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Graphical abstract

Carbon dioxide dissolution and ammonia losses in bubble columns for precipitated calcium carbonate (PCC) production

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Abstract:

The slag2PCC concept aims at transforming steelmaking slag into precipitated calcium carbonate (PCC) with market value. This paper reports on R&D work on two features that impact the overall performance and costs of slag2PCC as a carbon capture and utilisation (CCU) technology. Operating near ambient conditions, calcium is selectively leached from steelmaking slag using aqueous ammonium salt solvent, followed by carbonation using a CO₂-containing stream. Separators for removing spent slag and PCC connect two reactors for extraction and carbonation, respectively, between which the solvent solution is cycling. One requirement is effective conversion of the CO₂ fed to the system: while the dissolution of CO₂ is the rate-limiting step it is essential to minimise release of unreacted CO₂. Mixing the solutions enhances mass transfer. High-speed video recordings were made around mixers located at various heights in a bubble column, analysing CO₂ bubble swarm dissolution. A second feature studied are losses of ammonia (NH₃) from the solution. An outlet for unreacted gas presents a risk of NH₃ vapour release, which lowers solution alkalinity while adding costs. Multicomponent mixture mass transfer analysis showed that diffusion of NH₃ into CO₂ bubbles may be significant at least during initial stages of dissolution. Experimental findings were verified.

Keywords:

Mass transfer, Carbon dioxide (CO₂), Bubble swarm dissolution, Ammonia, Precipitated calcium carbonate (PCC), Carbon dioxide capture and utilisation (CCU)

1. Introduction

CO₂ mineral sequestration, binding CO₂ into a solid, environmentally benign carbonate material is seen by many as a CCU (carbon capture and utilisation) rather than CCS (carbon capture and storage) technology. The latter is then defined by transport by pipeline of pre-separated CO₂ to an underground storage site. The very slow large-scale deployment of such defined CCS results from the question of how the costs can be transformed into profit; in practice this means using the CO₂ for EOR (enhanced oil recovery), primarily in North-America. Indeed, in today's world (early 2019) 14 of 19 large-scale operating CCS projects are CCS-EOR projects storing / using ~ 29 Mt/a CO₂ while 5 CCS projects adding up to ~ 6.7 Mt/a CO₂ involve dedicated geological storage [1]. Obviously, using CO₂, the “U” of CCU is the key to economic viability and as a result the use of the abbreviation CCUS (carbon capture, utilisation and storage) is gaining ground.

CO₂ mineral sequestration can make use of the world's abundant magnesium silicate resources (for example waste piles from mining activities) or, although offering a much smaller capacity, alkaline industrial by-products and wastes such as steelmaking slags and phosphogypsum [2,3]. Quite a few process routes have been developed that divert such material streams from landfills by producing carbonates and other materials with market value, mitigating CO₂ emissions while generating revenue. Examples are (hydro) carbonates of magnesium and calcium, silica and several metallic elements varying from iron to copper, nickel, chromium and even rare earth metals (REEs). Typically the routes operate at (or near) ambient temperatures and pressures, in aqueous solutions, using chemical additives that can be recovered. For the current paper the product of primary importance is precipitated calcium carbonate (PCC) with market values in the range of 100 ~ 400 €/ton depending on particle size and crystal shape, for a high purity (> 99% CaCO₃) material. PCC finds many applications in papermaking, as filler or coating material in plastics, in paints, cosmetics and pharmaceuticals. (The steelmaking slag used for the work in this paper contained economically interesting amounts of vanadium, worth further study.)

Unfortunately, the international CCU/CCS community has difficulties positioning CO₂ mineral sequestration and its potential is grossly underestimated. One significant benefit of CO₂ mineral sequestration is that it can operate on CO₂-containing gas rather than pre-separated CO₂, removing the expensive CO₂ capture step from the process chain.

Arguments like “*Mineralisation is a niche opportunity not a global solution and is at very best CO₂ neutral as it only serves to recombine minerals that have been de-carbonated with the CO₂ they lost during processing*” [4] can be discarded as “fake news”. It is an accepted fact that

suitable magnesium silicate rock is available amounts that exceed the needs for large-scale CCS / CCUS and dwarf the capacity of geological formations for CO₂ storage [5]. These silicates, of course, do not release CO₂ during processing, apart from possible emissions from producing the electricity needed for rock crushing/grinding for which contributes very little to energy use (and CO₂ produced) during CO₂ mineralisation. And although many calcium-based industrial waste streams indeed derive from limestone (calcium carbonate), using a calcium-containing industrial waste stream rather than virgin limestone rock avoids the production of CO₂ by the heat source (i.e. fuel) needed for calcining the limestone to lime, calcium oxide, which adds 50% to the CO₂ resulting from the calcination [6].

One CCU / CCUS process that has been under development towards commercial application (in Finland) for more than a decade is the slag2PCC concept. The aim of the process concept – see Fig. 1 – is to produce a high quality PCC from steelmaking slags. More specifically, it uses steel converter slag from a basic oxygen furnace (BOF), an industrial by-product produced at a rate of several 100 Mt/a globally that mostly is landfilled. The slag2PCC route employs an aqueous solution of ammonium salt (chloride, nitrate or acetate) to selectively extract calcium from the slag in an extraction step, followed by carbonation in a second, carbonation step, with both steps operating at (close to) ambient temperatures and pressures. Ammonium salt solvent solution is cycled between the extraction and carbonation reactors via separators for the removal of spent slag and PCC product [7-11].

Fig. 1. The slag2PCC precept concept for PCC production from steelmaking slags

Conventional PCC production implies producing slaked lime, Ca(OH)₂, from lime, CaO, followed by carbonation. Notwithstanding the significant CO₂ emissions reduction of the slag2PCC route compared to conventional PCC production the scale-up to an industrial scale processing, say, ~25 t/h BOF slag faces several challenges/drawbacks:

- Dissolution of CO₂ bubble swarms in the aqueous solution is the rate-determining process step (which applies also to conventional PCC production)
- Ammonia may evaporate from the solutions and leave the process with exit gas (note that when operating on pure CO₂ there need not be any exit gas)
- Significant amounts of water may be needed to wash the PCC product (to recover solvent salt)

- Separation of the solids (slag residue and PCC product) from the aqueous streams is not trivial
- Not all calcium is extracted from the slag, and a significant amount of residual solids remains

Focussing on the carbonation reactor (see Fig. 1) this paper addresses the first two of these points, which we expected to be correlated.

2. Effect of mixing on CO₂ bubble swarm dissolution

Having earlier recognised that CO₂ dissolution into the aqueous solution in the carbonation reactor is the rate-determining step for PCC production [12] we have in detail studied the dissolution of CO₂ bubbles and bubble swarms in water and in salt-containing aqueous solutions. Not only does incomplete CO₂ dissolution give flawed performance from a CO₂ emissions mitigation point of view. It also introduces the risk of an ammonia slip as a result of possible ammonia transfer from the aqueous solution into CO₂ bubbles travelling upwards in the carbonation reactor, or via an overhead gas space in the carbonation reactor. This is addressed in section 3 of this paper.

Results we recently reported show (theoretically and experimentally) that 4 - 5 mm CO₂ bubbles released at the bottom of a 2 m column of water dissolve after rising approx. 1.6 - 1.9 m [13,14]. That work involved single droplets injected with short time intervals; this paper addresses bubble swarms. Mixing impellers were used as well, which should reduce the reactor height needed for bubble dissolution. This section analyses the impact of mixing on CO₂ or air bubble swarm dissolution.

Recently it was reported (for oxygen dissolution in water) that the Sherwood number quantifying the mass transfer for single rising bubbles is close to that for swarms for a given Reynolds number based on average vertical bubble rise velocity. This was found to hold for gas volume fractions up to 30%, for slow diffusion of the gas in the liquid (i.e. a high Péclet number). Moreover, it was stated that mass transfer conditions are similar to those for a bubble rising in a fluid at rest [15]. The results given below allow for analysing this for CO₂: Péclet numbers cannot be large for very small bubbles of a gas with a higher solubility in water than oxygen.

2.1. Experimental set-up and procedure

For analysis of the dissolution of CO₂ (or air) bubble swarms in water a 2 m high, 12.7 cm inner diameter polycarbonate bubble column was used, with a liquid volume of ~ 24.9 L, as in [14]. A mixer was added to the bubble column, scaled, similar to the column diameter to ½ the size of what was used in the 2×30 litres slag2PCC test set-up by Mattila [7,8]. Along a total length (height) of 2 m, four pitched blade mixers are located at 24.4 cm, 74.4 cm, 120.6 cm and 170.6 cm, respectively, from the gas distributor that also supports the mixer as shown in Fig. 2. This gas distributor, shown in more detail, has eight lines of four holes (0.5 mm) at 45° angles between the lines of holes.

Fig. 2. The bubble column used, with mixer, and a close-up of the gas distributor

Pure CO₂ or air was fed from a bottle equipped with a rotameter flow meter calibrated for air and CO₂ allowing for flows up to 0.9 and 0.5 l/min (STP), respectively. All tests were done at ambient conditions, with temperatures in the range 18.3 - 22.4 °C, with a gas flow of 0.25 l/min STP. The column solution was flushed and new (tap) water was taken when the solution pH, measured at the top of the column, dropped to values below 5.7, thus assuring < 5% saturation of water with CO₂. Impeller speed was 0, 50, 100, 150 or 200 rpm.

The image recording set-up consisted of a high-speed Photron camera SA3 Model 120K-M3 equipped with a 52 mm Nikon 200773 lens. To avoid reflections and shadows the lighting, supplied by a set of eight parallel arrangement of fluorescence tubes T5 39 W was put behind the column. Videos of 3 s (stored as three sections á 1 s) duration were taken at different heights: both the camera and the lighting vertical position could be adjusted. Most video recordings were taken around the mixing impellers and at the height of the gas inlet. The distance from the camera (lens) to the column was ±45 cm while the lighting was ±20 cm behind the column. This gave a window of ~15 cm used for all measurement heights. The special resolution of the system is 6.9 pixel/mm at a frame rate of 1000 images per second with a constant exposure of 1/2000.

Video recordings cannot be easily processed into bubble size and velocity distributions as a result of the use of only one plane of vision which implies that visibility of the bubbles coming out of or into the focal plane affects the bubble size and appearance. For more quantitative measurements a perpendicular frame (i.e. a second camera) would be needed. Nevertheless, one plane can be useful to provide a comparison point for bubble dissolution as the primary

goal of the measurements is to compare the effects of different mixing rates (impeller rpm) on bubble swarm dissolution. Therefore, the reporting below gives first a qualitative analysis of the recorded images, allowing for general statements on the effect of mixing, followed by a more elaborated algorithm (Matlab) – based analyses that aims at producing bubble size and velocity information, in the form of distribution functions. More detail on the set-up and size/velocity measurements is given elsewhere [14,16].

2.2. Qualitative analysis of images

An overview of “screengrabs” from the video recordings on CO₂ bubble swarm dissolution (0.25 l/min STP) in water at room temperature for five mixer rotational speeds and four heights above the gas distributor inlet) in the column is given in Fig. 3; two examples to be further discussed in more detail are given in Fig. 5.

Fig. 3 Summary of screenshots on CO₂ bubble swarm dissolution (0.25 l/min STP) in water at room temperature for five mixer rotational speeds and four heights (24.4, 74.4, 120.6 and 170.6 cm above the gas distributor inlet) in the column.

Before any digital tool – supported image analysis, several features can be distinguished from the images, apart from the obvious effect of bubble size decreasing with height, irrespective of mixing:

- For the lowest height, no clear effect of mixing (speed) is seen, although at the highest 200 rpm mixing rate the number of bubbles seems to be somewhat higher. For a constant flow rate, the number of bubbles formed at the distributor is unchanged. According to [14], for a single CO₂ bubble at this position the diameter would decrease from 5 mm to 4.5 mm, *i.e.* ~ 25% dissolution.
- For the second height, it can be seen that bubbles are smaller with increasing mixing speed. Perhaps a mixing speed still higher than 200 rpm would give still smaller bubbles. According to [14], for a single CO₂ bubble, at this position the diameter would decrease from 5 mm to 3 mm, corresponding to ~ 75% dissolution. Clearly, this is an important zone in the bubble column.
- For the third height, the effect of mixing is similar to what is seen at the second height but less clear since the bubbles are already quite small. According to [14], for a single CO₂

bubble, up to here the diameter would decrease from 5 mm to ~1.5 mm, approaching 98 % dissolution.

- For the fourth height, bubble sizes look similar for all mixing rates. A single bubble would be very small if not completely dissolved at this point [14].

Overall, the height section 0.5 – 1 m is where dissolution is most affected by mixing rate, judging from the size of the bubbles. Some explanation can be given using the analysis on single bubble rise in [14] – Fig. 12 of that is given here as Fig. 4. This suggests that bubble shape (given as aspect ratio) is important: wobbling bubbles in the lower section of the column are less affected by mixing since they exhibit non-vertical velocity components already, while the smallest bubbles in regions higher up are spherical and thus more hydrodynamically stable due to surface tension.

Fig. 4. Single dissolving CO₂ bubble shape vs. height in the column as reported in [14].

Increasing mixing speed from 0 to 200 rpm does increase bubble dissolution mainly in the middle section of the reactor; bubble sizes at height 3 (120.6 cm) at 0 rpm mixing appear not very different from those at height 2 (74.4 cm) at 200 rpm mixing. This is illustrated by Fig. 5.

Fig. 5. Bubble sizes at height level 3 (120.6 cm) 0 rpm (left) versus height 2 (74.4 cm) 200 rpm (right)

This analysis suggests that the positioning of mixing impellers can be optimised for the bubble dissolution: at certain ranges for the carbonation reactor height impellers can be omitted as they would not give any beneficial effect. For a bubble column reactor in which eventually solid particles are formed (as is the case for slag2PCC) this should be re-assessed since the motivation for using pitched blade impellers is to prevent the particles from settling towards the vessel bottom too fast.

2.3. Quantitative analysis of images

For a more conclusive analysis, an algorithm written in Matlab was used for image analysis. Due to the complex behaviour of the bubble swarm in a mixer environment, plus the effect of optical distortion due to the curvature of the vessel and the fluid surrounding the gas phase,

several processing steps are needed before bubble sizes and bubble swarm size distributions can be given:

1. Synchronisation, using a recording of the moving impeller without a bubble swarm. After this the impeller could be “subtracted” from the images
2. Optical correction to remove the optical distortion caused by the cylindrical vessel. For this, a grid pattern was immersed in water in a cylinder (identical to the bubble column) was used giving an image that allowed for defining a linear transformation as to correct for the distortion.
3. Filtering (using a Laplacian filter) and contrast enhancement
4. Colour of depth level for black-and-white conversion. Here values in the range 23 – 35 were used, optimised from a Pareto front after determining the number of bubbles seen vs. colour of depth (0 = black, 255 = white, for 8-bit processing)
5. A selection algorithm is used to determine the size distribution of a bubble swarm, as an average value over 1 s (= 1000 images)

Details of the data analysis procedure and more results than given here were recently reported elsewhere [16]; Fig. 6 gives results for CO₂ bubbles at the lowest and highest mixing impeller levels in the column, at 100 rpm. The error bars are based 100 ~ 200 bubbles present in the 1000 images recorded during one second, with bubbles moving through the image at 0.1 ~ 0.4 m/s. These results can be processed to a mean diameter value: this gives 3.90 mm for the first height level and 1.50 mm for the highest level. Assuming spherical volumes this suggests a volume reduction of ~ 94 %, not the full dissolution we observed earlier at this height level for single bubbles. For air bubbles the results show distributions similar to the left-hand Fig. 6, more or less unchanged for different heights. Processing the images shown in Fig. 5 gave mean diameters 1.83 mm (left) and 2.13 mm (right), respectively [16].

Fig. 6 CO₂ bubble size distributions at different height levels in the bubble column, during mixing at 100 rpm. Left: level 1 = 24.4 cm and right: level 4 = 170.6 cm above the gas inlet. (Colour of depth values 35 and 23, respectively, were used.) Error bars give standard deviation. Note different axes!

3. Losses of ammonia from the bubble column

The system $\text{CO}_2 - \text{H}_2\text{O} - \text{NH}_3$ is becoming increasingly important for CCUS applications. Ammonia offers an alternative for amine-based aqueous solutions for CO_2 capture, avoiding oxygen-containing gas degrading the solvent and giving a lower energy penalty for solvent regeneration, at the cost of slower chemisorption kinetics [17,18]. Most important here are the chilled and aqueous ammonia processes (CAP, AAP) operating at 2-10°C (preferably) or 25-40°C, respectively. Lower temperature gives less ammonia slip while the precipitation of ammonium salts is possible [19], although at room temperature formation of solid ammonium bicarbonate and carbamate in the gas was found [20].

Unlike conventional PCC production, the carbonation reactor solution contains dissolved ammonia that, similar to CAP or AAP CO_2 capture, may escape as an ammonia slip. Likewise, that would require downstream measures as to avoid excessive costs for make-up chemicals besides an impact on the environment. Ma and co-workers [21,22] recently studied mass transfer and ammonia escape during CO_2 capture in a bubble reactor, at 10-40 °C. Similar to earlier work at Aalto Univ. (see below) infrared (IR) gas analysis was used to measure ammonia concentrations in gas from the reactor.

3.1. Experimental work on release of ammonia and other gases

For this analysis only CO_2 bubbles, not air, are considered. Test results from earlier slag2PCC work at Aalto Univ. have been reported by Eloneva et al. [23] for lab-scale and later Said et al. [9] using the demonstration plant, for different ammonium salt solvent solutions. An FT-IR gas analyser Gaset (Temet Instruments DX-4000) was used to measure concentrations of H_2O , CO_2 and NH_3 in the gas leaving the carbonation reactor, containing a calcium-rich solution from BOF slag extraction.

At ÅA the release of NH_3 from the solution in the column was measured using a 1 litre of hydrochloric acid at $\text{pH} \approx 1.6$ washing bottle for gases leaving the column. At $\text{pH} 9$ in the column the solution in it contains $10\times$ the NH_3 needed to bring the washing bottle pH to neutral = 7 and a 5% release of the dissolved NH_3 would bring it to $\text{pH} > 2$. The solutions used in the column were 1) CaCl_2 and NH_4Cl (0.1 and 0.01 M, respectively) in water, 2) CaCl_2 and NH_4Cl as above, plus added NH_3 (25 %-wt NH_3 in water) to raise the pH to 9 - 10, making PCC

precipitation possible and 3) a solution produced from BOF slag using a 0.5 M NH_4Cl solvent solution. (For this, 1250 g BOF slag, as received in 2012 [8] was extracted in 25 litres (tap) water + NH_4Cl solution; after 1 h the solid residue was separated using an inclined settler. The clear, colourless solution was transferred to the bubble column and a few litres of water were added to fully fill the column. At that point, $\text{pH} = 9.83$.)

Results are summarised in Table 1. At Aalto Univ. a clear increase of NH_3 release was found at lab-scale when diluting the CO_2 feed with N_2 , at the same time lowering the release of water vapour, for solutions with NH_4NO_3 as the solvent salt. For a test with NH_4Cl the release of both NH_3 and water are much lower, about $\frac{1}{2}$ the releases measured with NH_4NO_3 solvent [23]. With the pilot scale unit, with a slag extraction product solution with NH_4Cl solvent, a clear effect of temperatures 45, 50 and 60°C was seen, with NH_3 concentrations in the gas from the carbonator increasing from 0.11 %-vol to above 2 %-vol [9]. Besides a lower temperature and despite the higher solvent concentration, lab-scale NH_3 losses may be lower as a result of a lower pH , as noted in [23].

Table 1. Experimental results on gaseous emissions from slag2PCC carbonation reactors

At ÅA, no rise in the pH level in the washing bottle was ever seen, not even after repeatedly adding aqueous ammonia solution to the reactor during the tests with mixed calcium and ammonium salts to raise the pH level as to allow for PCC crystallisation, nor while using the washing bottle solution for several tests in a row. This may be the result of the low temperature, the bubble swarms dissolving completely, or the low concentration of dissolved salts compared to the work at Aalto Univ.

3.2. Model description for ammonia mass transfer

While bubbles move upwards and dissolve in water, dissolved substances as well as water itself may be transferred into the bubbles, thus transporting material to the top of the bubble column. There, an overhead gas space may fill with vapour from which it may be vented or, if such space is not available, a gas flow leaves the column directly without equilibrating with the top of the solution.

The geometry of the bubbles and the concentration profiles of the three mentioned species in- and outside a bubble with diameter d_b are shown in Fig. 7. A two-film model with boundary layer thicknesses Δ_o and Δ_i at the bubble surface is used, noting that values for Δ_o and Δ_i differ for the chemical species considered.

Fig. 7. Impression of CO₂ bubbles rising and dissolving in a bubble column reactor and a simplified close-up of concentration profiles inside and outside a bubble

For the slag2PCC concept, CO₂ bubbles rise in a solution containing primarily Ca²⁺, OH⁻, HCO₃⁻, NH₄⁺ and Cl⁻ ions, besides (unless pH > 9.5) smaller amounts of CO₃²⁻. Thus, with dissolved NH₄⁺ ions seeking equilibrium with dissolved NH₃, NH₃(aq), dissolution of NH₃ into the CO₂ bubbles is a possibility. Likewise, water may diffuse into the bubbles. For other species (such dissolved air, *i.e.* N₂ and O₂) concentrations will be low or no significant driving force for diffusion exists (such as CaCl₂ or NH₄Cl). Thus, only H₂O, CO₂ and NH₃ mass transfer are considered below.

3.2.1 Dissolved molecular ammonia and carbon dioxide

For the mass transfer analysis the concentrations of dissolved molecular ammonia and carbon dioxide, NH₃ (aq) and CO₂ (aq) were calculated for solution pH values 7 - 10, using data for the dissolved salts and species in the Aalto Univ. carbonator reactors and the ÅA bubble column. Using HSC 5.1 as well as FactSage 6.4 software, Gibbs energy minimisation gave the equilibrium concentrations for the temperatures where experiments had been made, for the following species (with NH₄Cl solvent):

- Solid: CaO, Ca(OH)₂, CaCO₃, CaCl₂, NH₄Cl, NH₄HCO₃ and (NH₄)₂CO₃
- Aqueous solution: H₂O, NH₃ (aq), CO₂ (aq), ions NH₄⁺, Cl⁻, HCO₃⁻, CO₃²⁻, Ca²⁺, OH⁻, H₃O⁺
- Gas: CO₂, NH₃, N₂

The FactSage software allowed for adding several other nitrogen-species that weren't optional in HSC. Calculations implied increasing the amount of CO₂ (gas) fed to the solutions and follow the amounts of materials and phases while pH decreased.

Table 2. Dissolved ammonia and carbon dioxide for slag2PCC carbonation solutions, pH 7-10

Results (obtained with Factsage) are given in Table 2, showing that dissolved CO_2 concentrations increase 8 orders of magnitude when solution pH decreases from 10 to 7, while dissolved NH_3 concentrations decrease 2-3 orders of magnitude for the same pH change. In the pH interval studied, HCO_3^- ions will be the most abundant product of CO_2 dissolution. For pH 7 the value for dissolved CO_2 is close to the solubility of CO_2 . (A recent MSc thesis at Aalto Univ. dealing with the slag2PCC concept [24] notes that the difference between CO_2 solubility in pure water or in 1 M NH_4Cl is very small.) The potential for NH_3 diffusion to / into a CO_2 bubble will be highest at high pH values (confirming [23]) where the driving force of CO_2 dissolution (in opposite direction) is high too.

3.2.2 Transport of water from solution to bubbles

Since bubbles are fed as pure (or mainly) CO_2 into the solution, a driving force exists for H_2O to diffuse to and into the bubbles. With the liquid phase essentially being water (liquid molar fraction $x_{\text{H}_2\text{O}} \approx 1$) the equilibrium amount of water in the gas phase follows from Raoult's law, which gives for the equilibrium water molar fraction $y_{\text{H}_2\text{O}}$:

$$y_{\text{H}_2\text{O}} = \frac{p_{\text{sat}}}{p_b} \left(\frac{\text{mol}}{\text{mol}} \right) \quad (1)$$

At 20 – 25 °C the saturation pressure for water, p_{sat} , is 2330 – 3169 Pa. The total pressure p_b inside a bubble at height z (m) from the distributor plate inlet upwards into the 2 m water column equals

$$p_b = p^0 + (1 - \alpha) \cdot \rho_{\text{H}_2\text{O}} \cdot (2 - z) \cdot g + \frac{\sigma}{4d_b} \quad (\text{Pa}) \quad (2)$$

where p^0 = ambient pressure ≈ 101 kPa, bubble volume fraction α (here $\ll 1$), gravity g , water – CO_2 surface tension $\sigma \approx 0.072$ N/m, and bubble diameter d_b . At the gas inlet where $d_b \approx 5$ mm (2) gives $p_b \approx 120$ kPa. Laplace pressure contributes < 1 kPa to p_b until $d_b < 10$ μm , which is smaller than the image recording and processing resolution. Thus, $p_b = 110$ kPa can be taken as an height-averaged value which then with (1) gives $y_{\text{H}_2\text{O}} = 0.02 - 0.03$ for 20 – 25 °C, which confirms the findings of Eloneva et al. (for 30°C, where $p_{\text{sat}} = 4246$ Pa) [23]. At 45 – 60°C $y_{\text{H}_2\text{O}}$ may, however, increase to 0.1 – 0.2.

3.2.3 Simultaneous transport of CO_2 , NH_3 , H_2O between bubbles and solution

The three-component (ternary) mass transfer will be described by Maxwell-Stefan (MS) diffusion equations, with MS diffusion coefficients $\bar{D}_{i,j}$ rather than Fick's classical description using binary diffusion coefficients $D_{i,j}$ for species i with respect to j [25, 26]. For the gaseous and liquid phases the diffusivities $\bar{D}_{i,j}$ are calculated using the kinetic gas theory and the sphere-in-liquid theory, using the diffusion volumes for the species. Values for the $\bar{D}_{i,j}$ (with $\bar{D}_{i,j} = \bar{D}_{j,i}$) are given in Table 3, for a static pressure $p = 110$ kPa, liquid phase viscosity $\eta = 10^{-3}$ Pa·s, temperature range 20–50°C, using expressions in [26]. For the aqueous solution, $\bar{D}_{CO_2, NH_3}$ has little practical importance; gas phase CO_2 and NH_3 may form solid ammonium carbamate or, if water vapour is present, (bi) carbonate.

Table 3. Calculated Maxwell-Stefan diffusion coefficients for ternary system CO_2 , H_2O , NH_3 , in liquid (aqueous) phase and gas phase.

The surface renewal theory for bubbles of a few mm rising in a fluid allows for estimating the mass transfer coefficients on bubble in- and outside:

$$k_{i,j} = 0.4 \left(\frac{g^2 \Delta \rho^2}{\eta \rho} \bar{D}_{i,j}^3 \right)^{1/6} \left(\frac{m}{s} \right) \quad (3)$$

where $\Delta \rho^2 / \rho \approx \rho$ for the difference $\Delta \rho$ between liquid and gas phase density and liquid density ρ [26]. Values are given in Table 4 – the values for k_{CO_2, H_2O} correspond with the value $2 \dots 5 \times 10^{-4}$ m/s we recently reported for single CO_2 bubbles rising in water [14].

Table 4. Calculated mass transfer diffusion coefficients for ternary system CO_2 , H_2O , NH_3 , in liquid (aqueous) phase and gas phase.

As gas phase diffusivities are much higher than liquid phase diffusivities it is assumed that the gas inside the bubbles is well mixed. Also, the thickness of the boundary layer $\Delta_i = \bar{D}_{i,j} / k_{i,j}$ inside the bubble becomes of the same order of magnitude as the size of the bubble.

The transport equations to be solved for the molar fluxes $\dot{N}_{CO_2}$, $\dot{N}_{NH_3}$ and $\dot{N}_{H_2O}$ (mol/(s·m²)) from bubble to solution or *vice versa* are:

$$\begin{aligned}
 -\Delta x_{CO_2} &= \frac{\bar{x}_{NH_3}\dot{N}_{CO_2} - \bar{x}_{CO_2}\dot{N}_{NH_3}}{k_{CO_2,NH_3}\bar{c}} + \frac{\bar{x}_{H_2O}\dot{N}_{CO_2} - \bar{x}_{CO_2}\dot{N}_{H_2O}}{k_{CO_2,H_2O}\bar{c}} \quad \left(\frac{mol}{mol}\right) \\
 -\Delta x_{NH_3} &= \frac{\bar{x}_{CO_2}\dot{N}_{NH_3} - \bar{x}_{NH_3}\dot{N}_{CO_2}}{k_{CO_2,NH_3}\bar{c}} + \frac{\bar{x}_{H_2O}\dot{N}_{NH_3} - \bar{x}_{NH_3}\dot{N}_{H_2O}}{k_{NH_3,H_2O}\bar{c}} \quad \left(\frac{mol}{mol}\right) \\
 -\Delta x_{H_2O} &= \frac{\bar{x}_{CO_2}\dot{N}_{H_2O} - \bar{x}_{H_2O}\dot{N}_{CO_2}}{k_{CO_2,H_2O}\bar{c}} + \frac{\bar{x}_{NH_3}\dot{N}_{H_2O} - \bar{x}_{H_2O}\dot{N}_{NH_3}}{k_{NH_3,H_2O}\bar{c}} \quad \left(\frac{mol}{mol}\right)
 \end{aligned} \tag{4}$$

with molar fraction x in the aqueous solutions, $\Delta x = x_{bulk\ solution} - x_{bubble\ surface} = x - x^*$, and average value $\bar{x} = 1/2 \cdot (x_{bulk\ solution} + x_{bubble\ surface})$. Overall bulk concentration $\bar{c} \approx 55555\ mol/m^3$ is used for the aqueous solution, where $x_{H_2O} \approx 1$ and the surface concentrations are calculated using Henry's law for CO_2 and NH_3 , based on the composition of the bubble:

$$\begin{aligned}
 x^* &= \frac{p_b}{H}y \quad \text{for } NH_3 \text{ and } CO_2, \text{ with initially } y_{CO_2} = 1 \quad \left(\frac{mol}{mol}\right), \\
 x_{H_2O}^* &= 1 - x_{NH_3}^* - x_{CO_2}^* \quad \left(\frac{mol}{mol}\right)
 \end{aligned} \tag{5}$$

Values for x are taken constant (calculated from Table 2) and values for y vary as a result of transport which affects values for x^* . This gives changes in Δx and $\bar{x}$ and as a result changed fluxes $\dot{N}$. Henry coefficient NH_3 in water: $H\ (bar) = 1.71 + 0.053 \cdot T\ (^{\circ}C)$; CO_2 in water: $H\ (bar) = 412 + 49 \cdot T\ (^{\circ}C)$, using [27]. No correction for dissolved ions was made, as a correction by Wiesenberger and Schumpe (see e.g. [28]) gave little effect.

Bubble size changes as a result of imbalance between in- and outgoing mass transfer; experiments at ÅA suggest that CO_2 fluxes from a bubble are (much) larger than incoming fluxes of NH_3 and H_2O . Below, however, only fluxes immediately after entrance of a bubble into the carbonation reactor are analysed.

Fig. 8 gives the rates of diffusion of the three species in the aqueous phase, away from a bubble (a negative value implying diffusion towards a bubble) when a bubble is introduced to the solution. This is either as pure CO_2 (case a [23], $50^{\circ}C$ and case c, our data, $20^{\circ}C$) or as 50% CO_2 in N_2 (case b, [9], $30^{\circ}C$) where the N_2 is assumed non-dissolving.

Fig. 8 Diffusive fluxes of CO_2 , NH_3 and H_2O in the aqueous solution away from (> 0) or to (< 0) a bubble entering the carbonation reactor. Case a: Aalto Univ., demo plant $50^{\circ}C$, 100%

CO₂. Case b: Aalto Univ., lab-scale 30°C, 50% CO₂ in N₂. Case c: ÅA bubble column, 20°C, 100% CO₂.

The results in Fig. 8 confirm the experimentally recorded NH₃ emissions at Aalto (cases a,b) whilst none were seen at ÅA (case c.), presumably as a result of a lower temperature and much lower ammonium salt concentrations at ÅA. When surrounded by sufficiently high ammonium salt and dissolved ammonia concentrations, fluxes of NH₃ towards a bubble can exceed the fluxes of CO₂ (and water) away from a bubble. This opens a path for transporting NH₃ to the top of the reactor and eventually leaving it with a gas flow in the event that the reactor height is insufficient for complete dissolution of the rising bubble swarms.

As shown – looking at cases a) and b) in Fig. 8 –, solution pH combined with temperature determine in a complex way whether an NH₃ flux towards (and into) bubbles can locally override fluxes (out of and) away from bubbles, at least during the first stages of the dissolution process.

The here presented approach gives a tool for assessing or beforehand predicting this – it can be combined with numerical analysis of travelling bubbles through solutions with vertical concentration profiles of the important species. Nonetheless, future work with the slag2PCC demo-facility at Aalto should address the effect of the filling level of the carbonator reactor and the presence of overhead gas space.

4. Conclusions

This paper addresses two features of the slag2PCC process that need to be well understood while developing an academic activity to a commercial application: 1) the dissolution rate of CO₂ bubble swarms in aqueous solutions and how mixing impellers affect it, and 2) the release of ammonia, NH₃, from the solvent solution with exit gas, possibly the result of dissolved ammonia from the solution diffusing to and into CO₂ bubbles. High-speed video recording and image analysis shows that CO₂ bubble swarm dissolution is affected by mixing rate especially in the middle section of the bubble column where bubbles may still have an ellipsoidal shape but are no longer “wobbling”. This translates to (equivalent spherical) bubble sizes 1-3 mm. For reactor design this information can be used for positioning mixers and impellers. Diffusion of NH₃ in the solution towards a bubble (and eventually into it) is calculated to be a possibility,

using Maxwell-Stefan description for multi-component mass transfer: NH_3 diffusion may overrule the diffusive fluxes away from bubbles, depending in a complex way on temperature, pH and dissolved species concentrations. Experimental findings were verified.

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Nomenclature

BOF	Basic oxygen furnace
c	Concentration (mol/L or mol/m ³)
D	Diffusion coefficient (Fick) (m ² /s)
$\bar{D}$	Diffusion coefficient (Maxwell-Stefan) (m ² /s)
d_b	Bubble diameter (m)
g	Gravity acceleration 9.8 (m/s ²)
H	Henry coefficient (bar)
k	Mass transfer coefficient (m/s)
L	Litre
MS	Maxwell - Stefan
Mt/a	Million tonnes per annum
$\dot{N}$	Molar diffusion flux (mol/s/m ²)
$p, p^\circ, p_{\text{sat}}$	Pressure, Ambient pressure, Saturation pressure (Pa)
PCC	Precipitated calcium carbonate
STP	Standard temperature and pressure
x	Molar fraction in liquid (aqueous) phase (mol/mol)
y	Molar fraction in gas phase (mol/mol)
z	Height in column calculated from gas inlet (m)
ÅA	Åbo Akademi University
α	Volume fraction gas phase (m ³ /m ³)
Δ_i, Δ_o	Boundary layer thickness at bubble surface: inside or outside (m)
η	Dynamic viscosity (Pa·s)

ρ	Density (kg/m ³)
σ	Surface tension (N/m)
$x^*, \bar{x}, \Delta x$	Saturation value for x, Average value for x, Difference for x

References

- [1] Global CCS Institute > CO₂RE database > Resources > Facilities. Available at: <<https://co2re.co/StorageData>> [accessed 3.3.2019]
- [2] IPCC. IPCC Special Report on Carbon Dioxide Capture and Storage. NY, USA: Cambridge University Press, Cambridge, United Kingdom and New York; 2005, Chapter 7
- [3] Sanna, A., Uibu, M., Caramanna, G., Kuusik, R., Maroto-Valer, M., A review of mineral carbonation technologies to sequester CO₂. Chem. Soc. Rev., 2014; 43:8049-8080
- [4] Gale, J. GHGT-13 Panel Discussion on CO₂ Utilisation and Conversion, Nov. 24, 2016. Available at: <<https://ieaghg.org/ccs-resources/blog/ghgt-13-panel-discussion-on-co2-utilisation-and-conversion>> [accessed 26.11.2018]
- [5] Lackner, K.S., A guide to CO₂ sequestration, Science, 2003; 300 (5626): 1677-1678.
- [6] Eloneva, S., Said, A., Fogelholm, C.-J., Zevenhoven, R. Preliminary assessment of a method utilizing carbon dioxide and steelmaking slags to produce precipitated calcium carbonate. Appl. Energy 2012; 90: 329-334
- [7] Mattila, H.-P. Utilization of steelmaking waste materials for production of calcium carbonate (CaCO₃) [dissertation]. Turku, Finland: Åbo Akademi Univ.; 2014. Available at: <<http://urn.fi/URN:NBN:fi-fe2014092444878>> [accessed 24.1.2018]
- [8] Mattila, H.-P., Zevenhoven, R. "Designing a continuous process setup for precipitated calcium carbonate production from steel converter slag" ChemSusChem, 2014;7:903-913
- [9] Said, A., Laukkanen, T., Järvinen, M. Pilot-scale experimental work on carbon dioxide sequestration using steelmaking slag. Appl. Energy 2016; 177:602–611
- [10] Said, A. CO₂ sequestration by steelmaking slags for the production of precipitated calcium carbonate - From laboratory to demonstration stage [dissertation]. Espoo, Finland: Aalto Univ.; 2017. Available at: <<http://urn.fi/URN:ISBN:978-952-60-7399-6>> [accessed 24.1.2018]
- [11] Teir, S., Kotiranta, T., Pakarinen, J., Mattila, H.-P. Case study for production of calcium carbonate from carbon dioxide in flue gases and steelmaking slag. J. CO₂ Util. 2016; 14: 37-46

- [12] Mattila, H.-P., Grigaliūnaitė, I., Zevenhoven, R. Chemical kinetics modeling and sensitivity analysis of various process parameters for precipitated calcium carbonate production from steelmaking slags. *Chem. Eng. J.* 2012; 192:77–89
- [13] Legendre, D., Zevenhoven, R. A numerical Euler-Lagrange method for bubble tower CO₂ dissolution modelling. *Chem. Eng. Res. & Design* 2016; 111:49-62
- [14] Legendre, D., Zevenhoven, R. Detailed experimental study on the dissolution of CO₂ and air bubbles rising in water. *Chem. Eng. Sci.* 2017; 158:552-560
- [15] Colombet, D., Legendre, D. (Dominique), Risso, F., Cockx, A., Guiraud, P. Dynamics and mass transfer of rising bubbles in a homogenous swarm at large gas volume fraction. *J. Fluid Mech.* 2015; 763:254-285
- [16] Legendre, D., Zevenhoven, R. Image analysis assessment of the effect on mixing on aqueous dissolution of CO₂ and air bubble swarms in a bubble column. *Chem. Eng. Res. & Design – submitted*
- [17] Hanak, D.P., Biliyok, C., Manovic, v. Rate-based model development, validation and analysis of chilled ammonia process as an alternative CO₂ capture technology for coal-fired power plants. *Int. J. Greenh. Gas Contr.* 2015; 34:52-62
- [18] Mazari, S.A., Ali, B.S., Jan, B.M., Saeed, I.N., Nizamuddin, S. An overview of solvent management and emissions of amine-based CO₂ capture technology. *Int. J. Greenh. Gas Contr.* 2015; 34:129-140
- [19] Darde, V., Thomsen, K., van Well, W.J.M. Erling H. Stenby, E.H., Chilled ammonia process for CO₂ capture. *Energia Procedia* 2009; 1:1035-1042
- [20] Li, X., Hagaman, E., Tsouris, C., Lee, J.W. Removal of carbon dioxide from flue gas by ammonia carbonation in the gas phase. *Energy & Fuels*, 2003; 17:69-74
- [21] Ma, S., Chen, G., Gao, R., Jiaqi, W., Ma, L. Experimental research of ammonia escape in CO₂ absorption using ammonia solution in wetted-wall column. *Int. J. Greenh. Gas Contr.* 2016; 51:254-259
- [22] Ma, S., Chen, G., Zhu, S., Han, T., Yu, W. Mass transfer of ammonia escape and CO₂ absorption in CO₂ capture using ammonia solution in bubbling tower. *Appl. Energy* 2016; 162:354-362
- [23] Eloneva, S., Mannisto, P., Said, A., Fogelholm, C-J., Zevenhoven, R. Ammonium salt based steelmaking slag carbonation: precipitation of CaCO₃ and ammonium losses assessment. *Greenh. Gases: Sci. & Technol.* 2011; 1:305-3011
- [24] Sundermann, C.M. Production of calcium carbonate from steelmaking slag and captured CO₂- optimisation of the carbonation process and product quality [MSc thesis]. Espoo,

- Finland: Aalto Univ.; 2016. Available at: <<http://urn.fi/URN:NBN:fi:aalto-201612226258>> [accessed 24.1.2018]
- [25] Cussler, E.L. Diffusion mass transfer in fluid systems, Cambridge UK: Cambridge University Press, UK, 3rd Edition, 2009, Chapter 7
- [26] Wesseling, J.A., Krishna, R. Mass transfer in multicomponent mixtures. Delft: VSSD / Delft University Press, the Netherlands, 2000
- [27] Seader, J.D., Henley E.J. Separation process principles. John Wiley, 2nd Edition, 2006, Fig. 4.27
- [28] Buffo, A., Vanni, M., Marchisio, D.L. Simulation of a reacting gas-liquid bubbly flow with CFD and PBM: validation with experiments. Appl. Math. Modell. 2017; 44:43-60

Carbon dioxide dissolution and ammonia losses in bubble columns for precipitated calcium carbonate (PCC) production

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Fig. 1. The slag2PCC concept for PCC production from steelmaking slags

Fig. 2. The bubble column used, with mixer, and a close-up of the gas distributor

Fig. 3. Summary of screenshots on CO_2 bubble swarm dissolution (0.25 l/min STP) in water at room temperature for five mixer rotational speeds and four heights (24.4, 74.4, 120.6 and 170.6 cm above the gas distributor inlet) in the column.

Fig. 4. Single dissolving CO_2 bubble shape vs. height in the column as reported in [14].

Fig. 5. Bubble sizes at height level 3 (120.6 cm) 0 rpm (left) versus height 2 (74.4 cm) 200 rpm (right)

Fig. 6 CO₂ bubble size distributions at different height levels in the bubble column, during mixing at 100 rpm. Left: level 1 = 24.4 cm and right: level 4 = 170.6 cm above the gas inlet. (Colour of depth values 35 and 23, respectively, were used.) Error bars give standard deviation. Note different axes!

Fig. 7. Impression of CO_2 bubbles rising and dissolving in a bubble column reactor and a simplified close-up of concentration profiles inside and outside a bubble

Fig. 8 Diffusive fluxes of CO_2 , NH_3 and H_2O in the aqueous solution away from (> 0) or to (< 0) a bubble entering the carbonation reactor. Case a: Aalto Univ., demo plant 50°C, 100% CO_2 . Case b: Aalto Univ., lab-scale 30°C, 50% CO_2 in N_2 . Case c: ÅA bubble column, 20°C, 100% CO_2 .

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HIGHLIGHTS

- Image analysis on bubble swarms allowed for analysis of CO₂ and air dissolution
- Impeller rotational speed and positioning clearly affect bubble swarm dissolution
- Image-series averaged bubble swarm size distribution could be determined
- Possible release of ammonia from solvent salt via rising bubbles could be assessed
- Stefan-Maxwell diffusion analysis properly describes mass transfer to/from bubbles

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Table 1. Experimental results on gaseous emissions from slag2PCC carbonation reactors

Solvent salt	Gas mix feed % CO ₂ / % N ₂	Temp. °C	%-vol CO ₂ exit gas	%-vol H ₂ O exit gas	%-vol NH ₃ exit gas	% NH ₃ loss from solution	Ref.
^a NH ₄ NO ₃	100 / 0	30	~ 70	~ 3.2	0.2 – 0.3	0.42	[23]
^a NH ₄ NO ₃	50 / 50	30	~ 35	~ 3.0	0.2 – 0.3	0.68	[23]
^a NH ₄ NO ₃	25 / 75	30	~ 20	~ 2.8	0.2 – 0.3	0.83	[23]
^a NH ₄ Cl	50 / 50	30	~ 25	~ 1.5	0.1 – 0.2	0.35	[23]
^b NH ₄ Cl	100 / 0	45	no data	no data	0.11	no data	[9]
^b NH ₄ Cl	100 / 0	50	no data	no data	0.65	no data	[9]
^b NH ₄ Cl	100 / 0	60	no data	no data	0.30 – 2.0	no data	[9]
^c NH ₄ Cl	100 / 0	20	no data	no data	not detected	not detected	own data

^a Aalto Univ. lab-scale: extraction of 100 g steel converter slag (< 0.5 mm) in 1 L 2M solvent, at 30°C, 2h

^b Aalto Univ. demo plant: extraction of 20 kg steel converter slag (< 0.25 mm) in 170 L 1M solvent, at 20°C, 0.5 h

^c Åbo Akademi: salt solution of NH₄Cl (0.01 M) and CaCl₂ (0.1 M) with added aqueous NH₃ (25 %-wt in water) to raise pH to values > 9, in 24.9 L, ambient conditions.

Table 2. Dissolved ammonia and carbon dioxide for slag2PCC carbonation solutions, pH 7-10

Ca-salt mol /L	NH ₄ Cl mol/L	Temp. °C	Concentration CO ₂ (aq) & NH ₃ (aq) mol/L				Data ref.
			pH = 7	pH = 8	pH = 9	pH = 10	
~ 0.33 (13 g/l Ca ²⁺)	2	30	8×10 ⁻⁴ & 0.008	7×10 ⁻⁷ & 0.11	10 ⁻⁹ & 0.65	no data (pH < 10)	[23]
~ 0.5 (20 g/l Ca ²⁺)	1	50	0.006 & 0.004	5×10 ⁻⁵ & 0.06	9×10 ⁻⁹ & 0.35	5×10 ⁻¹¹ & 0.84	[9]
0.1 (CaCl ₂)	0.01 *	20	10 ⁻⁶ & 0.0009	2×10 ⁻⁷ & 0.006	2×10 ⁻⁹ & 0.039	< 10 ⁻¹⁰ & 0.092	own data

* Plus NH₃(aq) added to raise pH > 9

Table 3. Calculated Maxwell-Stefan diffusion coefficients for ternary system CO_2 , H_2O , NH_3 , in liquid (aqueous) phase and gas phase.

Temperature °C	Liquid $\bar{D}_{\text{CO}_2, \text{H}_2\text{O}}$ m^2/s	Liquid $\bar{D}_{\text{CO}_2, \text{NH}_3}$ m^2/s	Liquid $\bar{D}_{\text{NH}_3, \text{H}_2\text{O}}$ m^2/s	Gas $\bar{D}_{\text{CO}_2, \text{H}_2\text{O}}$ m^2/s	Gas $\bar{D}_{\text{CO}_2, \text{NH}_3}$ m^2/s	Gas $\bar{D}_{\text{NH}_3, \text{H}_2\text{O}}$ m^2/s
20	1.41×10^{-9}	1.49×10^{-9}	2.09×10^{-9}	2.02×10^{-5}	1.97×10^{-5}	3.02×10^{-5}
30	1.46×10^{-9}	1.54×10^{-9}	2.17×10^{-9}	2.15×10^{-5}	2.09×10^{-5}	3.20×10^{-5}
50	1.56×10^{-9}	1.64×10^{-9}	2.31×10^{-9}	2.40×10^{-5}	2.34×10^{-5}	3.58×10^{-5}

Table 4. Calculated mass transfer diffusion coefficients for ternary system CO_2 , H_2O , NH_3 , in liquid (aqueous) phase and gas phase.

Temperature °C	$k_{\text{CO}_2, \text{H}_2\text{O}}$ outside m/s	$k_{\text{CO}_2, \text{NH}_3}$ outside m/s	$k_{\text{NH}_3, \text{H}_2\text{O}}$ outside m/s	$k_{\text{CO}_2, \text{H}_2\text{O}}$ inside m/s	$k_{\text{CO}_2, \text{NH}_3}$ inside m/s	$k_{\text{NH}_3, \text{H}_2\text{O}}$ in m/s
20	3.22×10^{-4}	3.30×10^{-4}	3.92×10^{-4}	3.85×10^{-2}	3.80×10^{-2}	4.71×10^{-2}
30	3.27×10^{-4}	3.36×10^{-4}	3.98×10^{-4}	3.96×10^{-2}	3.91×10^{-2}	4.85×10^{-2}
50	3.38×10^{-4}	3.47×10^{-4}	4.11×10^{-4}	4.19×10^{-2}	4.14×10^{-2}	5.12×10^{-2}