

Research Article

Open Access



Feasibility of CO₂ desorption and electrolytic regeneration of potassium carbonate solution in an anion exchange membrane cell

Daxue Fu^{1,2}, Yukun Wang^{1,2}, Shikai Yu^{1,2}

¹Key Laboratory for Ecological Utilization of Multimetallic Mineral (Ministry of Education), Northeastern University, Shenyang 110819, Liaoning, China.

²School of Metallurgy, Northeastern University, Shenyang 110819, Liaoning, China.

Correspondence to: Daxue Fu, Key Laboratory for Ecological Utilization of Multimetallic Mineral (Ministry of Education), Northeastern University, NO. 3-11, Wenhua Road, Heping District, Shenyang 110819, Liaoning, China. E-mail: llow@126.com

How to cite this article: Fu D, Wang Y, Yu S. Feasibility of CO₂ desorption and electrolytic regeneration of potassium carbonate solution in an anion exchange membrane cell. *Miner Miner Mater* 2023;2:11. <https://dx.doi.org/10.20517/mmm.2023.19>

Received: 13 Jul 2023 **First Decision:** 20 Sep 2023 **Revised:** 7 Oct 2023 **Accepted:** 19 Oct 2023 **Published:** 23 Oct 2023

Academic Editors: Zenixole Tshentu, Shaoxian Song **Copy Editor:** Dong-Li Li **Production Editor:** Dong-Li Li

Abstract

In this work, an electrolytic process was introduced for coupled regeneration of potassium carbonate (K₂CO₃) solution and water electrolysis by using an anion exchange membrane cell. The process made the CO₂ separation from O₂ much easier with respect to the existing cationic exchange membrane process. The solution of K₂CO₃ was used in the cathode chamber to simulate the solution after absorbing CO₂. The solution of sulfuric acid (0.1 mol/L H₂SO₄) was charged in the anode chamber. The feasibility of the process was discussed. The effects of various operation parameters, including temperature, current density, and electrolysis time, were studied. The results indicate that both the yield rate of CO₂ and the current efficiency increase initially and decrease afterward with temperature. The yield rate of CO₂ increases while the current efficiency decreases with the current density. A low current density can reduce the energy consumption for producing the same amount of CO₂. The processes using anion exchange membrane electrolysis can regenerate the absorbent solution to achieve 89% current efficiency, and the simultaneous production of three pure gases, CO₂, H₂, and O₂, makes this method promising.

Keywords: Membrane electrolysis, Benfield, regeneration, carbon dioxide



© The Author(s) 2023. **Open Access** This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.



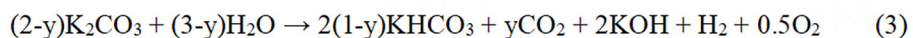
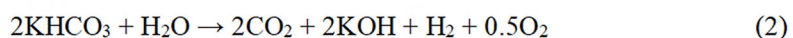
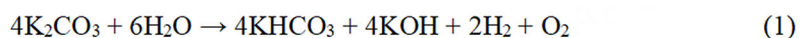
INTRODUCTION

In the past 40 years, the global climate and environment have been deteriorating, and the temperature has been rising. The use of fossil energy produces a large amount of carbon dioxide (CO₂), which makes the total amount of CO₂ in the atmosphere continue to rise, resulting in the greenhouse effect, rising sea levels, and frequent extreme weather. In order to improve its status, China has proposed a policy to achieve a carbon peak by 2030 and carbon neutrality by 2060. In 2020, carbon emissions in China reached 9.9 billion tons, of which CO₂ emissions from industrial flue gas accounted for the main part.

Pure CO₂ is an important chemical raw material, and its separation and purification in flue gas is the premise of its resource utilization. Some processes have been investigated and developed for separation and purification of CO₂, such as physical and chemical absorption^[1-6], membrane separation^[7-10], chemical looping^[11-13], and cryogenic separation^[14].

Chemical absorption is one of the most widely used methods in comparison with other post-combustion CO₂ absorption processes^[15]. Among those non-organic-based chemical solvents, including potassium carbonate (K₂CO₃), sodium carbonate, and aqueous ammonia, K₂CO₃ is the most effective, economical, and traditional solvent^[16]. The hot aqueous solution of K₂CO₃ has been widely used in the process of removing CO₂ such as natural gas sweetening or the production of pure hydrogen for ammonia synthesis^[17]. CO₂ is separated from the flue gas by chemical reactions between CO₂ and K₂CO₃ solution to produce potassium bicarbonate (KHCO₃). The absorbent is regenerated in subsequent steps, and CO₂ is desorbed by low pressure or high temperature.

The hot K₂CO₃ process (Benfield process) requires a considerable amount of heat for regeneration^[18]. Martin and Kubic^[19] developed an innovative process called Green Freedom for the capture and recovery of atmospheric CO₂ through ion-exchange-membrane electrolysis. In the new process, the recovery of captured CO₂ is realized by electrolytic stripping. The process was developed to recover CO₂ from rich K₂CO₃ solutions, and it drastically reduced the energy needed for CO₂ stripping and regeneration of the absorbent solution. In addition, Zhao *et al.* investigated the mechanism and energy consumption for this process^[20]. The electrolysis process is conducted in which CO₂ is released in three steps as the following: (1) No CO₂ release step- Reaction 1 takes place; (2) Enhanced CO₂ release step- Reaction 2 occurs to produce CO₂; (3) Steady CO₂ release step- CO₂ is released from this step through Reaction 3.



They concluded that energy requirements can decrease by around 16.6% for electrolytic regeneration processes and 25.8% for the total CO₂ capture and compression process using electrolytic regeneration.

However, the present electrolysis process can only obtain a mixture of CO₂ (~70%) and O₂ in the anode chamber^[16,19,20]. It is necessary to separate them by additional processes. In this paper, the authors introduced a modified electrolytic regeneration process by which three pure gases, CO₂, O₂, and H₂, are produced. Our process uses an anionic exchange membrane as compared to a cationic exchange membrane, as reported by other researchers^[19,20]. Because of the modification, CO₂ and O₂ are produced in the anode compartment, yet at two separate positions (membrane and electrode surfaces, respectively), thus making the CO₂ separation

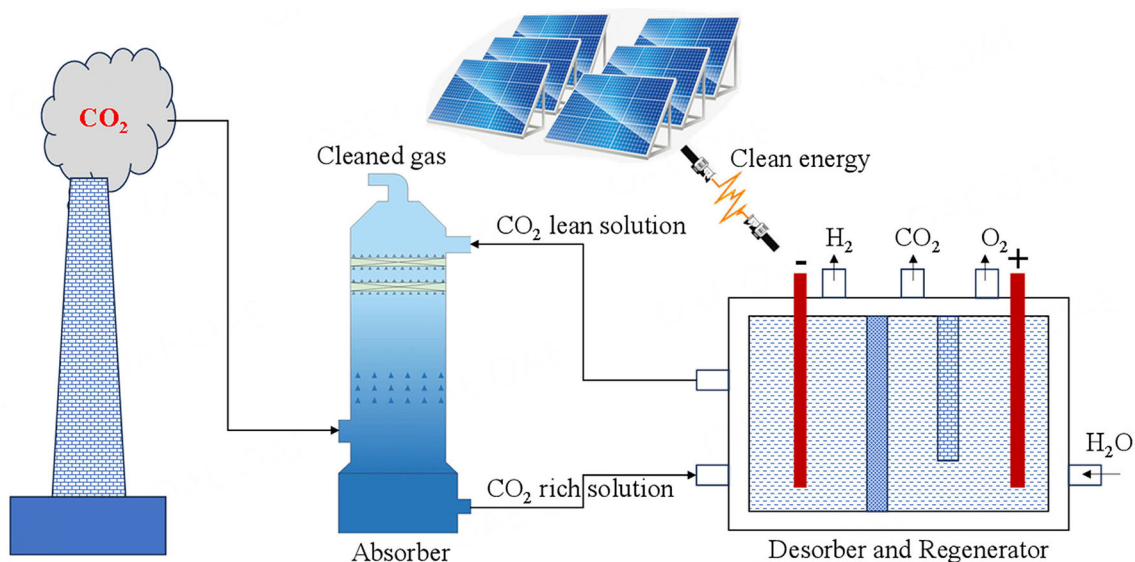


Figure 1. Chemical absorption system with the modified electrolytic regeneration process.

from O_2 much easier with respect to the cationic exchange membrane process. **Figure 1** shows a chemical absorption system with the modified electrolytic regeneration process. The CO_2 -rich solution is pumped into the electrolytic regenerator, in which desorption of CO_2 occurs with regeneration of the absorbent solution. The hydrogen as a by-product produced in the process and CO_2 can be done via catalytic reactions to form methanol^[21]. The electricity used in this process comes from clean energy.

In the paper, the regeneration mechanism of K_2CO_3 solution after absorption of CO_2 using the modified ion-exchange membrane electrolysis process and the effects of various operation parameters, including temperature, current density, and electrolysis time, have been studied.

METHODS

The solution of K_2CO_3 purchased with a purity of 99% (K_2CO_3) was used in the cathode chamber to simulate the solution after absorbing CO_2 . The solution of sulfuric acid (0.1 mol/L H_2SO_4) was charged in the anode chamber. The solution of 200 mL was used in the experiments. The cells were separated by the anion exchange membrane (Huamotech AEM8040). Titanium plate and Titanium plate with IrO_2 coating were used as the cathode and the anode, respectively. The electrolysis reactions were carried out at constant current density with an electrode area of 20 cm^2 . The whole cell was placed in a water bath to change the experimental temperature. The conductivity of the electrolytic solution was monitored by using a conductivity meter. The concentrations of K_2CO_3 and KOH in the electrolytic solution were determined by acid-base titration methods. The concentration changes in the electrolyte solutions were monitored by drawing samples at regular intervals and analyzing them by titration, and they were used to calculate the yield of CO_2 . The yield rate of CO_2 and the current efficiency were calculated by Eqs. (4) and (5), respectively.

$$w = (C_t - C_{t+1}) * V * 22.4 * 1000 \quad (4)$$

$$\eta = \frac{w * z * F}{j * S * 22.4 * 1000 * 3600} \quad (5)$$

Where w (mL/h) is the yield rate of CO_2 , $C_t - C_{t+1}$ (mol/L) the concentration changes of CO_3^{2-} at the interval of 1 h, V (L) the solution volume, 22.4 (L/mol) the molar volume of the gas, η the current efficiency, j (A/cm²) the current density, S (cm²) electrode area, z the number of electrons transferred and $z = 2$ in this work, and F the Faraday constant.

The energy requirement in the bench scale for producing CO_2 per unit volume was calculated as Eq. (6).

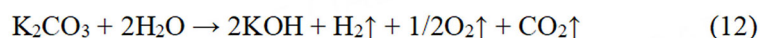
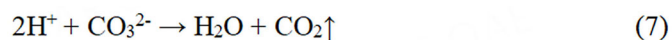
$$W = \frac{IU}{w} \times 1000 \quad (6)$$

Where W (kW·h/m³) is the energy requirement in the bench scale for producing CO_2 per unit volume, I (A) represents the electrolytic current, and U (V) signifies the average cell voltage after the electrolytic process is stabilized.

RESULTS AND DISCUSSION

Regeneration mechanism

Figure 2 shows an anion exchange membrane cell proposed in this work for electrolytic regeneration of KOH. The sulfuric acid (H_2SO_4) solution was charged in the anode chamber instead of the absorbent solution. Carbonate ions were transferred into the anode chamber by the AEM and reacted with H^+ according to Eq. (7). CO_2 was, thus, produced on the surface of the AEM in the anode chamber. The consumed H^+ was replenished by water electrolysis, and the simultaneous production of O_2 , according to Eq. (8), was on the surface of the anode. A partition could be added between the anode and the AEM to avoid the mixture of CO_2 and O_2 . In the cathode chamber, H_2 was produced from the water reduction reaction, and the absorbent KOH solvent was regenerated simultaneously according to Eqs. (9)-(11). The overall reaction of the cell can be summarized as Eq. (12).



It is worth noting that OH^- in the cathode chamber was also able to transfer into the anode chamber by the AEM and reacted with H^+ to produce H_2O , which is the main reason for the decrease of the current efficiency.

Stability of the electrolytic regeneration process

The changes of cell voltage, yield rate of CO_2 , and current efficiency with electrolysis time were investigated. Figure 3 shows the effect of electrolysis time on the cell voltage. The cell voltage increases with the current density, but the increase is disproportionate. The almost constant cell voltage throughout the electrolysis process indicated that the process was stable.

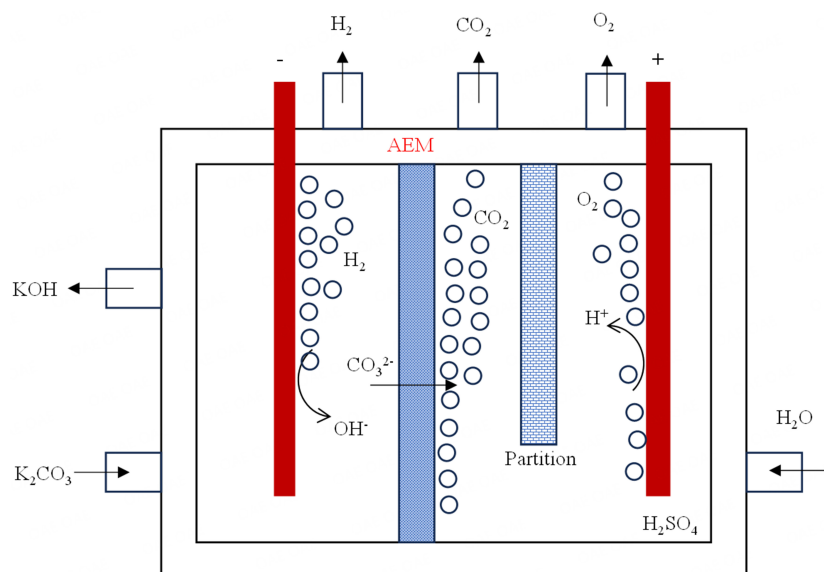


Figure 2. AEM cell for electrolytic regeneration of KOH with simultaneous H₂, O₂, and CO₂ generation.

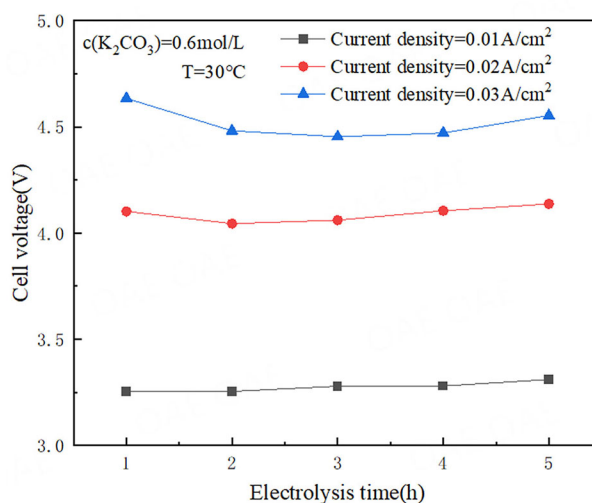


Figure 3. Effect of electrolysis time on the cell voltage.

Figure 4 shows the effect of electrolysis time on the yield rate of CO₂. The production rate of CO₂ dramatically decreases in the initial 2 h of electrolysis and tends to be stable in the following 3 h. The change of current efficiency with electrolysis time is shown in Figure 5. The current efficiencies are larger than 100% in the initial 2 h and tend to be stable in the following 3 h. In the initial stage, a large number of CO₃²⁻ exchange with AEM surface groups. The concentration of CO₃²⁻ in solution is thus reduced, but the exchange process is not the effect of the current.

Effect of temperature

It requires 2 h for the system to be stabilized, as mentioned above. The average values of yield rates of CO₂ and current efficiency were calculated by the data obtained from the 3rd to 5th h. Figure 6 shows the effect of temperature on yield rates of CO₂ and current efficiency. Both the yield rate of CO₂ and the current efficiency increase initially and decrease afterward with temperature. The initial upward stage is due to the increasing conductivity of the solution with temperature [Figure 7]. However, OH⁻ is easier than CO₃²⁻ to

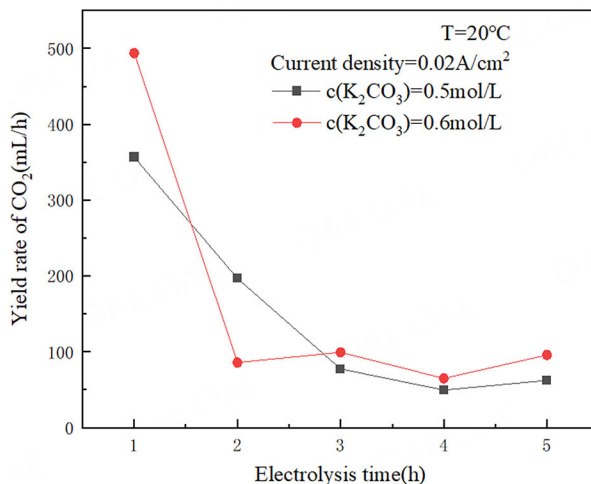


Figure 4. Effect of electrolysis time on the yield rate of CO₂.

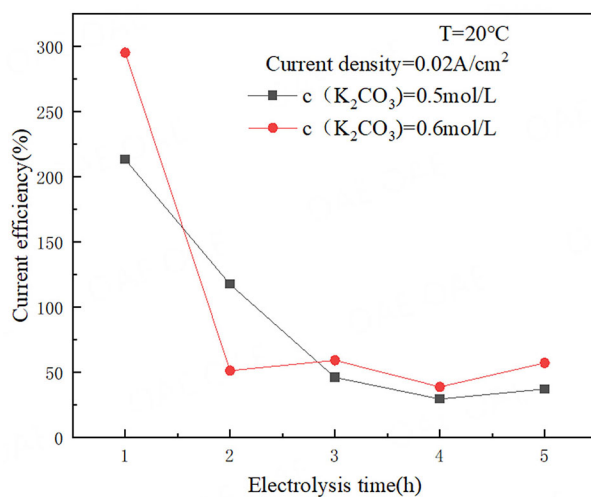


Figure 5. Effect of electrolysis time on current efficiency.

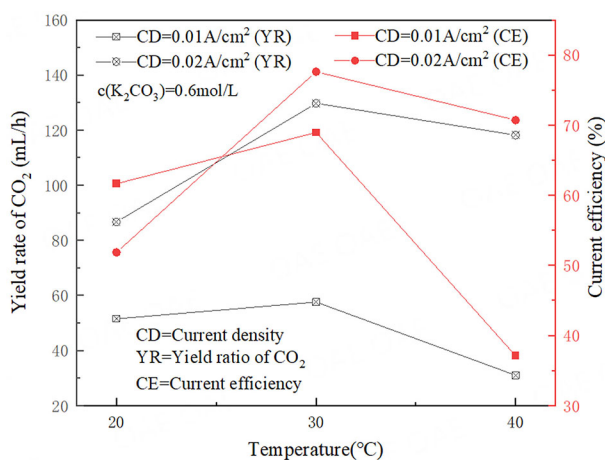


Figure 6. Effect of temperature on yield rates of CO₂ and current efficiency.

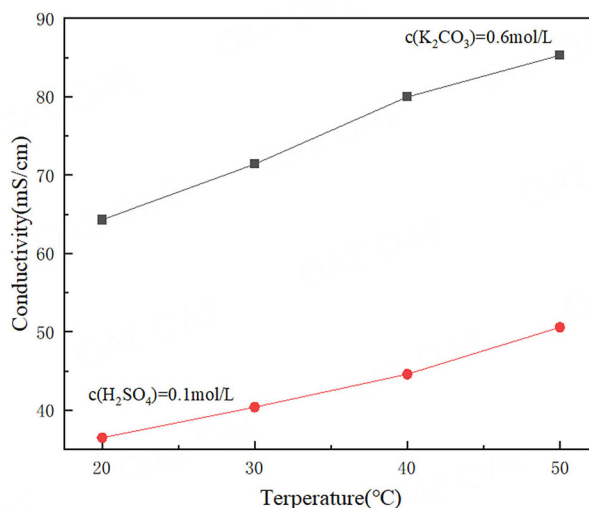


Figure 7. Effect of temperature on the conductivity of the solutions.

cross the AEM, resulting in a decreased trend with a further increase in temperature. The values of the yield rate of CO_2 and the current efficiency reached 129.7 mL/h and 77.6% at the conditions of 30 °C and 0.02 A/cm², respectively.

Effect of current density and CO_3^{2-} initial concentration

Figure 8 shows the synergistic influence of current density and CO_3^{2-} initial concentration on yield rates of CO_2 and current efficiency. The larger yield rate of CO_2 was obtained in a higher current density in Figure 8A, while the current efficiency has an opposite trend [Figure 8B]. The current efficiency is larger in a lower current density. The reason is that a larger number of OH^- ions are produced in a higher current density or a higher CO_3^{2-} initial concentration, resulting in a decrease of the current efficiency. The current efficiency reached 89% at the current density of 0.01 A/cm² and the CO_3^{2-} initial concentration of 0.7 mol/L.

Energy consumption

Figure 9 shows the effects of current density and CO_3^{2-} initial concentration on energy consumption. The energy consumption increases with current density. A low current density can reduce the energy consumption.

In conclusion, (1) the processes using membrane electrolysis can regenerate the absorbent solution to achieve 89% current efficiency, and the simultaneous production of H_2 makes this method promising; (2) CO_2 was produced on the surface of the AEM in the anode chamber, while O_2 was produced on the surface of the anode. The mixture of CO_2 and O_2 can be avoided by adding a partition between the anode and the AEM; (3) The effects of various operation parameters, including the temperature, the current density, and CO_3^{2-} initial concentration, have been studied. Both the yield rate of CO_2 and the current efficiency increase initially and decrease afterward with temperature. The yield rate of CO_2 increases while the current efficiency decreases with the current density. A low current density can reduce the energy consumption for producing the same amount of CO_2 .

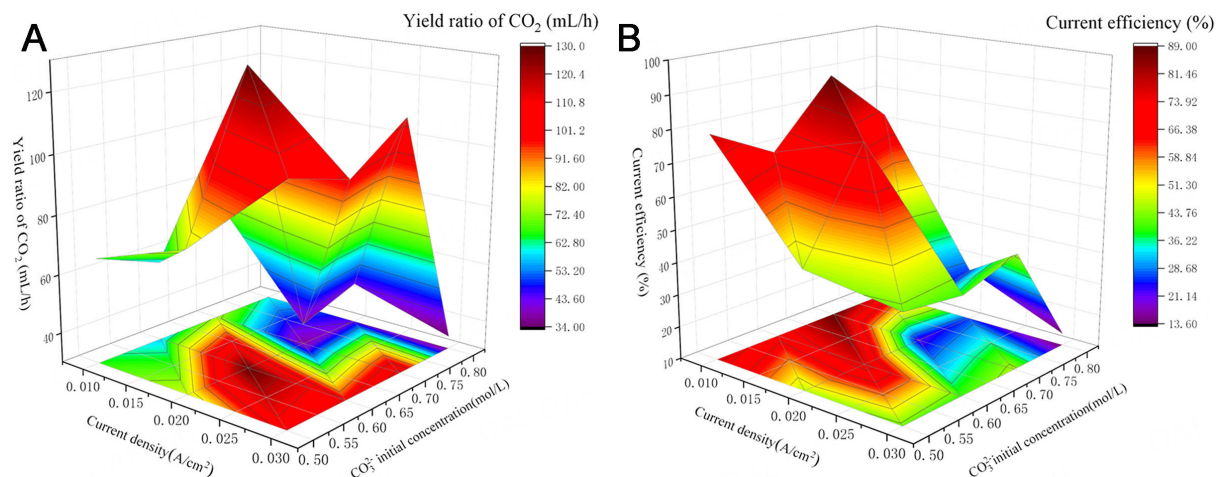


Figure 8. Effects of current density and CO_3^{2-} initial concentration on (A) yield rates of CO_2 and (B) current efficiency.

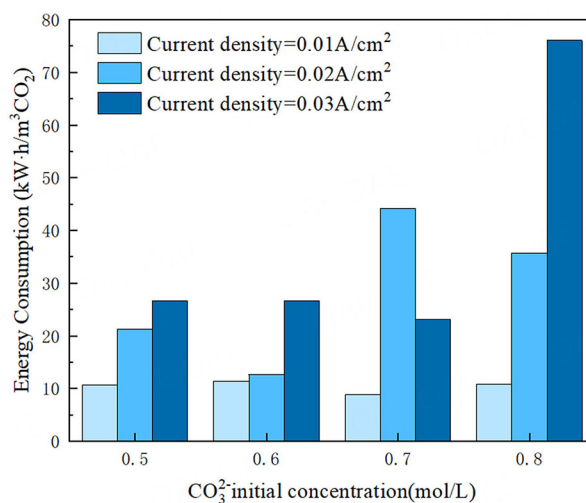


Figure 9. Effects of current density and CO_3^{2-} initial concentration on energy consumption.

DECLARATIONS

Acknowledgment

The financial support for this research from the National Natural Science Foundation of China (No. 52074203), the Fundamental Research Funds for the Central Universities under Grants (No. N2225019), and the Natural Science Foundation of Liaoning Province (No. 2022-MS-106) is gratefully acknowledged.

Authors' contributions

Investigation: Wang Y, Yu S

Visualization: Wang Y

Conceptualization, writing - review and editing: Fu D

Availability of data and materials

The corresponding author will provide the datasets used or analyzed during the current work upon reasonable request.

Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China under Grant (No. 52074203), the Fundamental Research Funds for the Central Universities under Grant (N2225019), and the Natural Science Foundation of Liaoning Province (2022-MS-106).

Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2023.

REFERENCES

1. Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO₂ capture with chemical absorption: a state-of-the-art review. *Chem Eng Res Des* 2011;89:1609-24. DOI
2. Rochelle GT. Amine scrubbing for CO₂ capture. *Science* 2009;325:1652-4. DOI PubMed
3. Osaka Y, Tsujiguchi T, Kodama A. Experimental investigation on the CO₂ separation performance from humid flue gas by TSA process. *Sep Purif Technol* 2018;207:77-82. DOI
4. Huang C, Liu C, Wu K, et al. CO₂ capture from flue gas using an electrochemically reversible hydroquinone/quinone solution. *Energy Fuels* 2019;33:3380-9. DOI
5. Breault RW, Spenik JL, Shadle LJ, et al. Carbon capture test unit design and development using amine-based solid sorbent. *Chem Eng Res Des* 2016;112:251-62. DOI
6. Ho MT, Allinson GW, Wiley DE. Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption. *Ind Eng Chem Res* 2008;47:4883-90. DOI
7. Powell CE, Qiao GG. Polymeric CO₂/N₂ gas separation membranes for the capture of carbon dioxide from power plant flue gases. *J Membr Sci* 2006;279:1-49. DOI
8. Favre E. Membrane processes and postcombustion carbon dioxide capture: challenges and prospects. *Chem Eng J* 2011;171:782-93. DOI
9. Ho MT, Allinson GW, Wiley DE. Reducing the cost of CO₂ capture from flue gases using membrane technology. *Ind Eng Chem Res* 2008;47:1562-8. DOI
10. Pohlmann J, Bram M, Wilkner K, Brinkmann T. Pilot scale separation of CO₂ from power plant flue gases by membrane technology. *Int J Greenh Gas Control* 2016;53:56-64. DOI
11. Hossain MM, de Lasa HI. Chemical-looping combustion (CLC) for inherent CO₂ separations - a review. *Chem Eng Sci* 2008;63:4433-51. DOI
12. Lyngfelt A, Leckner B, Mattisson T. A fluidized-bed combustion process with inherent CO₂ separation; application of chemical-looping combustion. *Chem Eng Sci* 2001;56:3101-13. DOI
13. Adánez J, de Diego LF, García-labiano F, Gayán P, Abad A, Palacios JM. Selection of oxygen carriers for chemical-looping combustion. *Energy Fuels* 2004;18:371-7. DOI
14. Tuinier MJ, van Sint Annaland M, Kramer GJ, Kuipers JAM. Cryogenic CO₂ capture using dynamically operated packed beds. *Chem Eng Sci* 2010;65:114-9. DOI
15. Koronaki I, Prentza L, Papaefthimiou V. Modeling of CO₂ capture via chemical absorption processes - an extensive literature review. *Renew Sustain Energy Rev* 2015;50:547-66. DOI
16. Liu N, Zhao X, Wang Y, Fei W. Electrolytic regeneration of decarbonising potassium carbonate solution. *Chin J Chem Eng* 2010;18:538-43. DOI
17. Kamps Á, Meyer E, Rumpf B, Maurer G. Solubility of CO₂ in aqueous solutions of KCl and in aqueous solutions of K₂CO₃. *J Chem Eng Data* 2007;52:817-32. DOI
18. Voldsund M, Jordal K, Anantharaman R. Hydrogen production with CO₂ capture. *Int J Hydrogen Energy* 2016;41:4969-92. DOI
19. Martin FJ, Kubic WL. Green freedom: a concept for producing carbon-neutral synthetic fuels and chemicals. Available from: <https://bioage.typepad.com/greencarcongress/docs/GreenFreedom.pdf>. [Last accessed on 20 Oct 2023].
20. Zhao X, Liu N, Wang Y, Fei W, Stevens GW. Study on the mechanism and energy consumption of CO₂ regeneration process by

membrane electrolysis. *Ind Eng Chem Res* 2011;50:8620-31. DOI

21. Chapel DG, Mariz CL, Ernest J. Recovery of CO₂ from flue gases: commercial trends. Available from: <https://citeseerx.ist.psu.edu/document?repid=rep1&type=pdf&doi=ce589caedf02f08164efb6a9fbca874e8e60cac6>. [Last accessed on 20 Oct 2023].