Study of Direct Air Capture (DAC) Using a KOH/K$_2$CO$_3$ Absorbing Solution for CO$_2$ Capture

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Abstract

Direct Air Capture (DAC) consists of sequestrating CO$_2$ from ambient air using absorption or adsorption mechanisms. Within the former, alkaline solutions, such as KOH, are generally used as the absorbing agent due to the high reached pH values favouring CO$_2$ absorption. However, these solutions' alkalinity induces high corrosivity and harmful properties, making them challenging to handle. The KOH/K$_2$CO$_3$ mixture solution is studied in this paper and proposed as an alternative to the more generally used strong base solution. This mixture solution aims at taking advantage of the low toxicity and corrosivity of K$_2$CO$_3$ solutions while still including a fraction of KOH. It guarantees sufficiently high alkalinity and counteracts K$_2$CO$_3$ poor mass transfer performance. The purpose of this paper is to have first estimations of the potential of KOH/K$_2$CO$_3$ solutions as the absorbing agent for carbon capture in ambient air by taking only equilibrium considerations and assuming an ideal aqueous solution. Within this framework, CO$_2$ removal efficiencies are calculated for various pH values and phase ratios, and then the results are compared with literature data. This comparison highlights the importance of kinetics limitations for CO$_2$ absorption in aqueous solutions. A significant part of this work is focused on the potential precipitation issues that may occur during CO$_2$ absorption. These issues' likelihood is compared for the case of a KOH/K$_2$CO$_3$ and a NaOH/K$_2$CO$_3$ solution. It turns out that precipitation is only encountered in the latter situation when extreme concentration conditions are encountered. In further work, the results should be refined by including the absorption kinetics and appropriately modelling the aqueous phase, accounting for the existing interactions. These factors may influence the conditions under which precipitation occurs. Nevertheless, the present study gives the necessary thermodynamics fundamental knowledge for addressing the challenges to be encountered in KOH/K$_2$CO$_3$ solutions.

Keywords: Direct air capture (DAC), KOH, K$_2$CO$_3$, removal efficiency, precipitation, equilibrium

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Nomenclature

V_{air}	Air volume entering the absorption unit (m³)
n^0_{CO2}	Number of CO$_2$ moles in the air entering the absorption unit (mol)
n^{eq}_{CO2}	Number of CO$_2$ moles in the air leaving the absorption unit (mol)
P^0_{CO2}	CO$_2$ partial pressure in the air entering the absorption unit (Pa)
P^{eq}_{CO2}	CO$_2$ partial pressure in the air leaving the absorption unit (Pa)
C_B	Strong base (KOH or NaOH) molar concentration (mol/L)
C_K	K$_2$CO$_3$ molar concentration (mol/L)
V_B	Strong base (KOH or NaOH) aqueous solution volume (L)
V_K	K$_2$CO$_3$ aqueous solution volume (L)

1. Introduction

One of the capital objectives pursued by the European Commission within its 2030 Climate Target Plan is to increase the ambition among international partners to limit the global temperature rise to 1.5°C. They propose to mitigate CO_2 emissions by at least 55% by 2030 [1]. One of the envisaged options is CO_2 capture from point source emissions, such as industrial chimneys, and also from the atmosphere to deliver negative emissions. This latter option is part of the Commission's strategic long-term vision and still requires scientific research to reach its maximum potential [2]. Direct air capture (DAC) technologies are based on adsorption or absorption processes. Using chemical absorption is a relevant option to face the challenge of the CO_2 dilution in the air.

1.1. KOH and K_2CO_3 as valuable chemicals for carbon capture

In the field of capture technologies, potassium carbonate (K_2CO_3) solutions are mainly used in post-combustion units as they present features addressing some drawbacks of the benchmark amine-based solutions. Most mature processes operate with monoethanolamine (MEA) as the absorbing agent and have been commercialised for many decades [3]. However, amine-based solutions are highly corrosive, incurring increased construction material costs, as well as the solution degrades at high temperatures and in the presence of oxygen, SO_x and NO_x [4, 5]. Comparatively, K_2CO_3 solutions present lower toxicity and corrosivity, making them easier to handle [6]. They are less prone to degradation due to their considerable chemical stability and can thus be used at a higher temperature, favouring absorption kinetics [7]. These solutions are also advantageous from an economic point of view as they benefit from a low vapour pressure, reducing solvent losses [6], and less regeneration energy demand due to the low heat of absorption [8]. The most severe drawback associated with K_2CO_3 utilisation is the slow kinetics, resulting in poor mass transfer performance and consequently increasing the required column heights and capital investment [4, 9]. Strong base solutions, such as KOH or NaOH, serve in absorption units sequestrating CO_2 from atmospheric air [10-12]. Carbon Engineering constructed the first DAC plant at pilot-scale in 2015 with a KOH solution, capturing 365 tonnes of CO_2/year at an estimated cost lying between $94 and $232/tonne of captured CO_2. This pilot plant includes a regeneration loop for the absorbing solution [12].

1.2. Benefits of using a KOH/K_2CO_3 blend solution for carbon capture

KOH solutions being highly alkaline, they incur corrosivity and handling issues. Furthermore, particularly corrosive solutions trigger the necessity of more expensive construction materials, increasing capital investment. In order to address this problem, the low toxicity and corrosivity of K_2CO_3 solutions can be beneficial. Unfortunately, using a K_2CO_3 solution alone would not be efficient for direct air capture applications, given the slow absorption kinetics and low gaseous phase concentration in CO_2, which is around 419 ppm [13]. KOH can be used in addition to K_2CO_3, intending to counteract these drawbacks. It is introduced in fewer quantities in contrast to its application alone, thus limiting the corrosivity. It is hence hoped to benefit from both the ease of handling of K_2CO_3 solutions and the capture efficiency of KOH solutions. This work aims to explore the first insights into assessing the potential of KOH/K_2CO_3 solutions for carbon capture from ambient air. All reasonings are based on the thermodynamic equilibria characterising the CO_2 absorption and hydration phenomena and assuming an ideal aqueous phase.

2. Chemical framework

2.1. CO_2 absorption by aqueous solutions

The understanding of CO_2 behaviour in aqueous solutions is paramount for describing its absorption in a KOH/K_2CO_3 solution. This section presents the equilibria ruling the transfer of CO_2 from the gas phase, air in this study case, to the aqueous phase, which encompasses the description of the different forms taken by CO_2 in the aqueous phase. When air is put in contact with an aqueous phase, an equilibrium translating the dissolution of the gaseous CO_2 ($CO_{2(g)}$) in the aqueous phase can be set up:

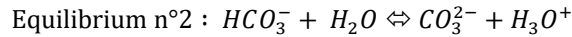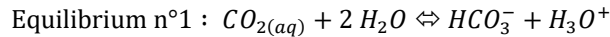$$\text{Henry's equilibrium} : CO_{2(g)} \Leftrightarrow CO_{2(aq)}$$
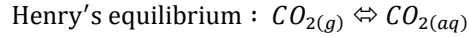
where $CO_{2(aq)}$ refers to an absorbed CO_2 molecule, which is still in the form of a CO_2 molecule, i.e. which has not yet been transformed, as shown in the following. From now on, $CO_{2(aq)}$ will be referred to as physically dissolved CO_2. The physical law used to describe this phenomenon is Henry's law, as portrayed by Eqn. 1:
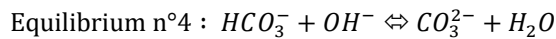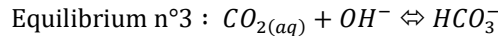
$$C_{CO2}^{eq} = H_{CO2}P_{CO2}^{eq} \tag{1}$$

C_{CO2}^{eq} represents the equilibrium molar concentration of physically dissolved CO_2 (mol/L) and P_{CO2}^{eq} the equilibrium CO_2 partial pressure (atm). Henry's law constant (H_{CO2}) for CO_2 equals 0.034 mol/(L*atm) at 25°C [14]. This law can only be applied if the gas behaves as an ideal gas and if the dissolved gas does not undergo any reaction in the solvent. The first assumption is respected in the present case regarding the low CO_2 partial pressure in the air. Concerning the second assumption, it turns out that dissolved CO_2 is implied in acid-base equilibria, meaning that Henry's law should theoretically not be used for the characterization of CO_2 absorption in aqueous solutions. Incidentally, an alternative to the classical Henry's law is proposed in Section 3.2.

CO_2 presents an acidic behaviour in aqueous solutions because of its hydration in carbonic acid (H_2CO_3), followed by the associated acid-base equilibrium. According to previous works [15-18], two different paths exist to describe CO_2 hydration in aqueous solutions, which depend on the pH value of this solution. For pH values below 8, the predominant path is called the water path:

$$\text{Equilibrium n°1} : CO_{2(aq)} + 2\,H_2O \Leftrightarrow HCO_3^- + H_3O^+$$

$$\text{Equilibrium n°2} : HCO_3^- + H_2O \Leftrightarrow CO_3^{2-} + H_3O^+$$

The first equilibrium of this path is the combination of two other steps in which physically dissolved CO_2 is first transformed into H_2CO_3 and then, into bicarbonate ions (HCO_3^-). However, carbonic acid does not exist in the aqueous phase and is directly converted, which is the reason why the first equilibrium is written as it is. The second hydration path, named hydroxide path, is observed for pH values above 10:

$$\text{Equilibrium n°3} : CO_{2(aq)} + OH^- \Leftrightarrow HCO_3^-$$

$$\text{Equilibrium n°4} : HCO_3^- + OH^- \Leftrightarrow CO_3^{2-} + H_2O$$

For pH values between 8 and 10, both paths simultaneously occur. Among the mentioned literature, some works [15, 16] state that for pH values below 8, the equilibrium n°4 replaces the equilibrium n°2, while others [17, 18] claim that equilibrium n°2 is observed in this pH range. In this work, it is assumed that for the bicarbonate/carbonate ions (CO_3^{2-}) equilibrium, the base is water for pH values below 8 and hydroxide ions (OH^-) for pH values above 10. In that way, a certain coherence is kept with the $CO_{2(aq)}/HCO_3^-$ equilibrium. Furthermore, HCO_3^- is more likely to react with OH^- at high pH values. Looking at these equilibria, it turns out that CO_2 exists in three different forms in aqueous solutions: physically dissolved CO_2, bicarbonate and carbonate ions. Each form preponderance is dependent on the pH value following the acid-base equilibria described above. A visualisation of the distribution of CO_2 among its possible forms as a function of pH is possible through the construction of a Bjerrum plot (see Fig. 1), using the equilibria described above and their respective constant (see Table 1 for their value). In this plot, the water path is represented by a straight line and the hydroxide path by a dashed line.

Fig. 1 pictures that the physically dissolved CO_2 concentration decreases with pH value to become almost negligible for pH values exceeding 10. It is drawn from this observation that the pH value should be higher than 10 to efficiently absorb CO_2. In this case, the equilibrium between gaseous and physically dissolved CO_2 can be shifted towards the aqueous phase, translating to a lower CO_2 partial pressure in the gaseous phase at equilibrium, which is the pursued

objective. This pH value is easily achieved with a KOH/K$_2$CO$_3$ solution as a 1 wt% solution of K$_2$CO$_3$ alone yields a pH value of 11.6.
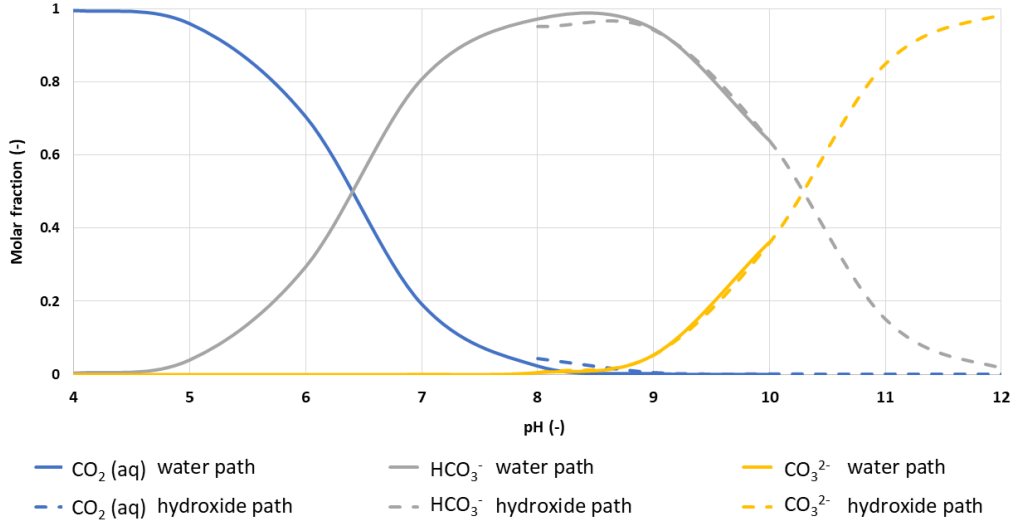

Fig. 1. Bjerrum plot describing the distribution of the different forms of CO$_2$ in aqueous solutions depending on the pH at 25°C

Table 1. Equilibrium constant values at 25°C

Equilibrium constant	Value	Reference
K_1	$4.19*10^{-7}$	[16]
K_2	$10^{-10.25}$	[19]
K_3	$4.25*10^7$	[16]
K_4	$10^{3.75}$	[19]

An important aspect to take into consideration with the distribution of the CO$_2$ forms is the temperature influence on the equilibrium constants and, thus, on the Bjerrum plot profiles. The literature [20] provides correlations (see Eqn. 2 to 5) to calculate equilibrium constants K_1 and K_2 at different temperatures (T in K):

$$pK_1 = -\log K_1 = \frac{3,404.71}{T} + 0.032786\,T - 14.8435 \qquad (2)$$

$$pK_2 = -\log K_2 = \frac{2902.39}{T} + 0.02379\,T - 6.4980 \qquad (3)$$

It can be demonstrated that $K_3 = K_1/10^{-14}$ and that $K_4 = K_2/10^{-14}$, from which the correlations describing the temperature dependency of K_3 and K_4 can be drawn:

$$pK_3 = -\log K_3 = -14 - \log K_1 = \frac{3,404.71}{T} + 0.032786\,T - 28.8435 \qquad (4)$$

$$pK_4 = -\log K_4 = -14 - \log K_2 = \frac{2902.39}{T} + 0.02379\,T - 20.4980 \qquad (5)$$

The validity of these correlations is assessed by calculating the equilibrium constant values at 25°C and comparing them with the values found in the literature and given in Table 2. The relative difference observed between literature

and calculated values being negligible, these correlations are assumed to be applicable for the construction of a Bjerrum plot at 25°C. However, given the lack of literature data, these correlations are assumed to be usable at other temperatures as well. It is worth highlighting that the equations were regressed by [20] for ideal solutions. In a more complex model, i.e. for non-ideal solutions, it is expected to observe larger deviations.

Table 2. Comparison of equilibrium constant values from literature and values calculated with Eqn. 2 to 5 at 25°C

Equilibrium constant	Value calculated with correlations	Value from literature	Relative difference (%)
pK_1	6.35	6.38	0.47
pK_2	10.33	10.25	0.78
pK_3	-7.65	-7.63	0.26
pK_4	-3.67	-3.75	2.13

Following this validation, the Bjerrum plot is thus generated at 75°C and compared with the curves obtained at 25°C, as depicted in Fig. 2. It must be specified that the pH 8 – pH 10 range in Fig. 2 is generated using the hydroxide path. This choice is arbitrary given the negligible difference between both paths within this range, as testified by the curves in Fig. 1. The curves comparison between 25°C and 75°C exhibits the equilibrium independence from temperature for pH values lower than 8. On the other side, when pH exceeds this value, it seems that for a given pH value, the higher the temperature, the further the equilibrium n°4 is shifted towards carbonate ions. Though, this variation remains slight. Thus, operating a CO_2 absorption unit at a higher temperature seems optimal for shifting the equilibrium. High temperatures also favour the absorption kinetics, suggesting that heating the solution before the absorption unit may benefit CO_2 transfer from both the equilibrium and kinetics sides. Although, the optimal operating temperature must be determined by accounting for the energy demand and the economics of the heating process.
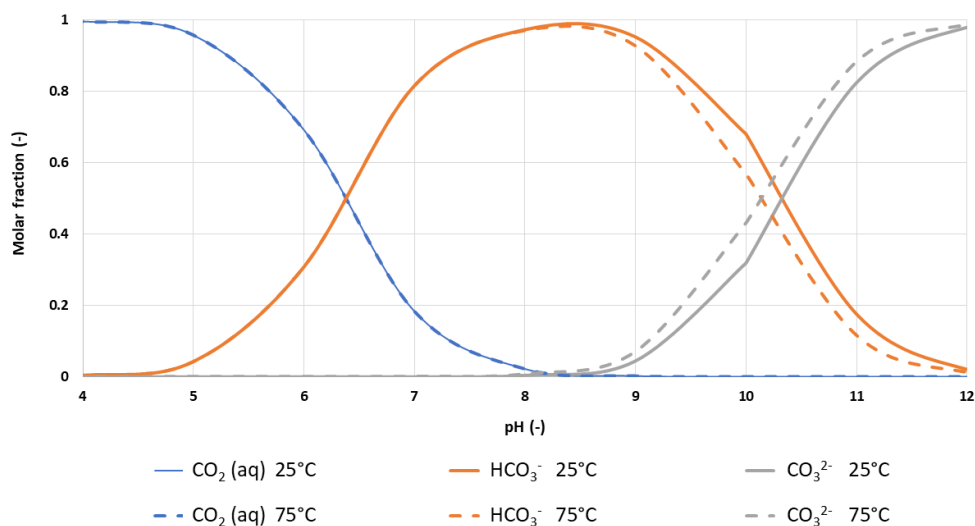

Fig. 2. Comparison of Bjerrum plots at 25°C and 75°C

## 2.2. Comparison of KOH and NaOH utilisation for CO2 absorption

NaOH solutions are already used in some absorption processes to capture CO_2 [3, 10, 11, 21, 22]. Thus, it is worth evaluating the difference between utilising a KOH/K_2CO_3 and a $NaOH/K_2CO_3$ solution, given the fact that they lead to equivalent pH values for equivalent concentrations. One of their main differentiation points is supposed to concern

the salt system existing in the solution, which can potentially lead to precipitation issues depending on the operating conditions. The identification of salts present in the solution is crucial because the solubility differs depending on the species, and, thus, salt precipitation appears under different conditions. The objective is to determine the solubility limits in each absorbing solution in order to identify the operating conditions such that the aqueous phase remains within the limits. In this way, it ensures the avoidance of any precipitation phenomena when operating an absorption unit. Indeed, absorption towers often include packings to optimise the mass transfer between the gaseous and aqueous phases and solid particle deposition resulting from salt precipitation would disturb the formation of a thin liquid layer at the packing surface and, thus, yielding lower mass transfer performance. Moreover, this deposition would induce a larger pressure drop across the absorption unit, moving the operating pressure away from its optimal value and inducing larger compression needs, which would have a detrimental effect on the DAC performance.

In order to determine the likelihood of precipitation issues, the first step is to identify all species possibly formed in the solution. Both absorbing solution options contain K_2CO_3, which dissociates in aqueous solutions:

$$\text{Dissociation n°1}: K_2CO_3 \Leftrightarrow 2\,K^+ + CO_3^{2-}$$
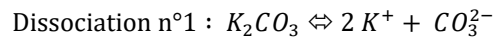
As discussed above, carbonate ions are also implied in an acid-base equilibrium. The reverse of equilibrium n°4 is considered for the carbonate/bicarbonate ions equilibrium, given that the studied solutions are alkaline enough to yield pH values exceeding 10. Moreover, KOH and NaOH, as strong bases, fully dissociate in aqueous solutions:

$$\text{Dissociation n°2}: KOH \rightarrow K^+ + OH^-$$

$$\text{Dissociation n°3}: NaOH \rightarrow Na^+ + OH^-$$
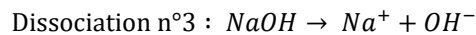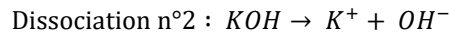
Looking at these reactions, the species present in the solution are potassium ions (K^+) and carbonate ions for the KOH/K_2CO_3 case. Bicarbonate ions are also yielded, given the carbonate/bicarbonate acid-base equilibrium. The strong base also produces OH⁻, mainly contributing to the high alkalinity of the system. In the case where NaOH substitutes KOH, sodium ions (Na^+) appear in the solution, decreasing the concentration of potassium ions, as K_2CO_3 is now their only source. It is thus possible to identify the ionic salts potentially formed with all these species in the solution. As shown in Table 3, four different salts may appear in the solution, namely sodium and potassium bicarbonates and carbonates. These ionic salts have no existence in solution, as they directly dissociate into their constitutive ions. However, if these ions' concentration is such that the solubility limit is reached, the corresponding salt will form and precipitate as a solid particle, thus leaving the aqueous phase.

Table 3. Ionic salts potentially formed in KOH/K_2CO_3 and NaOH/K_2CO_3 solutions

Cations/Anions	HCO_3^-	CO_3^{2-}	OH^-
K^+	$KHCO_3$	K_2CO_3	/
Na^+	$NaHCO3$	Na_2CO_3	/

Therefore, it is necessary to know the solubility limit of each salt, expressed as a maximum mass of salt dissolvable in 100 mL of water at 25°C. This solubility can then be used to determine the solubility product, which characterises each salt and helps to conclude whether or not a salt precipitates, given the molar concentration of each ion constituting this salt. The solubility and solubility product of each studied salt are given in Table 4.

Table 4. Solubility and solubility product of each studied salt at 25°C

Ionic salt	Solubility in water (g/100 mL)	Solubility product	Reference
K_2CO_3	111	2072.1 $(mol/L)^3$	[23]
Na_2CO_3	30.7	97.2 $(mol/L)^3$	[24]
$KHCO_3$	24.8	5.3 $(mol/L)^2$	[25]
$NaHCO_3$	10.3	1.3 $(mol/L)^2$	[26]

As previously mentioned, the solubility product value helps to determine the existence of salt precipitates in the solution. The approach is to calculate the ion product (Q) of a given salt, as exampled in Eqn. 6 for the general ionic salt A_mX_n and where the units are $(mol/L)^{m+n}$:

$$Q = [A^{n+}]^m [X^{m-}]^n \tag{6}$$

where the brackets refer to the ion molar concentration in the solution. Precipitation occurs when this ion product exceeds the solubility product of the corresponding salt. Thus, the higher the solubility product, the lower the precipitation likelihood. Regarding the solubility product values provided in Table 4, it turns out that bicarbonate salts are more prone to precipitation compared to carbonate salts. Therefore, the concentration of bicarbonate ions should be kept as low as possible to avoid precipitation issues, which can be done by operating at a high pH value and high temperature, as evidenced by Fig. 2. It also seems that sodium bicarbonate is less soluble than potassium bicarbonate, and this could be a reason to prefer the utilisation of KOH instead of NaOH. In order to elaborate on these potential precipitation issues, the absorption unit is studied in more detail in the next section. The ion product of the different studied salts is calculated for various operating conditions, i.e. various absorbing solution concentrations, to figure out the conditions to be avoided to exclude precipitation issues.

3. Modelling of the CO₂ absorption unit

3.1. Methodology

The model developed in this study is oversimplified as only equilibrium considerations are taken, along with the assumption of ideal solutions and gas phase. The model can be reduced to an absorption zone in which an air stream at atmospheric conditions is put in contact with an absorbing solution, which is either KOH/K_2CO_3 or $NaOH/K_2CO_3$. Various concentration combinations are studied, varying between 1 and 20 mol/L for the strong base and 1 and 8 mol/L for K_2CO_3.x It is assumed that both streams leave the absorption zone at equilibrium conditions. A graphical representation of this unit is proposed in Fig. 3. The brackets in this figure still refer to the ion molar concentration, with the superscript '0' indicating the concentration at the inlet and 'eq' at the outlet of the absorption zone.

The purpose of this simple model is twofold. On one side, the aim is to calculate the capture efficiency of a KOH (or NaOH)/K_2CO_3 solution based on equilibrium considerations. On the other side, it is desired to assess the ion product of each salt to conclude on their precipitated state presence. Some inputs are necessary for achieving those objectives, including the strong base and K_2CO_3 concentrations, their respective volume, the volume of treated air and the CO_2 partial pressure. Then, the overall procedure can be exposed as follows:

- Based on input data, calculation of the initial pH value of the absorbing solution. This step requires the solving of the reverse of Equilibrium n°4. Indeed, on top of the alkalinity brought by the strong base, K_2CO_3 also yields OH^- through the carbonate/bicarbonate equilibrium following its dissociation into its constitutive ions.
- Based on the CO_2 atmospheric concentration and the volume of treated air, calculation of the initial number of CO_2 moles (or initial mass) contained in the treated volume.

- Calculation of the number of CO_2 moles (or mass) absorbed by the solution by solving the equilibrium between gaseous and physically dissolved CO_2 (Henry's law), followed by Equilibria n° 3 and 4. This step enables the determination of each equilibrium concentration.
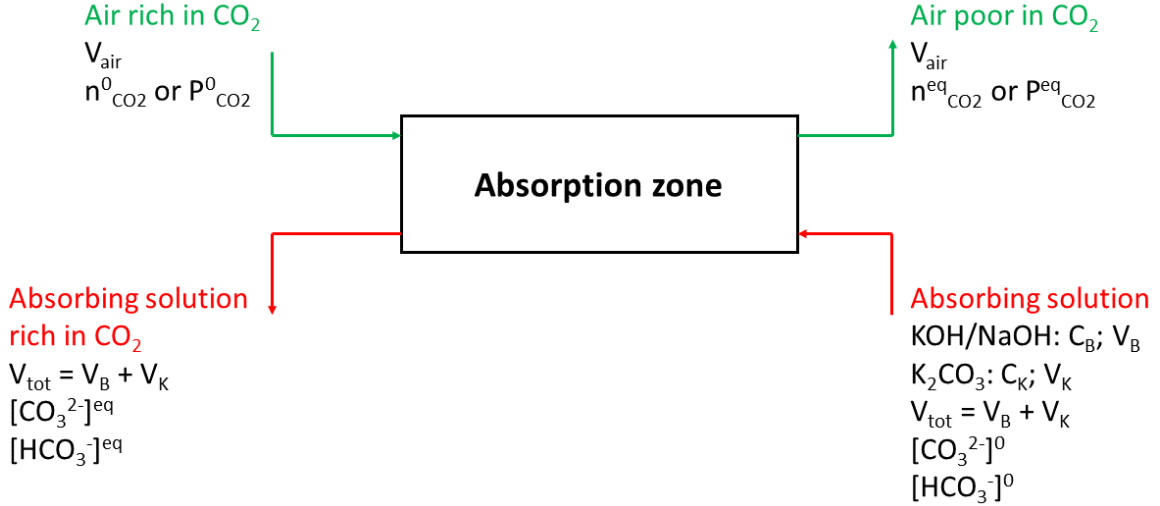- Calculation of removal efficiency and ion products.

Fig. 3. Graphical representation of the CO_2 absorption unit with boundary conditions

3.2. Effective Henry's law constant

Henry's law constant characterises the equilibrium existing between CO_2 present in the air and CO_2 present in the aqueous solution. This constant only accounts for physically dissolved CO_2 as it is the only species in solution which is effectively still a CO_2 molecule. In other words, this constant only describes a physical phenomenon, namely the dissolution of a gas into a solution with which it is in equilibrium. However, it is demonstrated above that CO_2 also exists in the form of bicarbonate and carbonate ions in the solution. Thus, another constant should be used to describe the equilibrium existing between gaseous CO_2 and all forms of CO_2 present in the solution. The formalism of Henry's law can still be used, but the physically dissolved CO_2 concentration is replaced by the concentration of all CO_2 forms present in the solution and Henry's law constant by an effective Henry's law constant (H'_{CO2}) defined in Eqn. 7:

$$[CO_2]_{tot,sol} = H'_{CO2} P_{CO2}^{eq} \qquad (7)$$

The concentration of all forms of CO_2 present in the solution can then be developed as in Eqn. 8:

$$[CO_2]_{tot,sol} = [CO_{2(aq)}] + [HCO_3^-] + [CO_3^{2-}] \qquad (8)$$

It is previously determined that the higher the absorbing solution pH, the greater its absorbing capacity. Thus, it can be supposed that the effective Henry's law constant should encompass this pH effect such that the greater the pH, the greater the value of H'_{CO2}, and, thus, the further the CO_2 equilibrium is shifted towards the aqueous solution, translating to a greater absorbing capacity. The mathematical development leading to this effective constant starts from Eqn. 8, which can be developed as in Eqn. 9:

$$[CO_2]_{tot,sol} = [CO_{2(aq)}] * \left(1 + \frac{[HCO_3^-]}{[CO_{2(aq)}]} + \frac{[CO_3^{2-}]}{[CO_{2(aq)}]} \right) \qquad (9)$$

Note that the brackets and *C* (both appearing in Fig. 3, for instance) both refer to a molar concentration, but in this case the former is used to lighten the writing. Then, replacing $[CO_2]_{tot,sol}$ using the effective Henry's law (see Eqn. 7), $[CO_{2(aq)}]$ with the original Henry's law (see Eqn. 1) and making pH appear in the parentheses by transforming both fractions with the definition of equilibrium constants K_3 and K_4 results in Eqn. 10:

$$H'_{CO2} = H_{CO2} * \left(1 + \frac{K_3 10^{-14}}{[H^+]} + \frac{K_3 K_4 10^{-28}}{[H^+]^2} \right) \tag{10}$$

This equation mathematically translates the pH effect on CO_2 absorption that was qualitatively discussed within the Bjerrum plot analysis. It shows that the higher the pH (equivalently lower the H^+ concentration), the greater the effective Henry's law constant and the better the solution absorbing capacity. This equation can finally be used when solving the equilibrium between gaseous CO_2 and CO_2 present in the aqueous solution (i.e., the absorbed CO_2), which enables the determination of equilibrium concentration and, thus, the assessment of removal efficiency and ion products. It is worth mentioning that Eqn. 10 can be evaluated at various temperatures with Eqn. 4 and 5 by using a correlation for the temperature dependency of Henry's law constant for CO_2 (H_{CO2}) [14].

3.3. CO_2 removal efficiency and comparison with other works

The CO_2 removal efficiency is defined as the relative amount (number of moles or mass) of CO_2 absorbed by the solution. The removal efficiency is presented in Eqn. 11, where the number of moles is used as the reference:

$$\eta = \frac{n_{CO2}^0 - n_{CO2}^{eq}}{n_{CO2}^0} \tag{11}$$

In this equation, the numerator represents the number of CO_2 moles absorbed by the solution. The influence of the absorbing solution pH on the CO_2 removal efficiency is evaluated in Fig. 4. The curves are generated for various phase ratios, another operating parameter determining the liquid-to-gas volumetric flow rate ratio. Fig. 4 highlights that a 100% removal efficiency is achievable, given that the absorbing solution alkalinity is high enough. This observation correlates with the analysis conducted on the Bjerrum plot, where it is demonstrated that a high pH value shifts the equilibrium fully towards the CO_2 present in the solution. A greater phase ratio tends to decrease the pH value for which the maximal efficiency is reached. Indeed, mass transfer is driven by concentration differences. Consequently, when the solution volume is reduced, the concentration in this phase increases more rapidly, thus diminishing the transfer driving force more strongly. Then, the absorbing solution pH should be increased to compensate for this effect and still reach the maximal efficiency at lower solution volume. More practically, other considerations must be taken to appropriately set those two parameters. A greater absorbing solution flow rate enables a lower operating pH, as depicted in Fig. 4, but a too large flow rate may incur increased operating costs, especially for regeneration purposes [28]. On the other hand, working with a milder absorbing solution flow rate requires to increase its concentration, which comes along with more corrosivity and, thus, higher material costs.

For comparison purposes, five data points comping from the literature [12, 21, 22, 27] are also included in this figure. The aim of comparing these equilibrium results with data from the literature is to apprehend the fact that kinetics limitations do exist when absorbing CO_2 with aqueous solutions. They are probably the reason why the removal efficiency does not reach as high values as the ones obtained from equilibrium considerations. The study case of Ayittey et al. [27] is interesting because it concerns a model for CO_2 absorption in flue gas with a K_2CO_3 solution. It shows that even if the CO_2 concentration in the gaseous stream is large (13 vol%), a 100% removal efficiency cannot be achieved in similar operating conditions. It highlights the poor mass transfer performance associated with the K_2CO_3 solutions. For the other works [12, 21, 22], the absorbing solution is a strong base (KOH or NaOH) and captures CO_2 from the ambient air. The removal efficiency is still lower than 100%, probably exhibiting kinetics limitations in these cases too. Furthermore, strong interactions certainly occur in the aqueous phase, limiting the utilisation of the ideal solution assumption. Then, it may be an explanation for obtaining lower efficiencies in these conditions.
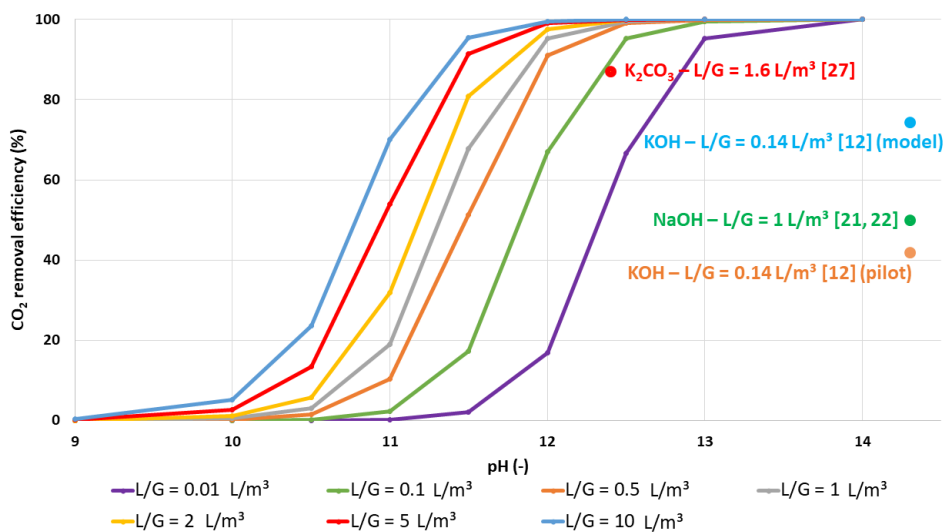
Fig. 4. Variation of the removal efficiency as a function of absorbing solution pH and phase ratio and comparison with literature [12, 21, 22, 27]

3.4. Potential precipitation of ionic salts

As previously explained, the ion product must be calculated for each studied salt to conclude whether it precipitates or not. Indeed, the ion product is compared with the solubility product of the corresponding salt; if it is greater, precipitation occurs. This verification is made for strong base (KOH or NaOH) concentrations varying between 1 and 20 mol/L and K_2CO_3 concentrations between 1 and 8 mol/L, assuming that both chemicals are used in equivalent quantities, i.e. the same volume, and a phase ratio of 1 L/m³. The results are presented in Fig. 5. They depict that the solubility limit is overcome for only one of the considered salts, which is sodium carbonate. This conclusion may seem unexpected regarding the solubility values presented in Table 4, where it can be seen that carbonate salts are more soluble than bicarbonate salts. However, the pH values reached by the absorbing solution are sufficiently high to consider all the absorbed CO_2 in the form of carbonate ions. Consequently, the concentration in bicarbonate ions is negligible, incurring a small ion product for bicarbonate salts, which remains far from their solubility limits, although this limit is lower compared to carbonate salts. Fig. 5 shows that for the carbonate salts, the higher the strong base concentration (C_B), the closer to the solubility limit. The inverse is observable for the bicarbonate salts. This phenomenon can be explained by a concentration in bicarbonate ions increasing at lower pH value, as outlined in the Bjerrum plot (see Fig. 1). It tends to rise the ion product of the bicarbonate salts when the strong base concentration is milder. However, the bicarbonate ions concentration is still negligible, making the ion product of bicarbonate salts almost independent of the strong base concentration, as depicted in the $KHCO_3$ and $NaHCO_3$ plots. In the latter case, the sodium ions concentration stemming from NaOH is not sufficient to counterbalance the small bicarbonate ions concentration, resulting in the independence of this ion product regarding the strong base concentration. There is yet a perceivable dependence for the $KHCO_3$ salt, as potassium ions are provided by both the strong base and the K_2CO_3 solutions.

In conclusion, it turns out that the only case in which precipitation could occur is when the absorbing solution is NaOH/K_2CO_3 with extreme concentrations. Indeed, the ion product of sodium carbonate exceeds its solubility product at high concentration values (at least 10 mol/L for the NaOH solution). In practical applications, it is expected to operate at lower concentrations since high pH values can be reached in milder operating conditions. This aspect could thus lead to the conclusion that precipitation is not an issue when absorbing CO_2 with a KOH (or NaOH)/K_2CO_3 solution. However, all considerations taken in this paper are equilibrium-based, on top of assuming ideal solutions. Then, it can be supposed that the conclusion related to precipitation issues would be different in real conditions as

none of the interactions existing in the aqueous solution is accounted for in this case. Even if these results must be refined by developing a more complex model including these interactions, the simplified model presented in this study shows that it is possible to observe precipitation when using NaOH, admittedly in extreme conditions, whereas precipitation issues do not occur when the absorbing solution is KOH/K_2CO_3. Although the assumptions made are strong, this result can be used as a first insight in deciding to adopt KOH over NaOH utilisation. The phase ratio influence should also be investigated in more detail. A lower solution flow rate would induce a larger pH decrease following CO_2 absorption and its acidification effect. It would result in a shift of the CO_2 species distribution towards bicarbonate ions (see Fig. 1). This would incur the ion product of bicarbonate salts to grow and potentially trigger their precipitation.
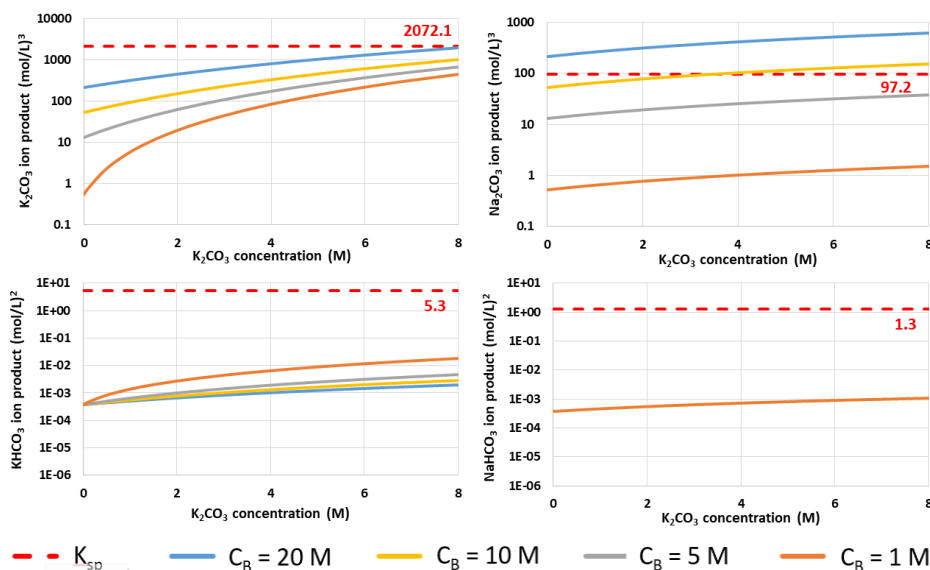

Fig. 5. Evolution of ion product of studied salts with the K_2CO_3 and KOH concentrations for a phase ratio of 1 L/m^3

4. Conclusion and perspectives

The main objective pursued within this paper was to get preliminary insights into the utilisation of a KOH/K_2CO_3 solution for CO_2 capture from ambient air. The discussion was centred on the calculation of removal efficiency and the effects of absorbing solution pH and phase ratio on this efficiency. A particular interest was also attributed to the study of potential precipitation issues, which may occur when using the considered solution and to the comparison of the use of KOH and NaOH within this framework. All considerations were equilibrium-based, and the aqueous phase was assumed to be an ideal solution. It was shown that a 100% removal efficiency is theoretically achievable with these assumptions, given sufficient alkalinity (between pH 12 and 13 for a phase ratio of 1 L/m^3). However, the results comparison with literature data highlighted the importance of kinetics limitations when absorbing CO_2 with aqueous solutions. The precipitation study showed that the KOH/K_2CO_3 solution does not present any precipitation issues within a large spectrum of operating concentrations. On the other side, when NaOH/K_2CO_3 is used, Na_2CO_3 precipitation appears for extreme concentration values. It is assumed to be a first insight for deciding between the utilisation of NaOH and KOH as, even with an oversimplified model where none of the interactions existing in the solution is accounted for, precipitation problems may appear with NaOH but not with KOH. It turns out that KOH provides faster kinetics [29], another reason for its possible prevalence upon NaOH utilisation.

In order to better assess the potential of KOH/K_2CO_3 solutions for CO_2 capture in ambient air, the two main assumptions taken in this work should be relaxed. Appropriate description and inclusion of the kinetics in the model

should be conducted to obtain a better estimation of this system performance, which can then be compared with other similar direct air capture installations [29]. Then, the aqueous phase modelling should imperatively be improved to account for the different interactions existing in the solution, especially at these high concentrations. The electrolyte non-random two-liquid (eNRTL) model is generally used [6, 27, 29]. It includes the presence of various interactions through activity coefficient calculation. A more robust model for the absorption unit should also be developed to consider the influence of other operating parameters, including temperature, pressure, etc. Finally, the modelling should include the regeneration step for the absorbing solution to assess the overall economic and energetic demand.

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