Research Article

A Novel Carbon Dioxide Desorption Phenomenon Using an Aqueous Potassium Acetate Solution

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Abstract: A novel CO_2 absorbent, 50–75 wt.% aqueous potassium acetate solution ($AcK_{(aq)}$), which showed a CO_2 absorption capacity of ~ 0.2 mol CO_2/mol, and could almost immediately completely desorb CO_2 on addition of 40 wt.% H_2O at 30 °C was investigated. This novel phenomenon seemed contrary to the *Le Chatelier's principle* because H_2O is a reactant in this system. After characteristics of products by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) pattern, the novel desorption behavior was attributed to the acid-base reaction between $KH(CH_3COO)_2$ and $KHCO_3$ precipitates within the absorbent sludge. As H_2O was added, both compounds re-dissolved and CO_2 was released. A similar observation was made when the absorbent sludge was heated to temperatures above 60 °C, owing to an increase in solubility with temperature. The mechanism of CO_2 captured and released by $AcK_{(aq)}$ was proposed in this study. This novel energy-saving CO_2 absorption and desorption behavior reveals that $AcK_{(aq)}$ has a high potential for application in the commercial production process.

Keywords: carbon dioxide, carbon capture, absorption, desorption

1. Introduction

Reducing the negative effects of global warming via carbon dioxide capture and storage (CCS) is an important area of research. According to the analysis from NOAA's Global Monitoring Lab, the global average atmospheric carbon dioxide was 414.72 ppm in 2021.[1] Many scientists have proposed exceptional and effective methods by which atmospheric or flue gas CO_2 can be captured, e.g., alkanolamine absorbents, including steric hindrance amines,[2-5] have been used extensively owing to their ability to quickly absorb carbon dioxide, NOx, and SOx. For example, Aghel et al.[6-9] reported that CO_2 captured by monoethanolamine or/and diethanolamine microchannel reactor. They proposed that the mass transfer efficiency was determined based on the CO_2 desorption percentage, volumetric liquid-side mass transfer coefficient ($k_L a_V$) and volumetric overall mass transfer flux ($N_{CO2} a_V$). The energy consumption per unit mass CO_2 (R) is also a key point of carbon capture and utilization (CCU) process. Unfortunately, during the absorbent regeneration process, a significant proportion of the alkanolamines is lost, and carcinogens such as nitrosamines may be produced[10-12] given that the desorption control conditions include high temperatures and pressures. Alternatively, metal hydroxides and carbonates, including potassium bicarbonate and sodium bicarbonate,[13-17] have been employed as absorbents in CO_2 capturing owing to their high stability and safety. However, their regeneration also requires high temperatures. Presently,

ionic liquids (ILs) are becoming an important focus for research in the field of CCS owing to their appreciable chemical and high thermal stabilities as well as low vapor pressures.[4,18,19] However, they are expensive, and their structures can be destroyed via hydration reactions, by the humidity in flue gases.

Particularly, typical CO_2 desorption processes are performed in high temperature ovens under high pressure. Therefore, the objective of this study was to explore the overall CO_2 absorption/desorption mechanism as well as the behavior of highly concentrated aqueous solution of potassium acetate (AcK, $CH_3COOK_{(aq)}$) as a CO_2 absorbent. A novel CO_2 desorption method that can be employed at 30 °C and atmospheric pressure was discovered during laboratory experiments conducted in this study. High purity CO_2 could be quickly desorbed from a CO_2-saturated AcK solutions by the addition of H_2O at room temperature. After CO_2 desorption, it was possible to regenerate the ultra-highly concentrated AcK aqueous solution ($AcK_{(aq)}$) for reuse as a CO_2 absorbent. This is a novel phenomenon that has not been explored in previous CCS-related studies. The overall absorption and desorption behavior of the novel absorbent was in accordance with Equation (1).

$$CH_3COOK_{(aq)} + H_2O_{(l)} + CO_{2(g)} \leftrightarrow KHCO_{3(aq)} + CH_3COOH_{(l)} \tag{1}$$
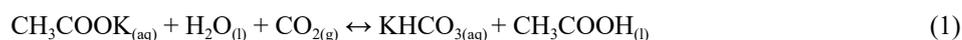
Interestingly, according to Equation (1), the addition of water will not favor CO_2 desorption. Therefore, this phenomenon seems to be contrary to the *Le Chatelier's principle* considering that according to Equation (1), H_2O is a reactant. During the experiments conducted in this study, it was observed that CO_2 could be easily and quickly desorbed from $AcK_{(aq)}$ by the addition of H_2O at 30 °C. This novel CO_2 absorption/desorption system is very suitable for Power-to-Gas (P2G) systems[20] considering that high purity CO_2 gas desorbed at 30 °C can be used to significantly reduce energy consumption. Furthermore, in P2G systems, the AcK aqueous solution could also be used as an electrolyte for the electrolysis of water to obtain hydrogen. In other words, all the steps in the P2G system could be performed at room temperature.

2. Materials and methods

All the chemicals used were analytical grade reagents, and they were used as supplied without any further purification. AcK (99.5 wt.%) was purchased from Sigma-Aldrich Co. Ltd., St Louis, MO, USA, while CO_2 (99 mol%) was purchased from Yunshan Co. Ltd., Yuanlin Chen, Changhua, Taiwan.

2.1 *Absorption of CO₂*

Aqueous solutions of AcK with different molalities (5, 10, 15, and 20 m) were prepared using AcK powder and deionized water. The CO_2 absorption experiments were performed at 30 °C in 1 h using a 300 mL bubbling reactor. The pure CO_2 gas was continuously supplied to the reactor at a flow rate of 50 mL/min using a flow controller, and the amount of CO_2 absorbed was determined using the weight method. The CO_2 absorption capacity of the aqueous AcK solutions was defined as the number of moles of CO_2/mole of AcK.

2.2 *Desorption of CO2*

The CO_2-saturated AcK solutions were desorbed by adding 10-40 wt.% distilled water at room temperature and amounts of CO_2 released were detected using the water displacement method. Additionally, similar desorption experiments were performed at 60, 70, and 80 °C using hot water baths.

2.3 *Characterization*

Fourier transform infrared (FTIR) spectra were recorded using a Perkin Elmer Frontier FTIR. The samples were mixed with KBr powder and pressed into tablets, and then analyzed over the range of 450 to 4000 cm^{-1} with a spectrum resolution of 4 cm^{-1}. The spectra were averaged over 64 scans at 30 °C. X-ray diffraction (XRD) patterns were recorded using a Bruker D2 PHASER XRD with Cu Kα radiation operated at 40 kV and 40 mA. The diffraction angles were scanned within a 2θ range of 20-80° at a scan speed of 4°/min.

3. Results

3.1 *Behaviors of CO$_2$ absorption*

The variation of the pH and the CO$_2$ absorption capacity of the absorbent with time is shown in Figure 1. Initially, the 20 m AcK aqueous solution had a pH value of 10.5, which decreased with increasing CO$_2$ absorption. Particularly, after 20 min of absorption, there was an increase in the turbidity of the aqueous AcK solution owing to the formation of a precipitate in the aqueous AcK solution, and after 40 min of absorption, the precipitation process resulted in the formation of a sludge (AcK sludge) as shown in Figure 2. Finally, the pH value of the aqueous AcK solution decreased to 7.8, and the maximum CO$_2$ absorption capacity was approximately 21.3 mmol/mol AcK. However, the CO$_2$ absorption capacity of AcK$_{(aq)}$ increases with an increase in AcK$_{(aq)}$ concentration as shown in Table 1. After CO$_2$ absorption, some precipitations were present in the 15 m AcK$_{(aq)}$ and none in the 5 and 10 m AcK$_{(aq)}$. As the concentration of AcK$_{(aq)}$ was below 10 m, the amount of CO$_2$ absorption was too low to act as an absorbent.
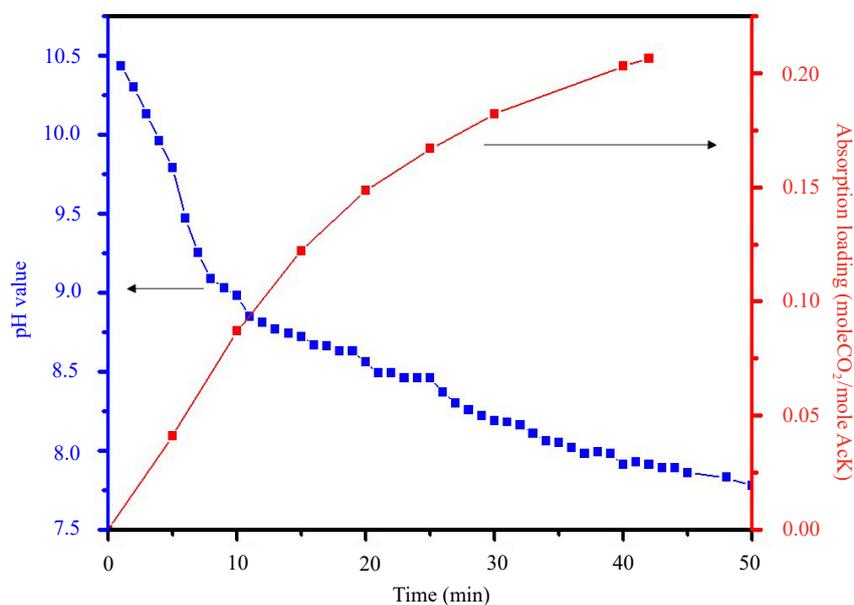
Figure 1. Variation of pH and CO$_2$ absorption loading of 20 m AcK$_{(aq)}$ absorbent with absorption time at 30 °C and atmospheric pressure
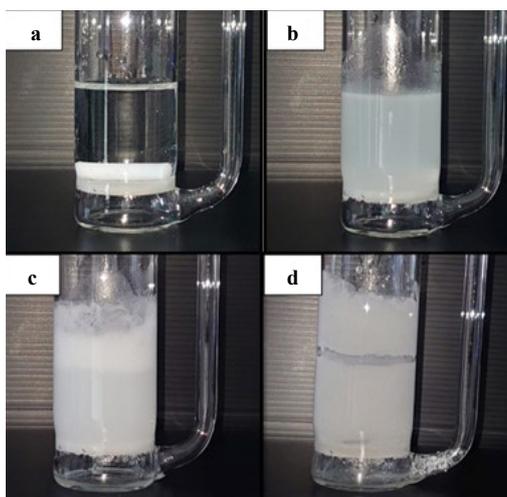
Figure 2. The turbidity and state of 20 m AcK aqueous after CO$_2$ absorption at (a) initial state; (b) after 20 min; (c) after 30 min; (d) after 40 min

[AcK] (m)	CO_2 loading* (mole CO_2/mole AcK)
20	0.206
15	0.142
10	0.089
5	0.005

*Absorption condition: $[CO_2]_{feed}$: 100%

Interestingly, CO_2 desorption from the aqueous AcK solution was easily initiated by the addition of H_2O as shown in the video included in the supplementary materials, i.e., within a short time, a large volume of CO_2 was rapidly released from the AcK sludge as water was added, and the absorbent was restored to a transparent aqueous solution. The quantity of CO_2 released depended on the amount of H_2O added as shown in Figure 3. When 10 wt.% and 40 wt.% H_2O were added, approximately 27% and more than 85% of CO_2 were released from the AcK sludge, respectively. A significant volume of high purity CO_2 could be released and collected from the absorbent by the addition of H_2O at 30 °C. Based on Equation 1, this particularly low energy consumption CO_2 desorption behavior of $AcK_{(aq)}$ seemed to contradict the *Le Chatelier's principle*. Considering that the H_2O is a reactant in this equation, its addition would rather favor the forward reaction. This observation was very interesting. Thus, the AcK sludge was further analyzed to investigate the possible CO_2 absorption/desorption mechanism of the aqueous $AcK_{(aq)}$ solution.
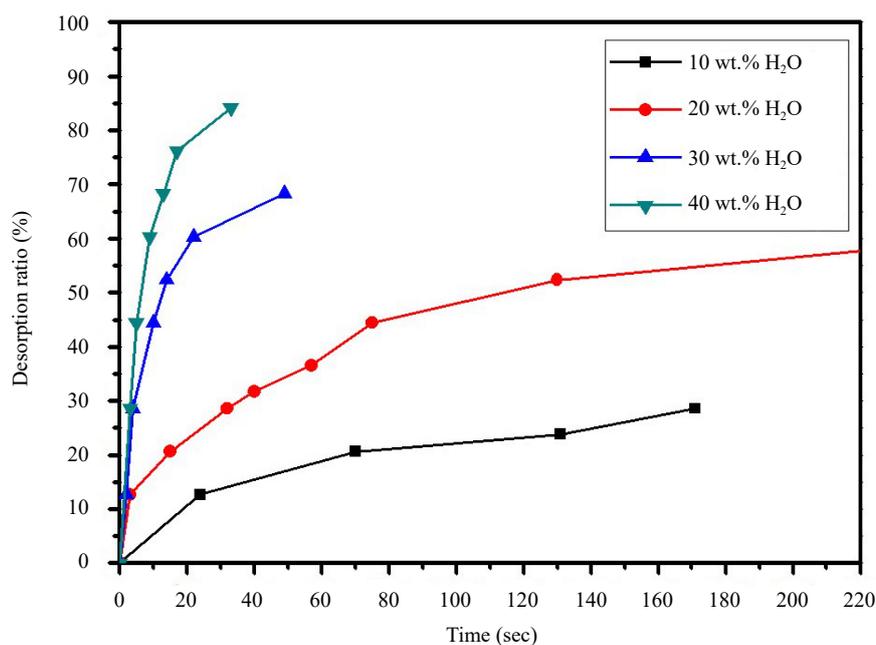
Figure 3. Variation of CO_2 desorption ratio out of 20 m AcK sludge with time resulting from the addition of different amounts of H_2O at 30 °C and atmospheric pressure

3.2 *Analysis of AcK sludge*

It is well established that the conversion of CO_2 to bicarbonate (HCO_3^-) or carbonate (CO_3^{2-}) depends on the pH of the aqueous solution. Given the high concentration of K^+ in the $AcK_{(aq)}$ absorbent, the formation of all possible species, including $KHCO_3$, $K2CO_3$, AcK, and AcK sludge were investigated using FTIR and XRD analyses. Considering all the FTIR spectra shown in Figure 4, the characteristic peaks of AcK sludge at 1650, 1400, 1000, 832, and 700 cm^{-1} reveal that the AcK sludge contained large amounts of $KHCO_3$. Additionally, the XRD diffraction pattern of AcK sludge also provided evidence that CO_2 absorption by $AcK_{(aq)}$ was in accordance with Equation (1), as shown in Figure 5. Based on the characteristic 2θ diffraction angles observed at 12°, 24.1°, 30.2°, 31.5°, and 34° ($KHCO_3$, ICDD 01-0976), $KHCO_3$ was the major constituent of the AcK sludge (AcK-CO_2). Tiny 2θ diffraction angles characteristic of K_2CO_3 and AcK were also observed in the diffraction pattern of the AcK sludge. In addition to the characteristic peaks of $KHCO_3$, H_2CO_3, and AcK, some unknown peaks at 2θ = 14.4°, 22.1°, 32.4°, and 39.7° were also observed in the XRD diffraction pattern of the AcK sludge. After diffraction pattern data comparison, these peaks were attributed to potassium hydrogen diacetate (PHDA, CAS #4251-29-0, $KH(CH_3COO)_2$), which was formed as a result of the hydrogen bonding established between the excess acetic acid and potassium acetate, a conclusion that is consistent with the CO_2 absorption pattern of the $AcK_{(aq)}$ system. When the ultra-highly concentrated aqueous AcK solution absorbed CO_2, K^+, and H_2O are consumed; thus, the amount of acetic acid increases according to Equation (1). The acetic acid then reacted with potassium acetate to form PHDA, which salted out of the ultra-highly concentrated aqueous AcK solution as a solid sediment owing to a decrease in solubility due to saturation. Similarly, for the same reason, $KHCO_3$ also salted out of the ultra-highly concentrated absorbent as a solid sediment. Therefore, CO_2 desorption from AcK sludge as a result of the addition of H_2O can be explained as follows. In addition to PHDA, which is an acidic compound that is used as a food additive, the AcK sludge also contains basic compounds ($KHCO_3$ and K_2CO_3); thus, it behaves like an effervescent tablet. Both PHDA and $KHCO_3$ were possibly decomposed and reacted resulting in the rapid release of CO_2 as H_2O was added to the AcK sludge causing them to dissolve.
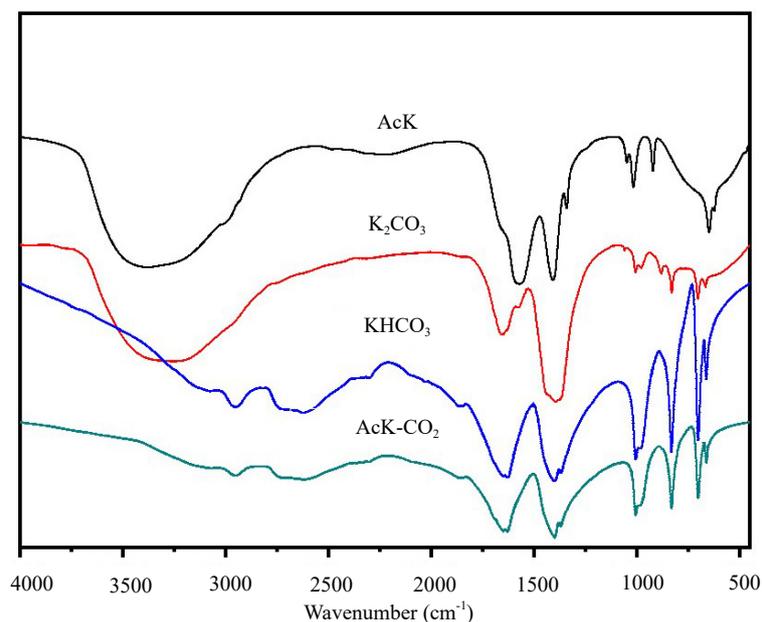
Figure 4. FTIR spectra of K_2CO_3, $KHCO_3$, AcK, and AcK sludge (AcK-CO_2)
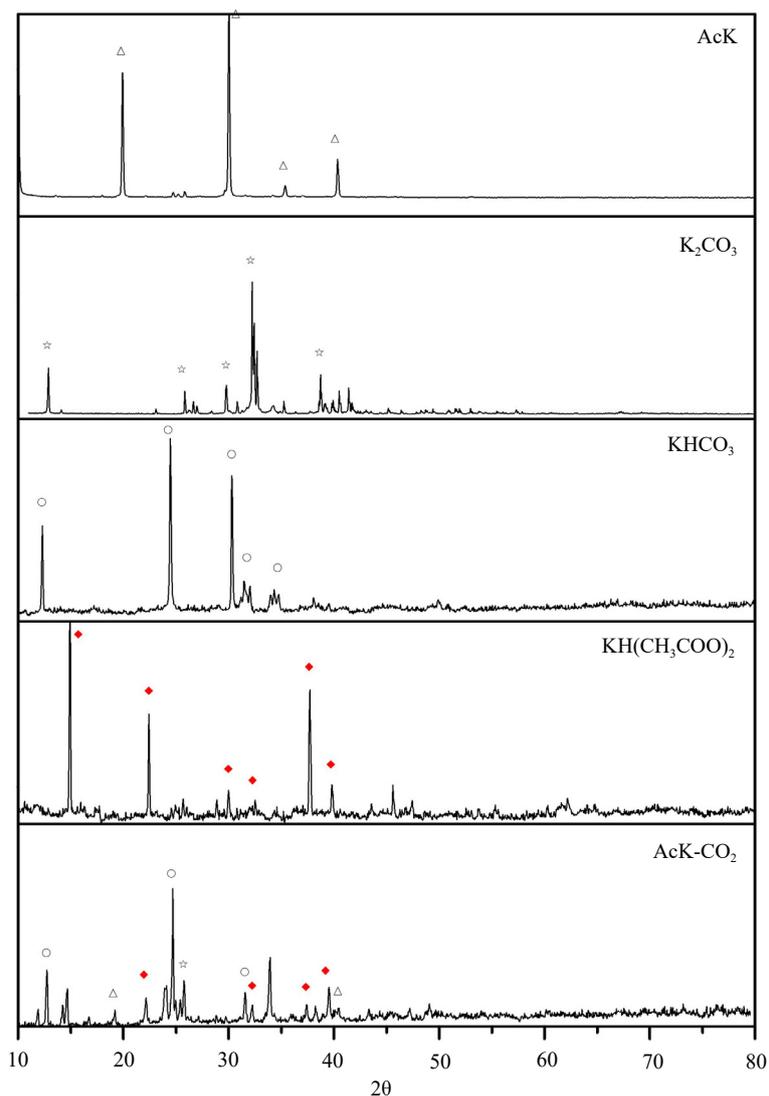
Figure 5. XRD diffraction pattern of K_2CO_3, $KHCO_3$, AcK, $KH(CH_3COO)_2$, and AcK sludge (AcK-CO_2)

3.3 *Effect of the temperature on CO_2 desorption*

The above mentioned results illustrate that CO_2 desorption out of AcK sludge can be achieved by the addition of H_2O to the AcK sludge owing to solubility when solvent volume increases. Another method by which the solubility of PHDA and $KHCO_3$ could be increased was by heating the solution. Thus, the relationship between the ratio of desorbed CO_2 and the temperature of the AcK sludge was investigated. The results show that the percentage of CO_2 desorbed out of the AcK sludge obviously depended on temperature (Figure 6). At 60 °C, the percentage of CO_2 that desorbed from the AcK sludge was greater than 60%, and at 80 °C, it was approximately 90%, indicating that the addition of water to the AcK sludge could be replaced by heating the AcK sludge to bring about the thermal desorption of CO_2. Therefore, as an absorbent, AcK has potential for application in commercial plants. Notably, the CO_2 desorption temperature and pressure for AcK absorbents are much lower than those required for amine absorbents. These lower desorption temperature and pressure conditions represent a lower energy consumption and an eco-operation requirement.
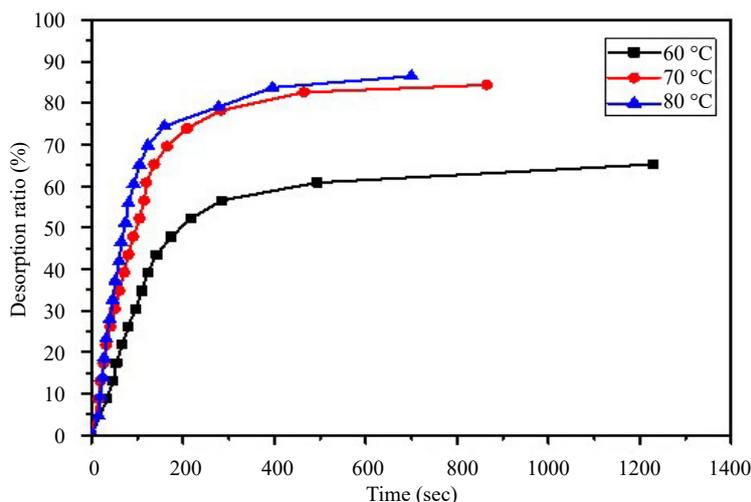
Figure 6. Variation of CO_2 desorption ratio of 20 m AcK-sludge with temperature

4. Discussions

The mechanism of CO_2 absorption and desorption by $AcK_{(aq)}$ is created and presented in Figure 7, in which four stages of CO_2 capture mechanism are evidenced. Firstly, HCO_3^- and CO_3^{2-} are formed when CO_2 is dissolved in the aqueous AcK solution resulting in a rapid decrease in pH. During this stage, $[HCO_3^-]$ will be higher than $[CO_3^{2-}]$ owing to the pH that is below 9. Secondly, as $[K^+]$ and $[HCO_3^-]$ increase to reach the solubility of $KHCO_3$, and thus, it starts to precipitate causing the $AcK_{(aq)}$ absorbent to become turbid, and when it becomes saturated with CO_2, the sludge state is obtained. Thirdly, acetic acid will be formed within the AcK sludge given that the K^+ is consumed by the CO_3^{2-}, and it will react with potassium acetate to form PHDA, which also precipitates out of the ultra-highly concentrated aqueous AcK solution as a solid sediment owing to a decrease in solubility brought about by saturation. Finally, as H_2O is added to the AcK sludge or as the AcK sludge is heated to temperatures above 60 °C, ultra-high purity CO_2 is released. When the CO_2 desorption results from the addition of H_2O, the final concentration of the absorbent is lower than its initial concentration. However, if thermal CO_2 desorption is employed, the concentration of the $AcK_{(aq)}$ absorbent typically remains unchanged.
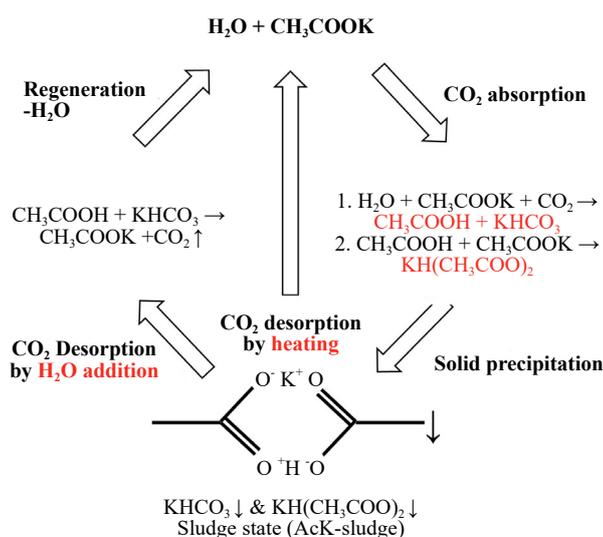
Figure 7. Schematic presentation of the CO_2 absorption and desorption mechanism for $AcK_{(aq)}$ absorbent

In summary, as an absorbent, $AcK_{(aq)}$ is a stable salt solution that does not result in the formation of secondary pollutants during CO_2 absorption and desorption. This novel desorption behavior was attributed to the dimer structure of $KH(CH_3COO)_2$, which was formed and precipitated within the $AcK_{(aq)}$. When water was added, the precipitated $KH(CH_3COO)_2$ and $KHCO_3$ re-dissolved and underwent an acid-base reaction that resulted in the release of high purity CO_2. This novel CO_2 absorption and desorption mechanism exhibited by $AcK_{(aq)}$ reveals that as a low-energy consumption CO_2 absorption/desorption system, $AcK_{(aq)}$ has a high potential for application in commercial production processes.

5. Conclusions

A novel CO_2 absorbent, $AcK_{(aq)}$, was explored in this study. The results showed that it could quickly and almost completely desorb CO_2 when 40 wt.% H_2O was added to it at 30 ℃ or when it was heated to temperatures above 60 ℃. This novel desorption behavior was attributed to the dimer structure of $KH(CH_3COO)_2$, which was formed and precipitated within the $AcK_{(aq)}$. When water was added, the precipitated $KH(CH_3COO)_2$ and $KHCO_3$ re-dissolved and underwent an acid-base reaction that resulted in the release of high purity CO_2. This novel CO_2 absorption and desorption mechanism exhibited by $AcK_{(aq)}$ reveals that as a low-energy consumption CO_2 absorption/desorption system, $AcK_{(aq)}$ has a high potential for application in commercial production processes. A pilot plant of the $AcK_{(aq)}$ absorption system is being constructed in the laboratory and further information will be published for the benefit of researchers and industry.

Supplementary Materials

Movie S1: The desorption of CO_2 by adding 40 wt.% water.

Author contributions

Jian-Sheng Shen: Investigation (equal); writing – original draft (equal). Cheng-Chien Wang: Writing – review and editing (equal). Chuh-Yung Chen: Review and editing (equal). Chen-Yang Lin: Assistant investigation.

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Conflicts of interest

There is no conflict of interest for this study.

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