rate (Q_G , 0.05×10^{-5} – $2.8 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$) upon: (a) methane purity in the gas exiting the HFMC; and (b) CO_2 flux. Fixed liquid flow rate (Q_L) $6.7 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$. Analogue absorbent NH_3 concentrations ranging 10 to 10000 $\text{gNH}_3 \text{ m}^{-3}$.

revealed that NH_4HCO_3 crystals had grown in situ on the membrane surface. Ion exchange regenerant was tested in the PP HFMC and resulted in in situ crystal formation which exited the HFMC in the absorbent and was collected in a coarse filter

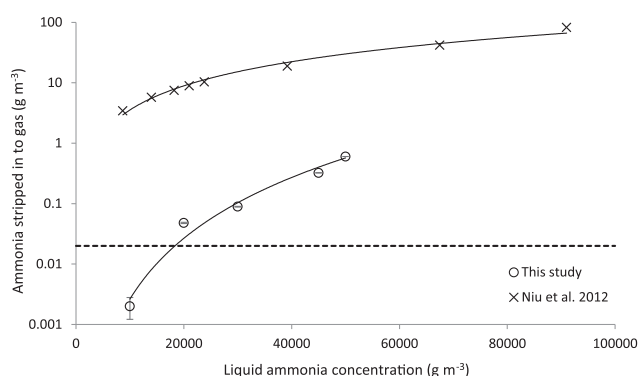


Fig. 4 – Effect of increasing NH_3 concentration on NH_3 slip into the gas phase. Fixed liquid and initial gas flow rates (Q_L , $1.67 \times 10^{-6} \text{ m}^3 \text{ s}^{-1}$; Q_G , $1.25 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$). The dotted line represents the concentration limit for NH_3 in biomethane for gas-to-grid and vehicular use (0.02 g m^{-3}).

(6–12 μm retention) for analysis (Fig. 7). The crystals were fine and amorphous in structure and were principally calcium carbonate ($CaCO_3$) although other cationic impurities including sodium, potassium and aluminium were also noted. In situ precipitation did not occur during return liquor assessment under identical hydrodynamic conditions to the IEX regenerant. Consequently, to enhance the likelihood for precipitation, the return liquor was recirculated in the HFMC until complete exhaustion of the absorbent. The crystalline solid was finally obtained through mild evaporation of the saturated return liquor. The EDX spectrum analysis suggested the crystal to be reasonably pure, comprising C, O and Na in a ratio indicative of sodium bicarbonate ($NaHCO_3$).

4. Discussion

A key finding from this study was that the low aqueous ammonia concentration present within environmental absorbents do enable chemical enhancement of CO_2 flux. The limiting aqueous NH_3 concentration needed to enhance CO_2 flux over water was between $100 \text{ gNH}_3 \text{ m}^{-3}$ and $447 \text{ gNH}_3 \text{ m}^{-3}$ with the upper value being indicative of the ammonium concentration reached in the IEX concentrate. This is above the ammonium concentration found in treated final effluent (around $10 \text{ g NH}_4^+ \text{ m}^{-3}$) which is commonly employed as the absorbent in water scrubbers for biogas upgrading at wastewater treatment works (Persson et al., 2007). An increase in pH of the 10 and 100 g m^{-3} ammonium/ammonia absorbents did not increase CO_2 flux (Fig. 2). When pH is increased from neutrality (pH 7) to pH 11, shifting the NH_4 –N equilibrium towards ca.100% free ammonia (Equation (5), SM 1). It is therefore asserted that since the increase in available reactant (ammonia) did not increase CO_2 flux, absorption within aqueous ammonia solvents below $100 \text{ gNH}_3 \text{ m}^{-3}$ is primarily governed by physical absorption. At aqueous ammoniacal nitrogen concentrations greater than 1000 g m^{-3} , a linear increase in CO_2 flux was demonstrated with an increase in pH (Fig. 2b) and is indicative of the chemical enhancement provided by the increase in available free ammonia (Esquiroz-Molina et al., 2013). Significantly, for the highest aqueous NH_4 –N absorbent concentration evaluated ($10,000 \text{ g m}^{-3}$), no further increase in CO_2 flux was noted as pH increased from pH10 to pH11 (Fig. 2a). This is analogous to the work of Esquiroz-Molina et al. (2013) and can be ascribed to the presence of an excess of free ammonia present in the reaction zone at the gas–absorbent interface at pH10, where the enhanced reactivity offsets the lower gaseous solubility constant thereby minimising liquid side resistance. Interestingly, in commercial aqueous ammonia packed column processes, pH is between 8.8 and 9.6 (Yeh et al., 2005) where the lower fraction of free ammonia available within this pH range can be tolerated through higher absolute NH_4 –N concentrations, which are typically in the range of $50,000$ – $100,000 \text{ g m}^{-3}$ (Puxty et al., 2010; Budzianowski, 2011a; Niu et al., 2012). Therefore within environmental absorbents, the reduced reactivity imposed by lower absolute NH_4 –N concentration can be offset by shifting the equilibrium toward free ammonia using mild pH correction.

Table 1 – Molecular masses and pure water solubilities of several binary carbonate and bicarbonate salts.

Name	Formula	Molecular mass g mol ⁻¹	Water solubility mol L ⁻¹ (20 °C)	Solubility product pK _{sp}	Ref.
Ammonium bicarbonate	NH ₄ HCO ₃	79.06	2.24	–0.70	Trypuć et al. (1998)
Sodium bicarbonate	NaHCO ₃	84.01	0.67	0.35	Trypuć et al. (1998)
Calcium carbonate	CaCO ₃	100.09	5.8 × 10 ⁻⁵	8.47	Haynes (2012)

Table 2 – Characterisation of raw wastewater matrices and subsequently derived absorbents.

Wastewater matrix	pH	NH ₄ -N g m ⁻³	Conductivity mS cm ⁻¹	COD g m ⁻³	TSS kg m ⁻³
Raw return liquor	8.3	2460	4.9	8400	5.6
Raw IEX regenerant	7.2	477	76.6	1060	
Filtered return liquor	11	2325	5.1	7900	4.6
Filtered IEX regenerant	11	477	76.6	1060	

An increase in absorbent temperature did not markedly enhance CO₂ flux within the environmental ammonia concentration range tested (Fig. 2). Zeng et al. (2011) also investigated the role of temperature (range 20–50 °C) in controlling NH₃–CO₂ reaction kinetics in 2–8% wt. aqueous ammonia and similarly noted only slight enhancement of the overall mass transfer coefficient between 20 and 40 °C (293–313 K), which is within the range where forward reactions are favoured (Bai and Yeh, 1997). The low temperature dependency potentially explains why the chilled aqueous ammonia process (temp. 1.7 °C) is commercially viable; the low temperature being favoured to limit ammonia slip (Valenti et al., 2009). In this study, an NH₃ concentration of 0.002 gNH₃ m⁻³ was measured in the gas phase for the 10,000 gNH₃ m⁻³ absorbent at a temperature of 20 °C which is an order of magnitude below the proposed gas phase ammonia concentration limit (0.02 gNH₃ m⁻³) for biomethane as a vehicle fuel or natural gas substitute (Persson et al., 2007; Environment Agency, 2013). Ammonia slip was demonstrated to be concentration dependent (Fig. 4) thus the low NH₃ slip recorded in this study can be explained by the lower environmentally relevant ammonia concentration range studied. However, NH₃ slip was also two orders of magnitude below that observed in a packed column

using aqueous ammonia within a similar concentration range (Fig. 4, Niu et al., 2012). Budzianowski (2011a) postulated that the difference in NH₃ slip was due to the hydraulic characteristics of each technology where the transport of NH₃ to the gas–liquid interface in packed columns was reasonably turbulent whereas the preferential laminar flow regime in HFMC (Re = 57–570 in this study) minimises the transport of NH₃ to the gas–liquid interface as NH₃ transport is limited to radial diffusion from the absorbent bulk to the boundary layer. Further, stagnant NH₃ within the gas-filled membrane pores, absent in column-based systems, will likely resist NH₃ mass transfer from the liquid phase, which could conceivably also play a role. Therefore, HFMCs appear practically advantageous to limit ammonia slip, and when coupled with the relatively low NH₃ concentration range used, enable a sufficiently clean produced gas for use.

At low gas flows, methane content in the gas outlet exceeded 98% (Fig. 3) which meets standards for biomethane (Persson et al., 2007). An increase in gas flow rate decreased methane content in the outlet gas but increased CO₂ flux into the receiving ammonia absorbent. In chemically reactive absorption systems, an increased gas flow often mediates solute flux (Esquiroz-Molina et al., 2013) as this permits replenishment of CO₂ at the solvent–membrane interface and sustains a high bulk gas CO₂ partial pressure (Zeng et al., 2013). At full scale, the balance between higher flux to reduce scale and maintenance of the outlet gas quality can be achieved through extension of reactor length (Noble and Stern, 1995). At the highest flux recorded using 10,000 gNH₃ m⁻³ aqueous ammonia absorbent, an overall absorption rate of 8.4 kmol m⁻³ h⁻¹ was recorded. For comparison, Zeng et al. (2013) reported an overall absorption rate of 2.37 kmol m⁻³ h⁻¹ from a 15% CO₂ v/v flue gas using 7.7% wt. aqueous ammonia in a packed column. This process comparison illustrates that analogous CO₂ fluxes can be achieved with lower concentration environmental aqueous ammonia absorbents through the process intensification provided by the HFMC. Chemical enhancement within the real matrices reached a plateau at a gas–liquid ratio of 15–19 (Fig. 5). The absorbent flow regime is characteristically laminar. Consequently the CO₂ loading applied at the high G/L ratio depletes the reactant within the immediate vicinity of the gas–liquid

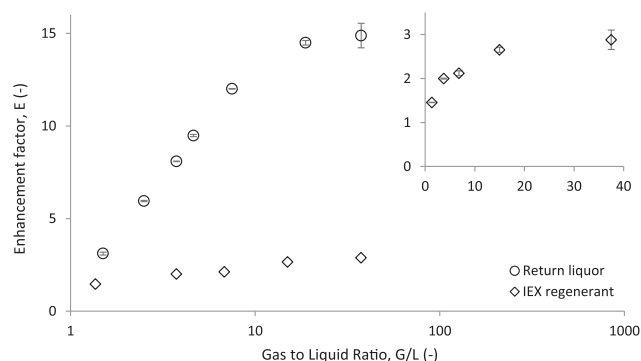


Fig. 5 – Effect of variable gas-to-liquid ratio upon enhancement factor (E, dimensionless), determined by ratio of CO₂ flux for return liquor or IEX regenerant (2325 g m⁻³ and 447 g m⁻³ respectively) against CO₂ flux in DI water.

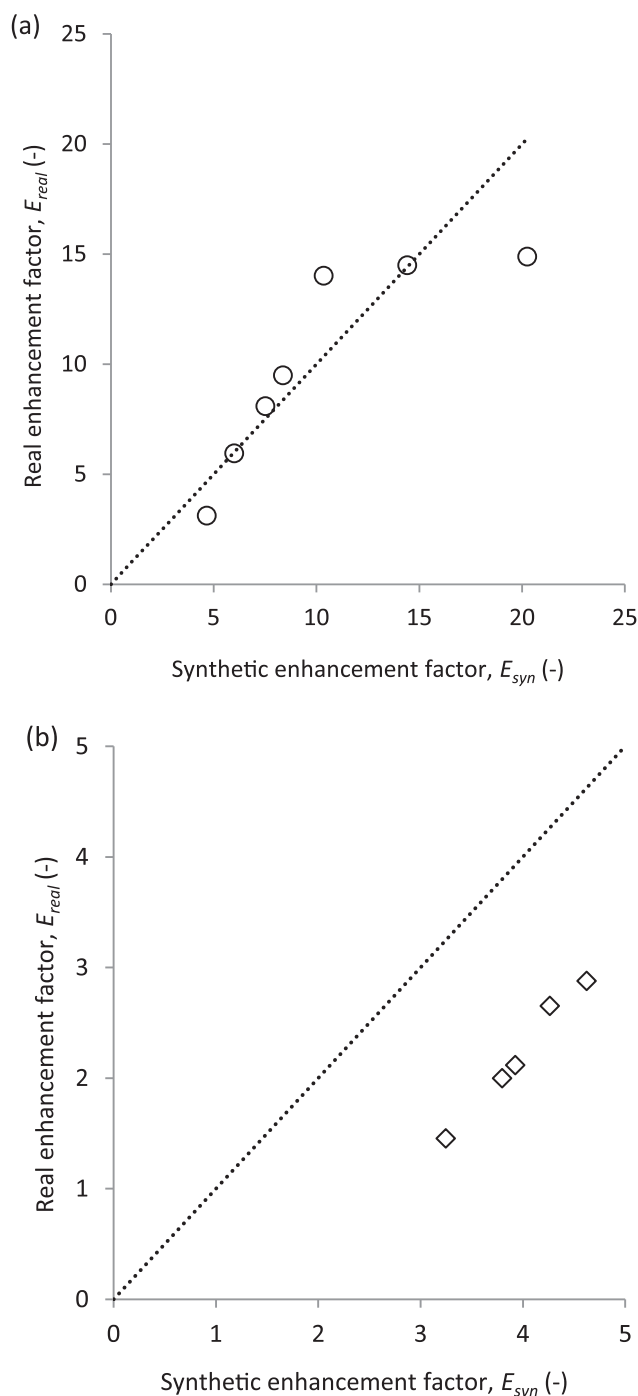


Fig. 6 – Effect of variable liquid flow rate (Q_L , 0.17×10^{-5} – $1.7 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$) upon enhancement factor (E , dimensionless) determined by ratio of CO_2 flux for (a) return liquor or (b) IEX regenerant against CO_2 flux in DI water. Parity line plotted for reference (dotted line).

interface and absorption rate then becomes limited by the radial diffusion of the reactant to the reactant plane (Dindore et al., 2005). Importantly, this demonstrates real environmental absorbents provide considerable enhancement of CO_2 flux versus water which is the absorbent currently favoured by water utilities (Persson et al., 2007). Chemical enhancement

provided by the return liquor was equivalent to that of the analogue indicating that enhancement was ostensibly a function of initial ammonia concentration. However, the IEX regenerant provided lower enhancement than an analogue of equivalent concentration which can be ascribed to the salt concentration (50 g L^{-1}) which is known to reduce the physical solubility of CO_2 into the absorbent (McLeod et al., 2013). Higher chemical reactivity can be engineered into the IEX regenerant through increasing ammonia concentration which is dependent upon the zeolites cation exchange capacity (CEC), and ammonium loading (Mackinnon et al., 2003). For example, Mackinnon et al. (2003) used a higher CEC zeolite (MesoLite) to provide a regenerant concentration of up to $10,000 \text{ gNH}_4\text{-N m}^{-3}$, which in this study has been shown sufficient to provide high CO_2 fluxes (Fig. 3).

A CO_2/NH_3 absorbent loading of $0.046 \text{ mol mol}^{-1}$ resulted from the maximum CO_2 flux achieved (Fig. 3). For these absorbent loading conditions (i.e. low loading and high pH) there is general agreement that the reaction product ammonium carbamate is favoured which is three times more soluble than ammonium bicarbonate and so does not readily precipitate (Mani et al., 2006; Budzianowski, 2011a). Data from Jänecke (1929) indicates that at a CO_2 loading of around $0.5 \text{ molCO}_2 \text{ molNH}_3^{-1}$ the equilibria shifts to favour bicarbonate (Equation (4)) and ammonium ions (Equation (5)) (Mani et al., 2006; Puxty et al., 2010) leading to preferential formation of ammonium bicarbonate (Equation (6)). In this study, this NH_4HCO_3 precipitation route was demonstrated under high CO_2 loading by bubbling CO_2 directly into the analogue ammonia absorbent (Fig. 7). Importantly, sequestration of both ammonia and CO_2 into precipitated NH_4HCO_3 eliminates the cost and complexity of solvent regeneration which represents a key barrier to uptake of chemical absorption (Mani et al., 2006). Following absorbent recirculation within the HFMC, ammonium bicarbonate crystals were also shown to preferentially form at the membrane surface. This is similar to the mechanism introduced by Di Profio et al. (2010) in the membrane crystallisation reactor which has been applied specifically for the enhancement of crystallisation kinetics. The authors proposed that the porous membrane surface provided cavities where solute molecules become trapped leading to localised supersaturated zones. Consequently, the use of the membrane for ammonia CO_2 absorption can enable ammonium bicarbonate crystallisation at lower CO_2 loadings than previously proposed in packed column investigation. The membrane's high controllability in favour of crystal growth versus nucleation can allow sufficiently sized crystals to detach due to the sheer of liquid flow and avoid scaling (Di Profio et al., 2010). However, pore wetting during operation can cause crystal formation within the fibre bore (McLeod et al., 2014). This can be avoided by selection of suitably hydrophobic membranes possessing small ($<0.2 \mu\text{m}$), circular pores in addition to solvents possessing high surface tension (such as highly electrolytic wastewaters).

In the IEX regenerant CaCO_3 was preferentially formed over NH_4HCO_3 due to its lower solubility (Table 1). The cations Na^+ , K^+ and Al^{3+} were also present within the precipitate due to co-separation by the cationic zeolite used. Ciambelli et al. (1985) fractionated a cationic IEX regenerant from an IEX

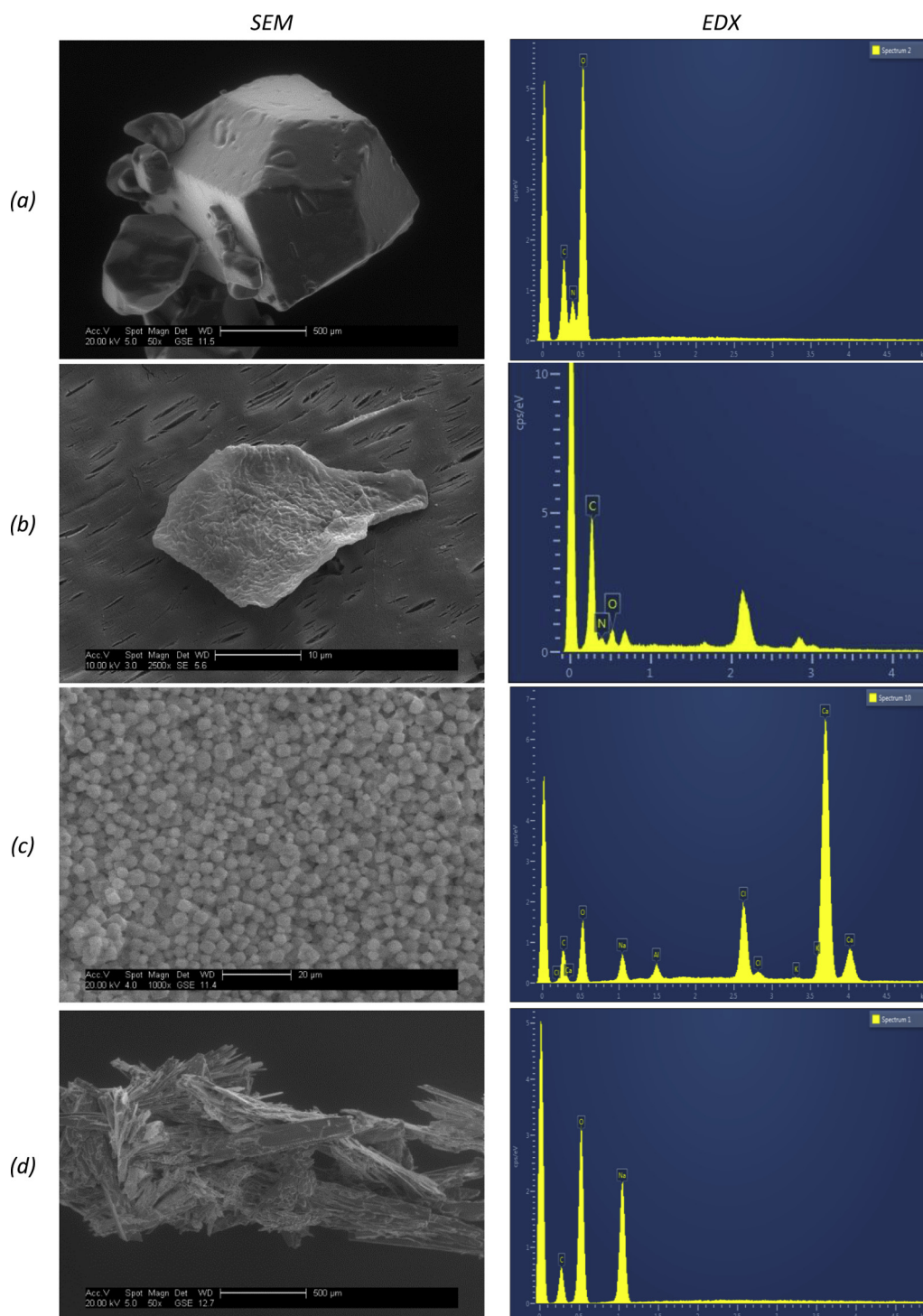


Fig. 7 – Scanning electron microscope (SEM) and energy dispersive X-ray (EDX) spectra of ammonium bicarbonate formed in situ by bubbling gas through bulk solvent and by nucleation on the membrane surface (a & b respectively), in situ calcium carbonate from IEX regenerant (c), and sodium bicarbonate from dehydration of return liquor saturated by CO₂ (d).

column used for ammonium separation and identified that the Ca²⁺ rich (and ammonia poor) regenerant fraction was first eluted from the IEX column ahead of ammonium. It is therefore proposed that further selectivity toward NH₄HCO₃ can be imparted when using IEX by more strict regulation of the regenerant cycle to favour ammonium. However, in the return liquor, sodium bicarbonate (NaHCO₃) was

preferentially precipitated due to its lower solubility constant and high [Na⁺] gradient. The high availability of [Na⁺] ions can be ascribed to the considerable sodium hydroxide addition needed to overcome the liquors buffering capacity to reach pH11. Interestingly, [Hecht et al. \(1990\)](#) demonstrated that equilibrium between NH₃ and NH₄⁺ (Equation (1)) can be successively re-established at low pH (i.e. pH7.8) following

consumption of the free NH_3 by solvent recirculation. Consequently, operation at lower pH will potentially provide more favourable conditions for ammonium bicarbonate precipitation due to the lower $[\text{Na}^+]$ gradient albeit at lower CO_2 fluxes.

To establish key financial benefits from this study, revenue generation from biomethane is compared to a conventional WWTW where biogas is used in CHP to produce electricity and $\text{NH}_4\text{-N}$ is treated by nitrification. The illustrative WWTW treats $500,000 \text{ m}^3 \text{ d}^{-1}$ total flow, $25,000 \text{ kgNH}_4\text{-N d}^{-1}$ ($50 \text{ gNH}_4\text{-N m}^{-3}$) and produces $3400 \text{ m}^3 \text{ h}^{-1}$ raw biogas (60:40/ $\text{CH}_4\text{:CO}_2$) which generates an annual revenue of $2.8 \text{ M}\text{€ y}^{-1}$ following subtraction of aeration costs ($2.9 \text{ M}\text{€ y}^{-1}$) which are assumed entirely attributable to nitrification (Table 3). The removal of trace H_2S and particulate impurities is assumed to be a uniform requirement for each scenario and therefore can be neglected for simplicity. However, if 100 ppmv H_2S in the biogas and a capacity of $0.3 \text{ kg sulfur kg}^{-1}$ carbon are assumed (Rautenbach and Welsch, 1994), then approximately 1 t of carbon media y^{-1} would be required for a $3400 \text{ m}^3 \text{ h}^{-1}$ biogas flow. Based on an ammonium mass balance from return liquors (Jaffer et al., 2001), 22% of the biogas flow can be upgraded with ammonia (78% to CHP), which yields an increased revenue of $1.3 \text{ M}\text{€ y}^{-1}$. A further $0.9 \text{ M}\text{€ y}^{-1}$ in revenue can be achieved through including NH_4HCO_3 recovery (total $5 \text{ M}\text{€ y}^{-1}$). Smaller illustrative WWTWs ($15,000 \text{ m}^3 \text{ d}^{-1}$), typically receiving lower strength raw influent ($25 \text{ gNH}_4\text{-N m}^{-3}$) and generating a 50% lower biogas flow per m^3 influent, will have a reduced nitrification demand upon the ASP and possess a lower return liquor flow (assuming no imported sludge); therefore a $41 \text{ K}\text{€ y}^{-1}$ baseline revenue via CHP is assumed. Based upon the stoichiometry of the NH_4HCO_3 product, 33% of the biogas flow may be directed towards upgrading, yielding an increased revenue of $33 \text{ K}\text{€ y}^{-1}$ ($74 \text{ K}\text{€ y}^{-1}$ total). Combined use of both CHP and upgrading is considered to be most feasible at full scale as some CHP capacity is needed to deliver heat for the AD. However, it is worth noting that up to 40% of the ammonium load can be attributed to the return liquors (Johnson, 2011) hence the projected revenue (based on 22%) can be considered conservative. Importantly, this added value could not be realised if exogenic chemicals (i.e. MEA) were used for biogas upgrading

due to the high cost of chemical regeneration ($-2.2 \text{ M}\text{€ y}^{-1}$) (Knudsen et al., 2009).

The capital cost of the membrane polymer can be determined by using the overall mass transfer coefficient (K_L , m s^{-1}) to calculate the membrane length needed to achieve a given CO_2 removal from the gas phase:

$$\ln\left(\frac{c_1}{c_0}\right) = \frac{-K_L a L}{V_L} \quad (9)$$

where L is the active membrane length (m), a is the specific surface area for the HFMC ($\text{m}^2 \text{ m}^{-3}$), V_L is the superficial liquid velocity (m s^{-1}), and c_0 and c_1 are the inlet and outlet dissolved CO_2 concentrations in the liquid respectively (Noble and Stern, 1995). A K_L of $1.53 \times 10^{-4} \text{ m s}^{-1}$ was observed in the present study using a return liquor chemical solvent. Module housing, piping, instrumentation and installation cost can be estimated using appropriate scaling factors (Shao et al., 2012), whilst the capital cost for solvent pumps (1 active, 1 reserve) was normalised against membrane surface area (1.67 € m^{-2} ; Judd, 2011) and assuming a 10 year lifetime. Therefore, for a 95% CH_4 biomethane output, a total HFMC installation cost of $50,200 \text{ € y}^{-1}$ assuming full-scale HFMCs (60% of total cost, Liqui-cel, 14x40 extra flow) at 40 € m^{-2} membrane area and a conservative 3 y membrane lifetime (Prasad and Sirkar, 1989). A payback time for a single module of just 9 d has negligible impact upon the economic benefit for the large WWTW. The reduced return liquor flow of the smaller WWTW requires only a single full-scale HFMC installation (8400 € y^{-1}). Although lower revenues result in a longer payback time (0.25 y) this is still reasonable and may be feasibly extended if less conservative membrane lifetimes (>10 y) are achievable (Prasad and Sirkar, 1989).

Full upgrading, where 100% of the gas load is used for biomethane production, increases revenue to $9.5 \text{ M}\text{€ y}^{-1}$ due to the higher incentivisation levy for biomethane (Read and Hofmann, 2011). Based on using IEX for harvesting NH_4^+ from primary effluent then 100% upgrading is theoretically achievable as mass balancing indicates the full ammonium load provides a mole ratio of 1.2:1 $\text{NH}_4\text{-N:CO}_2$ which is within range of the stoichiometric conversion (1:1 $\text{NH}_4^+/\text{CO}_2$ into NH_4HCO_3). With the inclusion of NH_4HCO_3 recovery to 100%

Table 3 – Characterisation of raw wastewater matrices and subsequently derived absorbents.

Scenario	Biogas utilisation	CHP ^c	Upgrade ^c	NH_4HCO_3 ^d	Aeration ^a	Total	Net gain ^e
Baseline	100% CHP 0% Upgrade	5.7	N/a	N/a	-2.9	2.8	N/a
Partial upgrading ^g	78% CHP 22% Upgrade ^b	4.4	2.1	N/a	-2.4	4.1	+1.3
Partial upgrading and recovering NH_4HCO_3 ^g	78% CHP 22% upgrade ^b	4.4	2.1	0.9	-2.4	5.0	+2.2
Full upgrading ^h	0% CHP 100% Upgrade	N/a	9.5	N/a	N/a ^f	9.5	+6.7
Full upgrading and recovering NH_4HCO_3 ^h	0% CHP 100% Upgrade	N/a	9.5	4.0	N/a ^f	13.5	+10.7

N/a – Not applicable to the specific scenario. CHP – Combined heat and power.

^a Aeration cost based solely on nitrification demand using: $4.34 \text{ kgO}_2 \text{ kgN}^{-1}$, oxygen transfer efficiency 15%, water depth 5 m.

^b Biogas split based on ammonia availability in return liquor using concentration and flow from Jaffer et al. (2001).

^c Biogas costs based on Read and Hofmann (2011).

^d Ammonium bicarbonate wholesale value based on Hernandez and Torero (2013).

^e Financial gain over baseline scenario (100% CHP plus nitrification).

^f Assumes 100% NH_4 utilisation for biogas upgrading, where mass balance across the example works demonstrates a mole ratio of 1.2:1 $\text{NH}_4^+ \text{-N:CO}_2$ which indicates an excess of $\text{NH}_4^+ \text{-N}$ given the stoichiometric conversion of NH_4^+ into NH_4HCO_3 is 1:1.

^g Using return liquors.

^h Using IEX regenerant following wastewater treatment.

upgrading, revenue is estimated to increase by $10.7 \text{ M}\pounds \text{ y}^{-1}$ versus the base case ($115 \text{ K}\pounds \text{ y}^{-1}$ in excess of the $41 \text{ K}\pounds \text{ y}^{-1}$ baseline for small works). Interestingly, the added value provided by selling NH_4HCO_3 as a fertilizer and the reduction in aeration costs (for nitrification) could reduce the financial risk in investing in biomethane, where uncertainty over the future value of biomethane incentives is currently impeding implementation of biogas upgrading facilities within the UK.

For the large example WWTW an IEX bed size of approximately 6000 t ($100,000 \text{ }\pounds \text{ y}^{-1}$) was estimated based upon literature values for clinoptilolite media CEC and cost (Aiyuk et al., 2004), with an annual media attrition of $>10\%$ is possible for full-scale IEX of municipal wastewater (Svetich, 1993). Based upon the operational IEX conditions in the present study and the maximum K_L observed for the IEX regenerant solvent ($1.4 \times 10^{-4} \text{ m s}^{-1}$); a membrane installation totalling $291,000 \text{ }\pounds \text{ y}^{-1}$ is estimated for a $95\% \text{ CH}_4$ biomethane. As a result a total payback time of just 14 d is anticipated for the combined IEX and membrane technologies. At a smaller scale WWTW the IEX bed capital cost approaches parity with the single full-scale HFMC required, incurring a combined capital cost of $10,000 \text{ }\pounds \text{ y}^{-1}$ with a payback time of roughly 0.1 y.

5. Conclusions

Aqueous ammonia absorbents in the concentration range identified in ammonia rich wastewaters have been shown to enable chemically enhanced CO_2 separation. Implementation of ecological solvents obviates the perceived challenges of chemical absorption where concerns regarding chemical handling and chemical cost can be precluded. The IEX regenerant provided less chemical reactivity than the return liquor due principally to the lower free ammonia concentration. The CO_2 absorption rate recorded using the high concentration NH_3 analogue ($10,000 \text{ g m}^{-3}$) demonstrated the potential of an optimised IEX process for ecological solvent production and were superior to those identified for packed columns in the literature where higher aqueous ammonia concentrations ($2\text{--}8\% \text{ wt.}$) are used. The enhanced absorption rate and low ammonia slip presented in this study can be attributed to the process intensification and specific hydrodynamic profile developed in HFMC technology. However, ecological solvents could still be of interest for retrofit to existing water scrubbers provided low ammonia slip can be achieved. The recovery of ammonium bicarbonate was illustrated but proved complex in real wastewater. Reaction product recovery can eliminate solvent regeneration, reduce wastewater treatment costs and provide a new revenue stream. Consequently, further investigation into more controlled methods of NH_4HCO_3 crystallisation in complex wastewaters is economically warranted and several possible options have been proposed.

Acknowledgements

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC, V/N: 08001923), Anglian

Water, Northumbrian Water, Severn Trent Water and Yorkshire Water for their financial support.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2014.09.010>.

REFERENCES

- Aiyuk, S., Xu, H., van Haandel, A., Verstraete, W., 2004. Removal of ammonium nitrogen from pretreated domestic sewage using a natural ion exchanger. *Environ. Technol.* 25, 1321–1330.
- Atchariyawut, S., Jiratananon, R., Wang, R., 2007. Separation of CO_2 from CH_4 by using gas-liquid membrane contacting process. *J. Membr. Sci.* 304, 163–172.
- Bai, H., Yeh, A.C., 1997. Removal of CO_2 greenhouse gas by ammonia scrubbing. *Ind. Eng. Chem. Res.* 36, 2490–2493.
- Budzianowski, W.M., 2011a. Benefits of biogas upgrading to biomethane by high-pressure reactive solvent scrubbing. *Biofuels Bioprod. Bioref.* 6, 12–20.
- Budzianowski, W.M., 2011b. Mitigating NH_3 vaporization from an aqueous ammonia process for CO_2 capture. *Int. J. Chem. React. Eng.* 9, A58.
- Ciambelli, P., Corbo, P., Porcelli, C., Rimoli, A., 1985. Ammonia removal from wastewater by natural zeolites. I. Ammonium ion exchange properties of an Italian phillipsite tuff. *Zeolites* 5, 184–187.
- Dindore, V.Y., Brilman, D.W.F., Versteeg, G.F., 2005. Hollow fiber membrane contactor as a gas-liquid model contactor. *Chem. Eng. Sci.* 60, 467–479.
- Di Profio, G., Curcio, E., Drioli, E., 2010. Supersaturation control and heterogeneous nucleation in membrane crystallizers: facts and perspectives. *Ind. Eng. Chem. Res.* 49, 11878–11889.
- Environment Agency, 2013. Revised Draft Quality Protocol for biomethane. LIFE08 ENV/UK/000208. Environment Agency, Reading, UK.
- Esquiroz-Molina, A., Georgaki, S., Stuetz, R., Jefferson, B., McAdam, E.J., 2013. Influence of pH on gas phase controlled mass transfer in a membrane contactor for hydrogen sulphide absorption. *J. Membr. Sci.* 427, 276–282.
- Hecht, V., Bischoff, L., Gerth, K., 1990. Hollow fiber supported gas membrane for in situ removal of ammonium during an antibiotic fermentation. *Biotechnol. Bioeng.* 35, 1042–1050.
- Hernandez, M.A., Torero, M., 2013. Market concentration and pricing behaviour in the fertilizer industry: a global approach. *Agric. Econ.* 44, 723–734.
- Jaffer, Y., Clark, T.A., Pearce, P., Parsons, S.A., 2001. Assessing the potential of full scale phosphorus recovery by struvite formation. In: 2nd International Conference on Recovery of Phosphates from Sewage and Animal Wastes, 12–14 March, Noordwijkerhout, Holland.
- Jänecke, E., 1929. Über das System H_2O , CO_2 und NH_3 . *Z. fuer Elektrochem.* 35, 716–728.
- Johnson, C., 2011. A carbonless, total nitrogen removal process. *Pollut. Eng.* 43, 20–23.
- Judd, S., 2011. The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment, second ed. Elsevier, Amsterdam.
- Knudsen, J.N., Jensen, J.N., Vilhelmsen, P.-J., Biede, O., 2009. Experience with CO_2 capture from coal flue gas in pilot scale: testing of different amine solvents. *Energy Procedia* 1, 783–790.

- Kozak, F., Petig, A., Morris, E., Rhudy, R., Thimsen, D., 2009. Chilled ammonia process for CO₂ capture, 1, 1419–1426.
- Kuntke, P., Smiech, K.M., Bruning, H., Zeeman, G., Saakes, M., Sleutels, T.H.J.A., Hamelers, H.V.M., Buisman, C.J.N., 2012. Ammonium recovery and energy production from urine by a microbial fuel cell. *Water Res.* 46, 2627–2636.
- Mackinnon, I.D.R., Barr, K., Miller, E., Hunter, S., Pinel, T., 2003. Nutrient removal from wastewaters using high performance materials. *Water Sci. Technol.* 47, 101–107.
- Makhloufi, C., Lasseugette, E., Remigy, J.C., Belaisaoui, B., Roizard, D., Favre, E., 2014. Ammonia based CO₂ capture process using hollow fiber membrane contactors. *J. Membr. Sci.* 455, 236–246.
- Mani, F., Peruzzini, M., Stoppioni, P., 2006. CO₂ absorption by aqueous NH₃ solutions: speciation of ammonium carbamate, bicarbonate and carbonate by a ¹³C NMR study. *Green. Chem.* 8, 995–1000.
- McAdam, E.J., Pawlett, M., Judd, S.J., 2010. Fate and impact of organics in an immersed membrane bioreactor applied to brine denitrification and ion exchange regeneration. *Water Res.* 44, 69–76.
- McLeod, A., Buzatu, P., Autin, O., Jefferson, B., McAdam, E.J., 2014. Controlling shell-side crystal nucleation in a gas-liquid membrane contactor for simultaneous ammonium bicarbonate recovery and biogas upgrading. *J. Membr. Sci.* <http://dx.doi.org/10.1016/j.memsci.2014.07.063>.
- McLeod, A., Jefferson, B., McAdam, E.J., 2013. Quantifying the loss of methane through secondary gas mass transport (or 'slip') from a micro-porous membrane contactor applied to biogas upgrading. *Water Res.* 47, 3688–3695.
- Nii, S., Takeuchi, H., 1992. Removal of CO₂ by gas absorption across a polymeric membrane. *J. Chem. Eng. Jpn.* 25, 67–72.
- Niu, Z., Guo, Y., Zeng, Q., Lin, W., 2012. Experimental studies and rate based process simulations of CO₂ absorption with aqueous ammonia solutions. *Ind. Eng. Chem. Res.* 51, 5309–5319.
- Noble, R.D., Stern, S.A., 1995. *Membrane Separations Technology: Principles and Applications*. Elsevier, Amsterdam.
- Patterson, T., Esteves, S., Dinsdale, R., Guwy, A., 2011. An evaluation of the policy and techno-economic factors affecting the potential for biogas upgrading for transport fuel use in the UK. *Energy Policy* 39, 1806–1816.
- Persson, M., Jonsson, O., Wellinger, A., 2007. Task 37 – Biogas Upgrading to Vehicle Fuel Standards and Grid Injection. IEA Bioenergy, pp. 8–9.
- Prasad, R., Sirkar, K.K., 1989. Hollow fiber solvent extraction of pharmaceutical products: a case study. *J. Membr. Sci.* 47, 235–259.
- Puxty, G., Rowland, R., Attalla, M., 2010. Comparison of the rate of CO₂ absorption into aqueous ammonia and monoethanolamine. *Chem. Eng. Sci.* 65, 915–922.
- Rautenbach, R., Welsch, K., 1994. Treatment of landfill gas by gas permeation – pilot plant results and comparison to alternatives. *J. Membr. Sci.* 87, 107–118.
- Read, A., Hofmann, F., 2011. Does biogas scrub up? *Mater. Recycl. World* 2, 20–21.
- Rongwong, W., Boributh, S., Assanumrungrat, S., Laosiripojana, N., Jiratananon, R., 2012. Simultaneous absorption of CO₂ and H₂S from biogas by capillary membrane contactor. *J. Membr. Sci.* 392–393, 38–47.
- Shao, P., Dal-Cin, M., Kumar, A., Li, H., Singh, D.P., 2012. Design and economics of a hybrid membrane-temperature swing adsorption process for upgrading biogas. *J. Membr. Sci.* 413–414, 17–28.
- Shuangchen, M., Huihui, S., Bin, Z., Gongda, C., 2013. Experimental study on additives inhibiting ammonia escape in carbon capture process using ammonia method. *Chem. Eng. Res. Des.* 91, 2775–2781.
- Svetich, R., 1993. Long-term use of clinoptilolite in the treatment of sewage at Tahoe-Truckee Sanitation Agency, Truckee, California. In: *Zeolite'93, Occurrence, Properties and Utilization of Natural Zeolites*, Boise, Idaho, June 20–28.
- Thornton, A., Pearce, P., Parsons, S.A., 2007. Ammonium removal from digested sludge liquors using ion exchange. *Water Res.* 41, 433–439.
- Valenti, G., Bonalumi, D., Macchi, E., 2009. Energy and exergy analysis for the carbon capture with the chilled ammonia process (CAP). *Energy Procedia* 1, 1059–1066.
- Yeh, J.T., Resnik, K.P., Rygle, K., Pennline, H.W., 2005. Semi-batch absorption and regeneration studies for CO₂ capture by aqueous ammonia. *Fuel Process. Technol.* 86, 1533–1546.
- Zeng, Q., Guo, Y., Niu, Z., Lin, W., 2011. Mass transfer coefficients for CO₂ absorption into aqueous ammonia solution using a packed column. *Ind. Eng. Chem. Res.* 50, 10168–10175.
- Zeng, Q., Guo, Y., Niu, Z., Lin, W., 2013. The absorption rate of CO₂ by aqueous ammonia in a packed column. *Fuel Process. Technol.* 108, 76–81.