We are IntechOpen,
the world's leading publisher of Open Access books
Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Synergistic Effect on CO$_2$ Capture by Binary Solvent System

Quan Zhuang and Bruce Clements

Additional information is available at the end of the chapter

Abstract

CO$_2$ absorption into a binary solvent system was studied using a batch-mode gas/liquid absorption apparatus. The binary system composed of potassium carbonate (K$_2$CO$_3$) and piperazine (PZ) showed a strong synergistic effect, whereby the binary solvent performed better than either of the individual solvents for CO$_2$ absorption. The other pairs of solvents tested (K$_2$CO$_3$/monoethanolamine (MEA) and K$_2$CO$_3$/NaOH) showed no synergistic effects. The results indicate that this synergistic effect only occurs with specific pairs of solvents. The mechanism for the synergistic effect is postulated that the activated CO$_2$ on PZ migrates to K$_2$CO$_3$, or a more reactive intermediate complex between K$_2$CO$_3$ and PZ is formed.

Keywords: post-combustion, carbon capture, binary solvent, synergy effect, piperazine, potassium carbonate, CO$_2$ absorption

1. Introduction

There has been a growing concern over greenhouse gas emissions as they are considered to be the direct cause of global warming [1, 2]. Postcombustion capture technology is widely being studied for capturing CO$_2$ produced in power generation plants [3–5]. Compared with other CO$_2$ capture technologies such as oxy-fuel combustion and integrated gasification combined cycle (IGCC), postcombustion capture is regarded as the most probable technology to be first employed when carbon capture becomes a reality in the near future in terms of technology

readiness level, flexibility, and economics [6]. Postcombustion capture technology uses liquid solvents to make efficient contact with CO_2-containing flue gas, during which CO_2 interacts and reacts with the solvent and is removed from the flue gas stream. After absorption, the CO_2-laden solvent undergoes a regeneration operation, releasing pure CO_2 which is then compressed, transported, and sequestered. The regenerated solvent, now at lean state, is returned to start the next cycle of CO_2 capture. The whole operation is a continuous process. The same or similar technologies have been applied for decades for natural gas purification and syngas CO_2 separation [7–9]. For greenhouse gas CO_2 mitigation applications, commercial solvents such as amine, potassium carbonate, and methanol are currently being tested, however, improved solvents are required to reduce the cost and increase the efficiency of postcombustion capture systems. At the moment, solvents that are being developed for CO_2 capture include nonconventional amines, aqueous ammonia, amino acids, ionic liquids, and mixtures of two or more solvents, i.e., hybrid systems [10, 11].

Potassium carbonate is known to be used in industrial CO_2 separation processes, such as Benfield and Catcarb [12], as the main solvent with or without proprietary additives. It has advantages over amines: lower cost, lower heat of absorption, thermal stability, nonvolatile, less corrosiveness, low toxicity, and environmentally friendly. A major downside for using K_2CO_3, however, is its slow absorption rate and low CO_2 absorption capacity, resulting in poor CO_2 mass transfer rate relative to amines. The way to overcome the aforementioned shortcomings of K_2CO_3 is to add promoter, i.e., a hybrid solvent. Hybrid solvent systems have the potential to perform better than the individual components alone. Physicochemical properties of different solvents can supplement each other. Synergistic effect or cooperative effect of hybrid solvents has been found in applications in other areas such as extraction and coal swelling [13, 14]. The mechanisms of the synergistic effects are suggested to be engendered by thermodynamics and hydrogen bonding.

We have been studying CO_2 absorption using an aqueous potassium carbonate solvent solution with the addition of other solvents in an attempt to improve CO_2 absorption performance. In this chapter, we report results of a synergistic effect that became apparent during these studies. When small amount of piperazine (PZ) is added to the potassium carbonate solution, both CO_2 absorption rate and capacity are significantly enhanced, exceeding the mathematical sum of the CO_2 absorption rate and the capacity of the individual solvents.

Piperazine itself is an active absorbent for CO_2 [15]. For some engineering reasons, it has only been used as an additive or a promoter to other common CO_2 capture amines [16]. With amine solvents, piperazine has shown promotional effect. For instance, the CESAR-1 solvent is an aqueous blend of AMP (2-amino-2-methyl-1-propanol) and PZ which showed a reduction of about 20% in the regeneration energy and 45% in the solvent circulation rate compared to those of MEA-based CO_2 capture process under similar process condition [17].

There have been some reports on the promotional/synergistic effect on CO_2 capture by K_2CO_3 and PZ [18]. This study builds upon previous achievements and provides convincing experimental evidence of the synergistic effect.

2. Experimental

A batch-mode liquid-gas absorption apparatus was constructed in CanmetENERGY, Ottawa. A schematic and a photo of the apparatus are shown in **Figure 1**. All of the connections within the system are vacuum-proof. The volume of the four-neck flask is 690 ml. The solute gas used in the experiment is a mixture of CO$_2$ and air (49 v% of CO$_2$). CO$_2$ absorption tests were carried out at 21℃ (room temperature). The flask was placed in a water bath to maintain a constant temperature (CO$_2$ absorption is exothermic). First, the flask was purged by the solute gas for 10 min. Then all of the valves of the flask were closed, leaving the gas in the flask at ambient pressure. After this, 10 ml of solvent was introduced into the flask by opening the two valves of the funnel, and then closing them quickly so that the flask becomes a closed system with gaseous solute in contact with liquid solvent. The liquid was agitated by a magnetic stirrer at 350 rpm (there was no difference on the CO$_2$ absorption results with rpm in the range of 300–400). When the CO$_2$ was absorbed, the pressure in the flask decreased. This pressure was monitored with a solid state pressure sensor/transducer (PX209-30V15GI) from Omega. A monotonous pressure declining curve was obtained, revealing the CO$_2$ absorption kinetics (rate of decline) as well as capacity (the final level-off of the decline).

1. Funnel for liquid solvent introduction
2. CO$_2$/air gas inlet
3. Pressure sensor to computer
4. Purge outlet
5. Water bath to maintain constant temperature
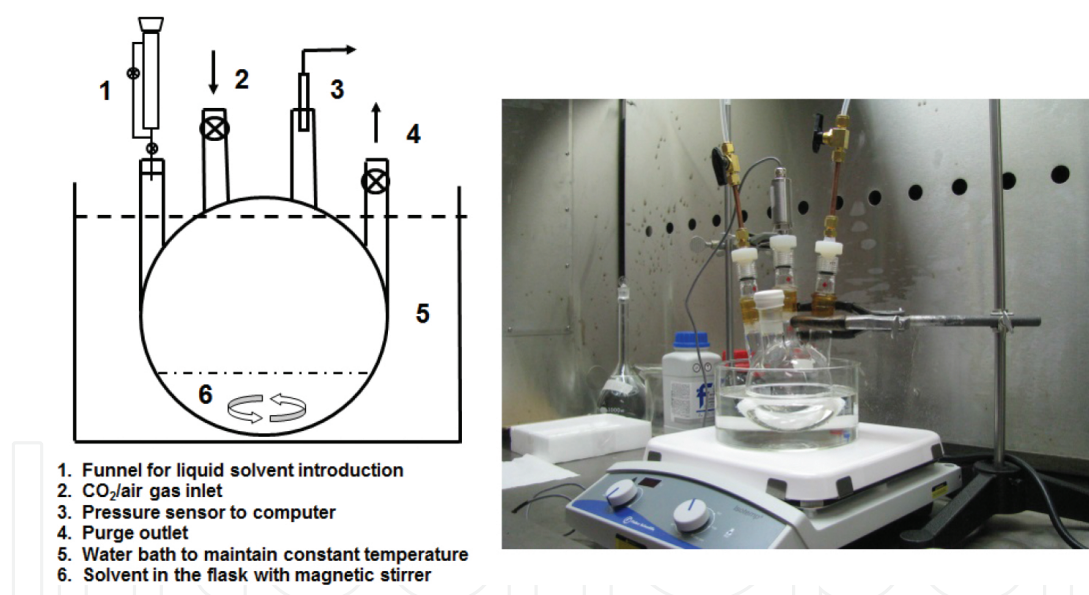6. Solvent in the flask with magnetic stirrer

Figure 1. Batch mode gas-liquid absorption apparatus.

The solvents used and their concentrations in aqueous solution are shown in **Table 1**. In the test, the primary solvent was aqueous potassium carbonate, K$_2$CO$_3$. Other solvents were used as secondary promoters to see if there was a synergistic effect between the primary and secondary solvents. The hybrid solvents were obtained by mixing the individual solvents (shown in **Table 1**) with certain ratio (quantity in ml). Water was added to adjust the effective concentration and the final volume in a test.

Three test series were completed, one for each of the secondary solvents. These included:

<u>Test Series 1—K_2CO_3 (primary solvent) with PZ (secondary solvent)</u>

- 7 ml K_2CO_3/3 ml H_2O (K_2CO_3 represents its solution in **Table 1**)

- 3 ml PZ/7 ml H_2O (PZ represents its solution in **Table 1**)

- 7 ml K_2CO_3/3 ml PZ

<u>Test Series 2—K_2CO_3 (primary solvent) with MEA (secondary solvent)</u>

- 7 ml K_2CO_3/3ml H_2O

- 3 ml MEA/7 ml H_2O (MEA represents its solution in **Table 1**)

- 7 ml K_2CO_3/3 ml MEA

<u>Test Series 3—K_2CO_3 (primary solvent) with NaOH (secondary solvent)</u>

- 7 ml K_2CO_3/3 ml H_2O

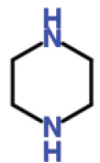- 3 ml NaOH/7 ml H_2O (NaOH represents its solution in **Table 1**)

- 7 ml K_2CO_3/3 ml NaOH
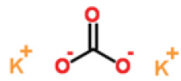
Solvent	Molecular. formula	Density (g/cm³)	Molar mass (g/mol)	Concentration used (% wt)	Structure
Potassium carbonate	K_2CO_3	2.43	138.21	33	
Piperazine (PZ)	$C_4H_{10}N_2$	1.98	86.14	16	
Ethanolamine (MEA)	C_2H_7NO	1.01	61.08	15	
Sodium hydroxide	NaOH	2.13	40.00	15	

Table 1. Properties of chemicals and solvents used in the experiment.

3. Results and discussion

The CO_2 absorption results for test series 1 are shown in **Figure 2**. After the solvent was introduced into the flask filled with CO_2/air, the chemisorption occurred as demonstrated by the pressure decrease. From the results in **Figure 2**, it can be seen that K_2CO_3 showed a slow absorption rate and low absorption capacity. Piperazine's CO_2 absorption rate was faster and

had higher capacity. When the two solvents were mixed, the binary solvent system absorbed more CO$_2$ at an even faster rate. The mathematical sum of the individual CO$_2$ absorption curves of the K$_2$CO$_3$ and piperazine (the sum of the green curve and the light blue curve) is shown in **Figure 2** as well (dark blue line). It is clear that the binary solvent system performed much better for CO$_2$ absorption than the mathematical sum of the individual solvents. The two curves (orange and purple in **Figure 2**) showing the CO$_2$ absorption results of the binary solvent system from two different tests under the same conditions indicate that the apparatus worked very well with a high degree of repeatability.
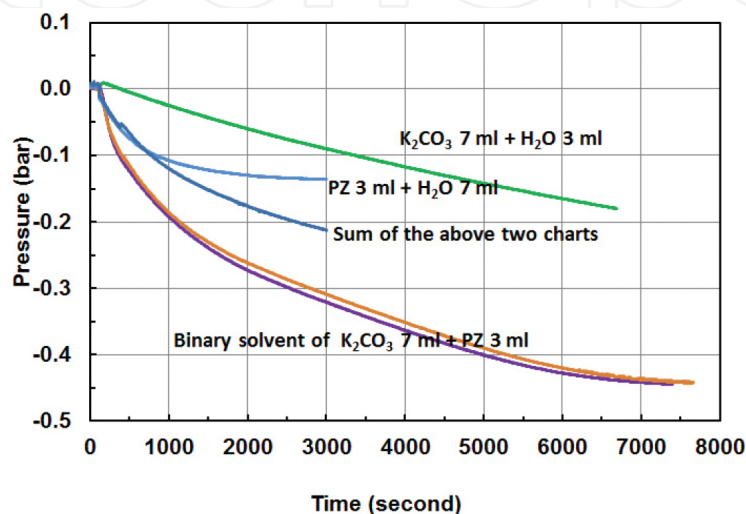

Figure 2. Test series 1—CO$_2$ absorption with binary solvent system of K$_2$CO$_3$ and piperazine.

The test results of the binary solvent system of K$_2$CO$_3$ and MEA are shown in **Figure 3**. The component solvents of K$_2$CO$_3$ and MEA were of similar effectiveness for CO$_2$ absorption. The binary solvent system showed only a slight synergistic effect.
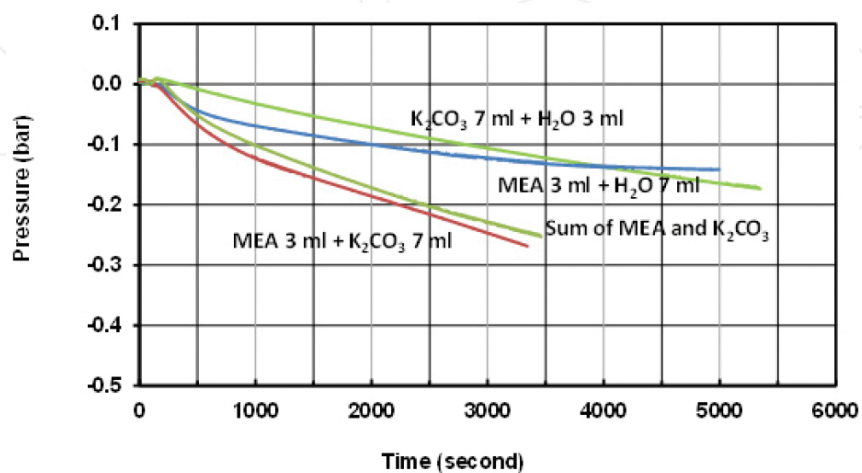

Figure 3. Test series 2—CO$_2$ absorption with binary solvent system of K$_2$CO$_3$ and MEA.

In order to investigate the necessary and/or sufficient conditions for the synergistic effect of a stronger CO_2 solvent with a milder solvent (e.g., PZ with K_2CO_3), the binary solvent system of K_2CO_3 with NaOH was tested (**Figure 4**). It can be seen from **Figure 4** that, although NaOH is a much stronger CO_2 solvent than K_2CO_3, the binary solvent system of K_2CO_3 and NaOH does not show any synergistic effect.
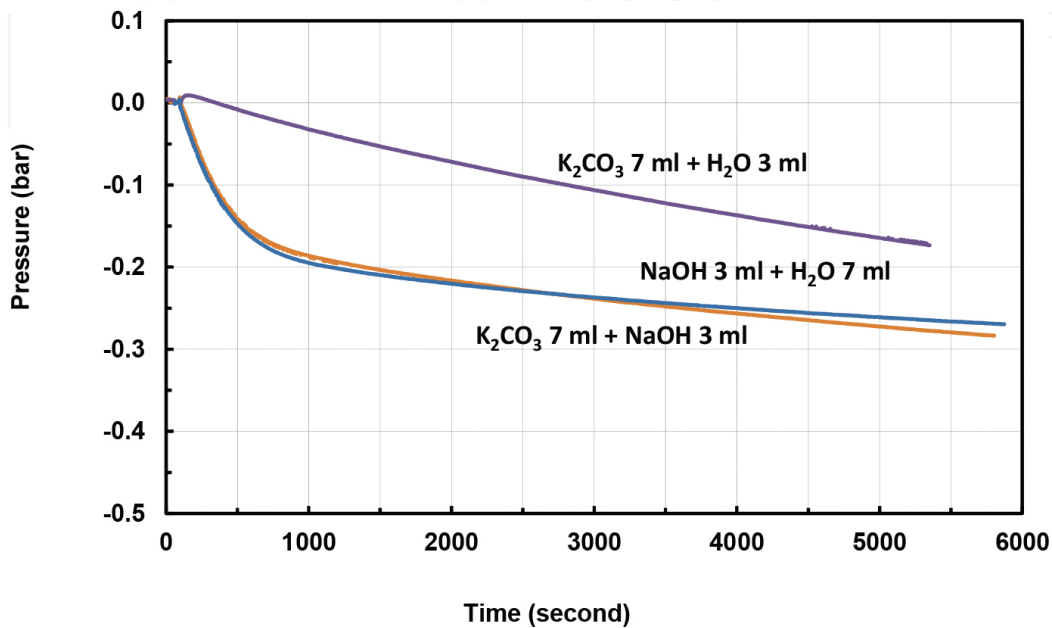

Figure 4. Test series 3—CO_2 absorption with binary solvent system of K_2CO_3 and NaOH.
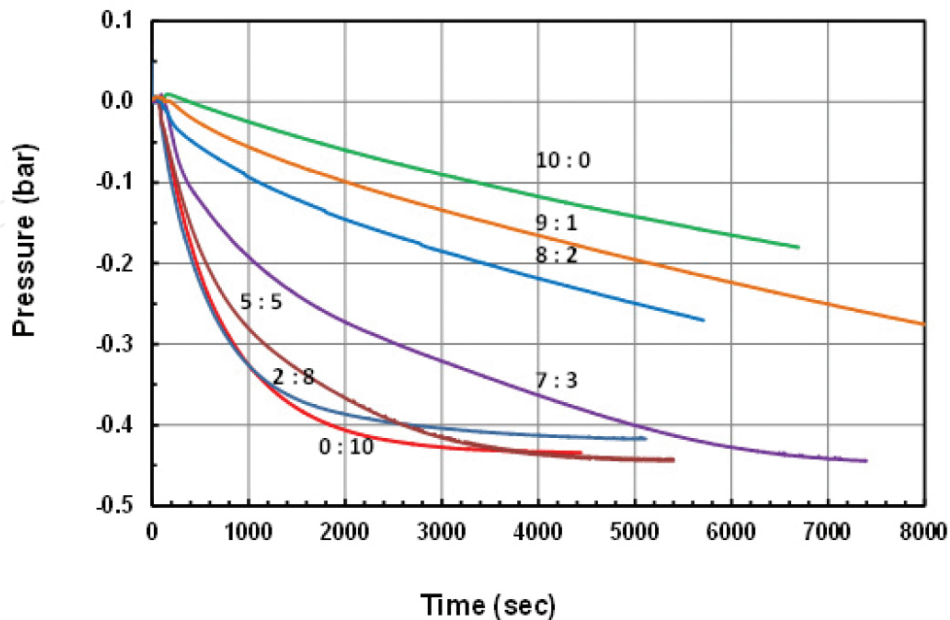

Figure 5. The CO_2 absorption by binary solvent versus the ratio of K_2CO_3:PZ.

Therefore, it is a necessary but not a sufficient condition for a binary solvent system with different CO_2 absorption capacities and kinetics to generate synergistic effect. Among the three pairs, only the binary solvent of K_2CO_3 and PZ showed a positive synergistic effect on CO_2 absorption.

As shown by our experiment (**Figure 2**) and others [19], PZ is a stronger and faster CO_2 solvent than K_2CO_3. When the ratio of K_2CO_3 and PZ was varied, the CO_2 absorption curves shifted from the curve of K_2CO_3 to the curve of PZ, as shown in **Figure 5**. The binary solvent systems between the two pure solvents exhibit synergistic effect. Illustrated in **Figure 6** is the synergistic performance of the binary solvent as well as the relationships with the two pure solvents (this is only a general illustration).
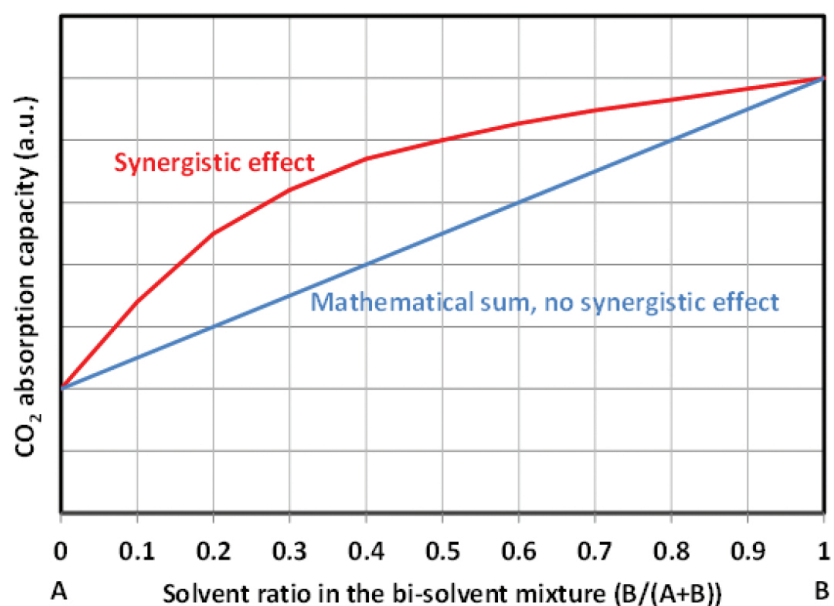

Figure 6. Illustration of synergistic effect by a binary solvent system, e.g., K_2CO_3/PZ.

PZ is an expensive solvent. Whether or not it is suitable, alone, as a CO_2 capture solvent is still being explored in terms of thermal stability, corrosiveness and cost, etc. [19]. As shown by this study, it is promising to apply a binary solvent of K_2CO_3 and PZ at a ratio that maximizes the synergistic effect on CO_2 capture. Savings from operating at this condition could be realized in terms of solvent cost, reduction of the absorber and regenerator sizes due to the improved CO_2 absorption rate and capacity. More effective solvents would require smaller absorbers and regenerators, leading to lower capital costs.

J. Tim Cullinane and Gary T. Rochelle have reported the promotional effect of K_2CO_3 and PZ by kinetics [18]. They concluded that the promotional effect comes from the kinetics of the two individual solvents and that the two solvents absorb CO_2 independently. These cannot explain the observations of this study. The promotional or synergistic effect of PZ to K_2CO_3 has been suggested to occur through an intermediate formed between CO_2 (aq) and PZ [20–22]. This hypothesis, however, still needs to be verified experimentally. Our results indicate that there may be a more interactive mechanism affecting the hybrid solvent performance. Having a

binary solvent system with one solvent more effective than the other is a necessary condition for the synergistic effect (the pairs of K_2CO_3 and PZ, K_2CO_3, and NaOH), but not a sufficient condition (K_2CO_3 and NaOH). There must be other reasons behind the synergistic effect. Here we postulate two mechanisms:

- CO_2 transition (or spill over or migration): CO_2 is reactivated by solvent B forming a labile state [[B] · [CO_2]$_{(aq)}$], then transfers or migrates to solvent A to finish CO_2 absorption (**Figure 6**). Likely hydrogen bonding is involved.

- Reactive complex intermediate structure between the two solvents: in the CO_2 absorption system, there occur some kind of interactions between the two solvents by hydrogen bonding or local ionic attraction, forming a more reactive intermediate complex [A·B] with improved CO_2 absorption ability.

The factors of electron donner strength, dielectric constants, solubility parameters of the individual absorbent, and hydrogen-bonding/nonhydrogen-bonding may influence the degree of synergistic effects. There needs more research work to capture and characterize the reactive intermediate complex or transition state, to prove or disprove these postulated mechanisms.

4. Conclusion

The idea of combining solvents to improve absorption is effective for piperazine and K_2CO_3. These two solvents interact together and generate a greater absorption than each of the individual solvents. The other solvents, i.e., MEA and NaOH, when mixed with K_2CO_3 did not improve CO_2 absorption, implying that the synergistic effect only occurs selectively between specific pairs of solvents. The solution of 3 ml piperazine with 7 ml potassium carbonate is the optimal ratio that increases CO_2 absorption using the least amount of piperazine. The results of these tests show the possibility of using piperazine and K_2CO_3 solution at an industrial scale. If correctly implemented, it would result in savings in capital by reducing the absorber size compared to use K_2CO_3 alone. The next step for this project is to apply these results within a larger system. The major conclusions from the tests conducted are summarized below:

- A synergistic effect between K_2CO_3 and piperazine was observed.

- This synergistic effect only happens between this specific pair of solvents and is not universal. Other than the thermodynamic reasons behind the effect, there seems to be some additional mechanism that enhances the reaction (potentially a labile [CO_2] formation followed by migration or some more reactive intermediate complex structure formed between the two solvent molecules).

- 3 ml piperazine/7 ml K_2CO_3 ratio is the most effective (faster absorption rate and higher absorption capacity).

Acknowledgements

Author details

Quan Zhuang* and Bruce Clements

*Address all correspondence to: quan.zhuang@canada.ca

Natural Resources Canada, CanmetENERGY, Ottawa, Ontario, Canada

References

[1] Kathryn A. Mumford, Yue Wu, Kathryn H. Smith, Geoffrey W. Stevens, "Review of solvent based carbon-dioxide capture technologies", Front. Chem. Sci. Eng. 2015, 9(2): 125–141.

[2] IPCC Report, 2014 and the previous annual editions.

[3] Yasaman Mirfendereski, "Techno-Economic Assessment of Carbon Capture and Sequestration Technologies in the Fossil Fuel-based Power Sector of the Global Energy-Economy System", Master Thesis, Technische Universität Berlin, May 2008.

[4] Quan Zhuan, Bruce Clements, Ying Li, "From ammonium bicarbonate fertilizer production process to power plant CO_2 capture", Int. J. Greenhouse Gas Control, 2012, 10: 56–63.

[5] Quan Zhuang, Richard Pomalis, Ligang Zheng, Bruce Clements, "Ammonia- based carbon dioxide capture technology: issues and solutions", Energy Procedia, 2010, 4: 1459–1470.

[6] Bruce G. Miller, Clean Coal Engineering Technology, Elsevier, Burlington, USA, 2011.

[7] Salako Abiodun Ebenezer, "Removal of carbon dioxide from natural gas for LNG production", Institute of Petroleum Technology Norwegian University of Science and Technology, 2005.

[8] Chao Chen, "A technical and economic assessment of CO_2 capture technology for IGCC power plants", Ph.D. Thesis, Carnegie Mellon University, 2005.

[9] Barry Burr and Lili Lyddon, "A comparison of physical solvents for acid gas removal", GPA 2008.

[10] Young Eun Kim, Jeong Ho Choi, Sung Chan Nam, Yeo Il Yoon, "CO_2 absorption capacity using aqueous potassium carbonate with 2-methylpiperazine and piperazine", J. Ind. Eng. Chem., 2012, 18: 105–110.

[11] Gary T. Rochelle, Frank Seibert, "CO_2 capture by absorption with potassium carbonate", DOE Final Report, December 2007.

[12] B. Amerijiafari, F. Grange, H. Ford, "Alternative concepts for supplying carbon dioxide for enhanced oil recovery projects", DOE Final Report, 1980.

[13] Yongseung Yun, Eric M. Suuberg, "Cooperative effects in solvent swelling of a bituminous coal", Energy Fuels, 1998, 12: 798–800.

[14] Izuru Matsubayashi, Yuko Hasegawa, "Thermodynamic consideration for solvent effects in the synergistic extraction of europium (III) with pivaloyltrifluoroacetone and 1,10-Phenonthroline", Anal. Sci., 2001, 17: 221–223.

[15] Francis Bougie, Maria C. Iliuta,"CO_2 absorption in aqueous piperazine solutions: experimental study and modeling", J. Chem. Eng. Data, 2011, 56: 1547–1554.

[16] Derks, P.W.J., "Carbon Dioxide Absorption in Piperazine Activated N-Methyldiethanolamine", PhD thesis, University of Twente, The Netherlands, 2006.

[17] Eva Sanchez Fernandez, "Novel process designs to improve the efficiency of postcombustion carbon dioxide capture", Ph.D. Thesis, Universidad Complutense de Madrid, 2013.

[18] J. Tim Cullinane, Gary T. Rochelle, "Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine", Chem. Eng. Sci. 2004, 59: 3619–3630.

[19] David H. Van Wagener, Gary T. Rochelle, Eric Chen, "Modeling of pilot stripper results for CO_2 capture by aqueous piperazine", Intl. J. Greenhouse Gas Control, 2013, 12: 280–287.

[20] R. Ramazania, S. Mazinanib, A. Jahanmiria, B. Van der Bruggen, "Experimental investigation of the effect of addition of differentactivators to aqueous solution of potassium carbonate: absorption rate and solubility", Intl. J. Greenhouse Gas Control, 2016, 45: 27–33.

[21] A.L. Shrier, P.V. Danckwerts, "Carbon dioxide absorption into amine-promoted potash solutions", Ind. Eng. Chem. Fundam. 1969, 8: 415–423.

[22] G. Astarita, D.W. Savage, J. Longo, "Promotion of CO_2 mass transfer in carbonate solutions", Chem. Eng. Sci. 1981, 36: 581–588.