UDC 66.074.332

CONTROL OF CO_2 ABSORPTION BY NaOH SOLUTION USING pH, CONDUCTIVITY AND TITRATION MEASUREMENTS

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Received 23.01.2023
Accepted 11.04.2023

***Abstract**: The article deals with the issue of CO_2 utilization by sodium hydroxide absorption. Sodium hydroxide (NaOH) is able to react with CO_2 under atmospheric conditions to form carbonate or bicarbonate ions in solution. This study focuses on the absorption of CO2 by an alkaline solvent in a bubble column. Carbonate or bicarbonate ions were measured during carbonization using pH, conductivity and titration.*
***Keywords:** carbon dioxide, sodium hydroxide, conductivity, titration, absorption*
DOI: 10.32737/2221-8688-2023-2-123-131

Introduction

More than 81% of the world's energy needs are met by the consumption of fossil fuels (such as coal, oil, and natural gas), which result in emissions of pollutants such as nitrogen oxides, carbon monoxide, and hydrocarbons and greenhouse gases [1,2]. CO_2 is the main greenhouse gas emitted as a result of human activity. Therefore, the problem of CO_2 utilization is urgent. CO_2 utilization is achieved through chemical, electrochemical, photochemical, and biochemical methods. These studies are summarized in a comprehensive review of publication [3] and patent [4].

Photo-catalytic reduction provides for the use of light to convert CO2, while biochemical reduction is due to the use of enzymes and electrochemical reduction to the use of electrical energy. The reduction of CO2 products can include methanol, formic acid, CO, methane, ethylene, and gasoline. The review outlines recent advancements in the understanding and development of CO_2 reduction through the above-mentioned methods [3].

The current status of CO_2 capture patents and technologies was reviewed on the basis of the Espacenet patent database. Over 1000 patents were issued, with 60% published since 2000. There has been a sharp increase in the number of patents over the last 2 years. The top four sources of patents are Japan, the US, WIPO and China [4].

Despite the fact that the removal of CO2 from the atmosphere using NaOH is an energy-consuming process, research in this area is also ongoing [5-7].

In [6], it is proposed to use dissolved sodium hydroxide to remove CO_2 from the air, followed by its regeneration and precipitation of calcite. The calcite then decomposes to form lime and CO_2.

A prototype contactor was developed to measure the CO_2 capture efficiency of NaOH spray and the energy requirements for full-size contactors. The contactor was designed to have a downward-flow, concurrent design for simple construction and maintenance of the particle trap system. The CO_2 concentration was measured using an infrared gas analyzer, and carbonate concentration was measured in periodic liquid samples. The experiment also recorded temperature, relative humidity, and pressure drops [7].

Simulation and modeling studies of the absorption process of carbon dioxide with sodium hydroxide are included in several studies [8,9].

In [9] study evaluated different models for the enhancement factor that consider the impact of chemical reactions on mass transfer. Four mass transfer rate models and two enhancement factor models were used to simulate gas-fluid mass transfer in a bubble column and then experimental data were compared. The Henket1 model was found to be the most accurate and the Hlawitschka model was better than a constant enhancement factor model. The mass transfer model had little effect on the final pH variation in the reaction.

By using a membrane system, studies were carried out to obtain Na_2CO_3 crystals by CO_2 capture [10,11].

The process based on a membrane contactor for crystallizing $Na_2CO_3x10H_2O$ was proposed in the study [10] as the final step in capturing CO_2. The performance of an osmotic membrane distillation-crystallization setup was evaluated by considering the effect of flow rates, concentration of the feed and osmotic solution, and feed temperature on mass and heat transfer coefficients.

The study [11] evaluated the potential of using membrane crystallization to recover Na_2CO_3 from aqueous streams for CO_2 sequestration. The impact of various crystallization conditions (concentration and flowrate of Na_2CO_3 solution and osmotic solution, and type of osmotic solution) on process performance was determined. Results showed that the concentration of the osmotic solution and the flowrate of the Na_2CO_3 solution were key parameters that influenced the process.

The paper [12] compares the performance of a traditional packed column and a novel membrane contactor for CO_2 absorption. The results showed that the membrane contactor performed well as compared to the conventional column and even offered a higher intensification factor due to its compact and modular design.

The paper [13] examines the use of NaOH aqueous solution as an absorbent for capturing CO_2 from flue gas. The CO_2 absorption reaction occurs in consecutive steps, resulting in the production of Na_2CO_3 and $NaHCO_3$. The reaction rate and capture efficiency are found to be highly dependent on the NaOH concentration. The mass ratio of absorbed CO_2 that participates in the production of Na_2CO_3, $NaHCO_3$ was calculated.

The goal of this research is to establish the conditions for the formation of compounds that may result from the reaction of CO_2 and NaOH under low flow rates of CO_2 and low concentrations of NaOH in a laboratory setting, and to identify the most effective methods for controlling the process.

Experimental

NaOH aqueous solution was prepared by dissolving NaOH powder (Chemical, 98%) in distilled water. Different concentrations of the absorbent solution (NaOH) were shown in the study. The pH and conductivity X (mS/cm) values of the concentrated solutions of the NaOH, Na_2CO_3 and $NaHCO_3$ which had been prepared from commercial materials with a chemical purity of approximately (95-98%) were measured before the experiment.

The flow rates of the feeding gas (CO_2) were 20-500 ml/min. The main purpose of the study was to determine the conditions for full capture of CO_2 gas under laboratory conditions. This process included capturing CO_2 in a scrubbing column with NaOH solution. CO_2 capture experiments were conducted on laboratory scale setup. The reactor system was designed for this experiment. Reactors with the same diameter and 3 different volumes ($1000 cm^3$, $2550 cm^3$ and $7000 cm^3$) were analyzed in the study. Carbon dioxide was taken from a cylinder of compressed CO_2, its flow rate is controlled by a mass flow controller. Finally, two mass flow controllers are present at the top and bottom of the column to measure the flow rate in the two sections of the column through the use of electronic pressure sensors placed inside the console. The degree of capture of the gas was established by measuring the inlet and outlet flow rates of the gas. The schematic diagram of this setup is shown in Fig. 1.

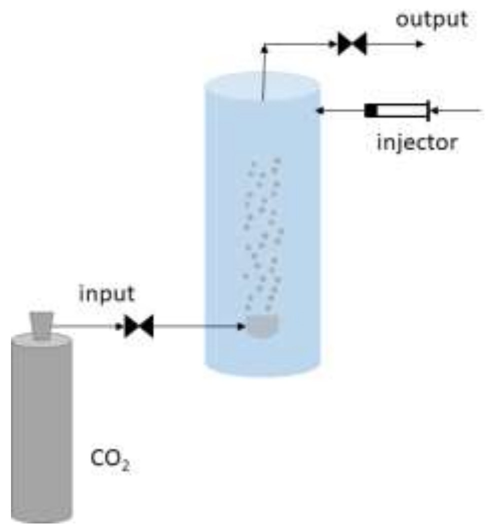

Fig. 1. Experimental setup for the chemisorption of CO_2 into NaOH.

In order to analyse the liquid samples, the double indicators method used. This method involves the use of phenolphthalein and methyl orange.

Results and discussion

Initial pH of the absorbent solution plays a crucial role in establishing the mass transfer rate of gases into liquids. The pH of the solution varied from 12.7 to 13.7 by changing the NaOH concentration at 25 °C (Fig 2). The pH of the solution slowly grew as NaOH concentration increased. Similar results were also typical for conductivity values (Fig 2).

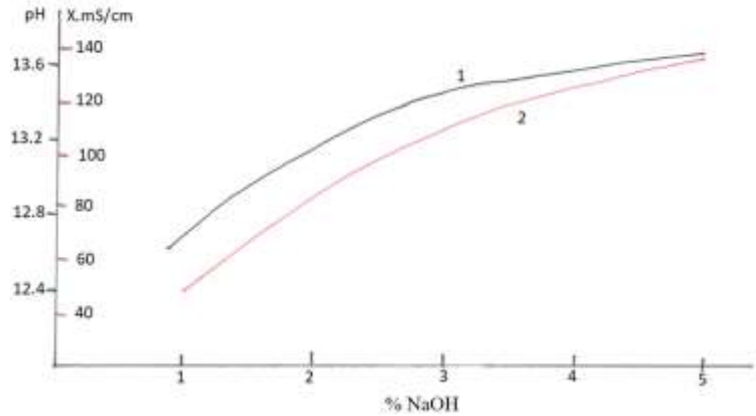

Fig. 2. pH (line 1) and conductivity (line 2) values of NaOH solutions depending on percent concentration at 25 °C

The effects of temperature on pH and conductivity were also studied by heating the scrubbing solution with immersion tank heater to vary the temperature of the Na_2CO_3 and $NaHCO_3$ solution at different saturation ratios from 25°C to 30°C. The pH and conductivity values for Na_2CO_3 and $NaHCO_3$ can be seen at Fig. 3 and Fig. 4 respectively. The results shown in Fig. 4 indicate that, at less alkaline pH, there was an increase in the conductivity, characterized by the incorporation of the CO_2 as HCO_3^- in the liquid phase, whereas, at a more alkaline pH, the conductivity decreased.

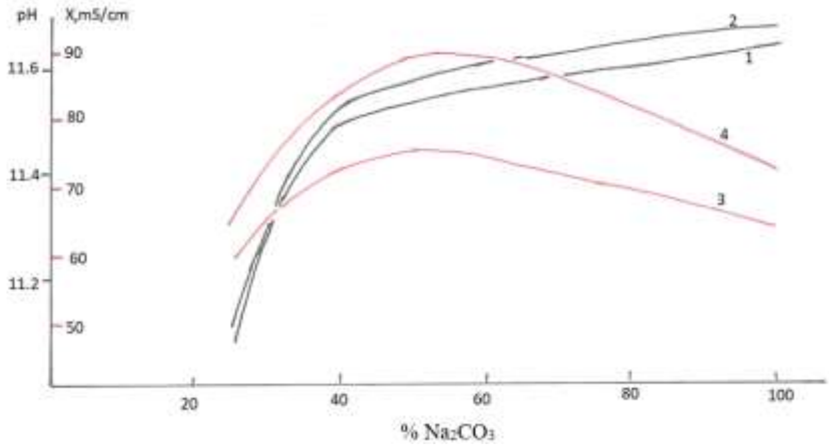

Fig. 3. pH and conductivity values of different Na_2CO_3 saturated solutions line 1 and 3 belongs at 25 °C, line 2 and 4 belongs at 30 °C

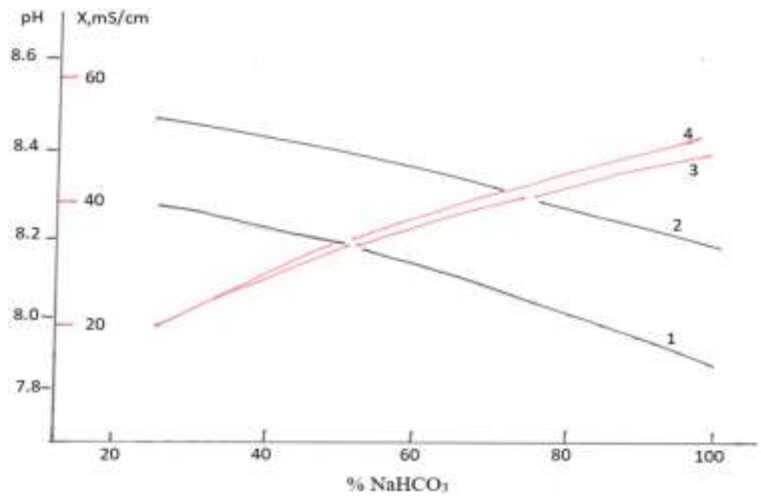

Fig. 4. pH and conductivity values of different $NaHCO_3$ saturated solutions line 1 and 3 belongs at 25 °C, line 2 and 4 belongs at 30 °C

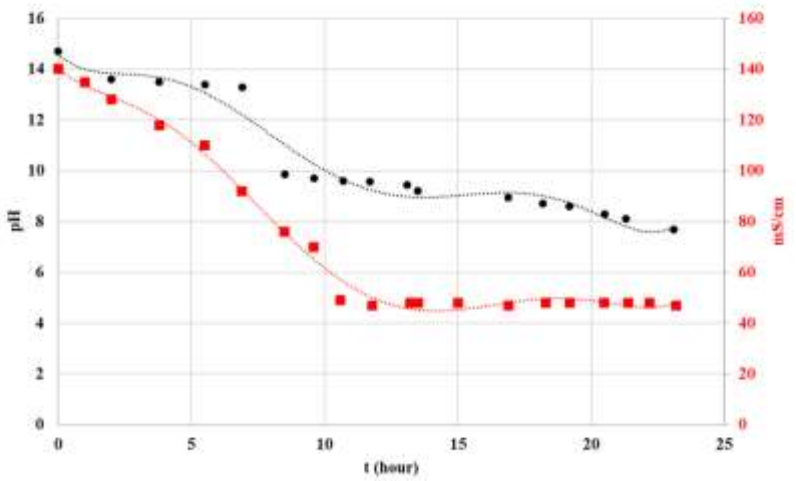

Fig 5. pH and specific conductivity change during absorption CO_2 in NaOH solution. V (CO_2) =50 ml/min, C (NaOH) =5%

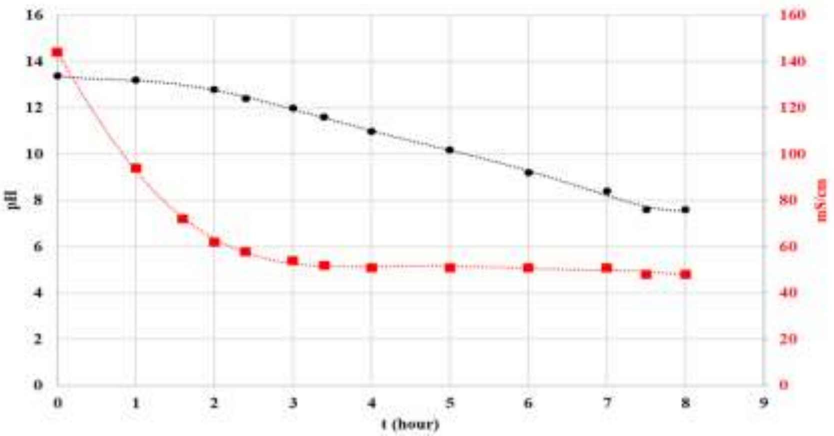

Fig. 6. pH and specific conductivity change during absorption CO_2 in NaOH solution. V (CO_2) =200 ml/min, C (NaOH) =5%

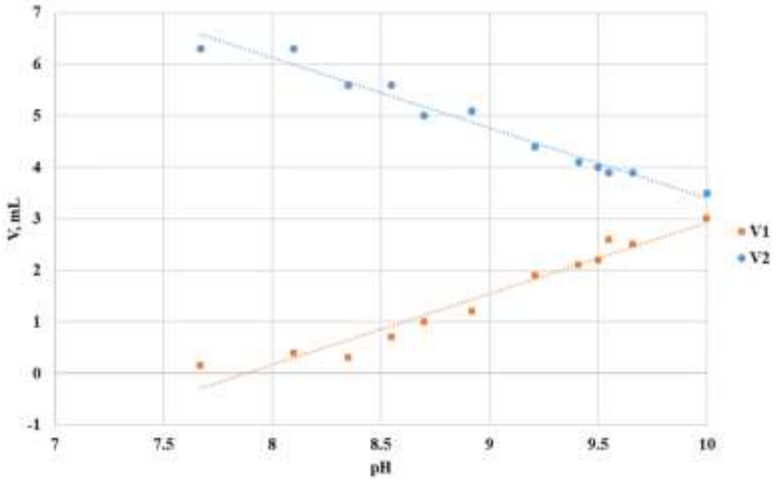

Fig 7. Determination mixture of $NaCO_3$ and $NaHCO_3$ with different value of pH in absorption CO_2 (V=200 ml/min) at 5% NaOH by titration. V_1 –titration - present phenolphthalein, V_2-titration - present methyl orange.

The CO_2 absorption in NaOH was measured using a pH and conductivity for 50 ml/min (Fig 5) and 200 ml/min (Fig 6) flow rates at long-term experimental studies.

The presence of HCO_3^- ions in a wide pH range (4.5-12) CO_2+NaOH environment is shown with the Bierrum graph [14-16].

In the study, pH and conductivity changes in the system were investigated in the absorption studies of CO_2 gas (31.5% by mixing with a N_2) at 1-5% range concentrations of NaOH solution. Experimental conditions do not permit full capture of the feed gas [13]. In our study, the range of the selected gas flow rate, the dimensions of the reactors we used, and the amount of solution used made it possible to ensure that the given CO_2 gas was kept completely.

Fig. 7 presents the specification of Na_2CO_3 and $NaHCO_3$ mixture in the function of the pH when phenolphthalein and methyl orange indicators are used. The sample taken from alkaline medium is titrated with HCl and two indicators (phenolphthalein and methyl orange) that change color and indicate what species is in the solution during titration. This method is used differently whether or not NaOH is still present in the solution. After reaching pH = 10.0, a sample was taken each time (5 ml) at a different pH from the reaction mixture starting from this value and titrated with 0.911 N HCl solution after the addition of phenolphthalein indicator (consumption V_1). The same process was done with the addition of methyl orange indicator (consumption V_2).

Fig. 8 presents the determination of Na_2CO_3 and $NaHCO_3$ mixture via titrimetric analysis method. When the pH value is 10.67 as a result of the reaction between a CO_2 flow rate of 100 ml/min and a 5% concentrated NaOH solution, a sample was taken each time (5 ml) at a different pH from the reaction mixture starting from this value and titrated with 0.0915 N HCl solution. As can be seen from Fig. 8, V=48 ml and pH=7.41 corresponds to the equivalent point and the titration of the NaOH + Na_2CO_3 mixture is completed. At V=74 ml and pH=3.5, the formation of $NaHCO_3$ is completed. According to the results of these analysis, the amount of $NaHCO_3$ formed at each reached pH-value was calculated.

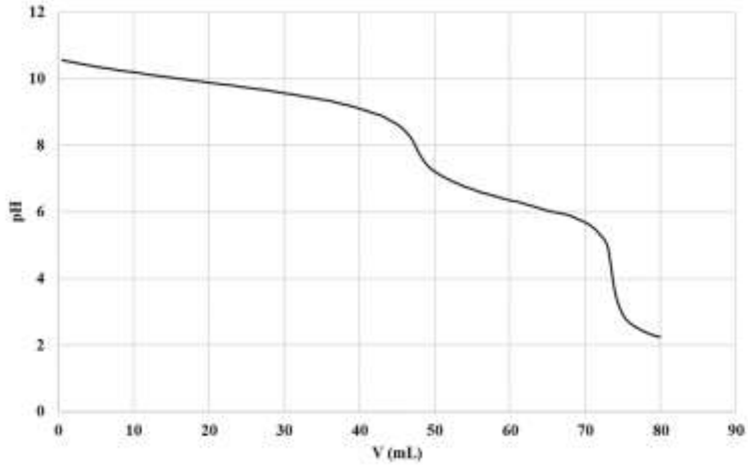

Fig 8. Titrimetric analysis mixture after absorption CO_2 (V=100 ml/min) in %5 NaOH, at pH=10.7

The reaction of CO_2 with water to form bicarbonate and hydrogen ions is important at low pH values. As the OH^- ions are consumed, i.e. the pH is lowered, the CO_2 converts into bicarbonate ions [17]. The results of the experiments conducted in the study are indicative that $NaHCO_3$ formation is possible at high pH values.

Effects of different operating and design parameters, including concentration of NaOH solution, absorbent solution volume flow rate and total gas flow rate on CO_2 removal efficiency were analyzed. The operating conditions of the all experiments conducted with the absorption column are reviewed in Table 1.

Table 1. Experimental conditions for absorption column

No	Molarity (M) (NaOH)	Total Volume (cm^3)	Flow Rate (ml/min) (CO_2)	Inlet Pressure (psi) (CO_2)	CO_2 feed time (hour)	pH (end of experiment)	Conductivity (mS/cm) (end of experiment)	Product
1	0.25	1000	50	13.56	3	7.64	16.68	$NaHCO_3$
2	0.5	1000	50	13.56	6	7.80	24.4	$NaHCO_3$
3	0.75	1000	100	13.56	6.5	9.16	36	Na_2CO_3 + $NaHCO_3$
4	1.25	1000	100	13.68	6	9.20	51	Na_2CO_3 + $NaHCO_3$
5	1.25	2550	50	14.16	6.5	9.43	48.6	Na_2CO_3 + $NaHCO_3$
6	1.25	2550	200	14.16	7	7.92	49	$NaHCO_3$
7	1.25	2550	400	14.16	3.2	7.72	51.3	$NaHCO_3$
8	2.5	7000	500	15.89	7	11.84	66.9	Undissolved CO_2

When using the NaOH solution, it was found that there emerged different products when the total gas flow rate rose from 50 to 200 mL/min in the same total reactor volume. Experimental results showed that the total gas flow rate has a remarkable effect on the CO_2 removal efficiency [18].

As can be seen in the experiment number 8 (Table 1), CO_2 gas inlet flow rate is 500 mL/min but the gas flow rate at the reactor exit is approximately 250 mL/min after 7 hours due to the gas flow rate added to the reactor and the high concentration of NaOH in the reactor. 50% of the gas entering the system leaves the reactor without reacting. Since the temperature formed in the reaction reaches high values (80-90 ^{0}C), it causes the gas to leave the reactor without reacting. In other experiments, no gas is released from the reactor at the end of the experiment.

In order to understand the presence of compounds formed in the reaction, phenolphthalein and methylorange indicators were placed in the reaction reactor. The color change observed during the reaction of the indicators added into the reactor is given in Fig. 8. Since the NaOH concentration is high in the initial state of the reaction, the phenolphthalein indicator is colored dark red. Then, as CO_2 continued to be fed into the reactor, a light red color was observed with the formation of CO_3^{2-} ions. At that, CO_2 gas converts existing CO_3^{2-} ions to HCO_3^- ions starting from the upper part of the reactor (color of both indicators is visible in the reactor). After complete conversion, only the color of the methyl orange indicator is visible in the reactor. Color fuel changes into yellow which indicates that all carbonate has reacted to form bicarbonate.

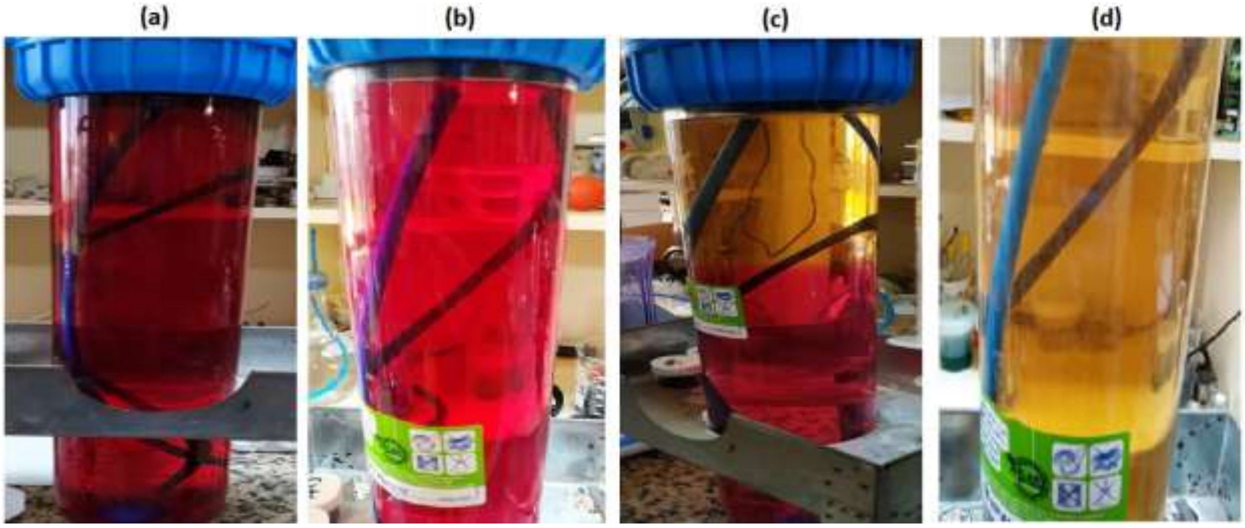

Fig. 8. (a) Color in high concentration of NaOH; (b) Color change phenolphthalein after forming Na_2CO_3; (c) Forming mixture of Na_2CO_3 + $NaHCO_3$ color phenolphthalein and methylorange (d) Color fuel change to yellow after $NaHCO_3$ is completely obtained.

Conclusion

We followed the formation of carbonate and bicarbonate ions depending on pH value of the NaOH + CO_2 system. Control over product formation can be measured not only by titrimetric analysis, but also by pH and conductivity measurement of solutions.

References

1. Eppinger J. and Huang K.W. Formic acid as a hydrogen energy carrier. *ACS Energy Letters.* 2017, vol. 2(1), pp. 188-195.
2. Brouwer J. On the role of fuel cells and hydrogen in a more sustainable and

renewable energy future. *Current Applied Physics*. 2010, vol. 10, pp. 9-17.
3. Yaashikaaa P.R., Senthil Kumara P., Sunita J. Varjanic, Saravanand A. Review. Article A review on photochemical, biochemical and electrochemical transformation of CO_2 into value-added product. *Journal of CO_2 utilization.* 2019, vol. 33, pp. 131-147.
4. Bingyun Li, Yuhua Duan, David Luebke, Bryan Morreale. Advances in CO_2 capture technology: A patent review. *Applied Energy*. 2013, vol. 102, pp. 1439-1447.
5. Mahmoudkhani M., Heidel K.R. Ferreira J.C., Keith D.W. Cherry R.S Low energy packed tower and caustic recovery for direct capture of CO_2 from air. *Energy Procedia*. 2008, vol.1, pp. 1535-1542.
6. Frank S. Zeman and Klaus S. Lackner. Capturing Carbon dioxide directly from the atmosphere directly from the atmosphere. *World Resource Review*. 2004, vol. 16, no.2, pp. 157-173.
7. Joshuah K. Stoaroff, David W. Keith and Gregory V. Lowry. Carbon Dioxide Capture from Atmospheric Air Using Sodium Hydroxide Spray. Environ. *Sci. Technol.* 2008, vol. 42, pp. 2728–2735.
8. Manuel Krauß, Roland Rzehak. Reactive absorption of CO_2 in NaOH: An Euler-Euler simulation study. *Chemical Engineerig Science*. 2018, pp. 199-214. https://doi.org/10.1016/j.ces.2018.01.009,
9. Junda L., Ping Z., Liu L., Si C., Yanpo S., Hongjie Y. CFD modeling of reactive absorption of CO2 in aqueous NaOH in a rectangular bubble column: comparison of mass transfer andenhancement factor model. *Chemical Engineering Science*. 2021, vol.30, p. 116218. https://doi.org/10.1016/j.ces.2020.116218
10. Ruiz Salmón I., Janssens R., Luis P. Mass and heat transfer study in osmotic membrane distillation crystallization for CO2 valorization as sodium carbonate. *Separation and Purification Technology*. 2017, vol. 176, pp. 173–183.
11. Luis P., Van Aubel D., Van der Bruggen B. Technical viability and exergy analysis of membrane crystallization: Closing the loop of CO2 sequestration. *International Journal of Greenhouse Gas Control.* 2013, vol. 12, pp. 450–459.
12. Israel Ruiz Salmón, Nicolas Cambier and Patricia Luis, CO2 Capture by Alkaline Solution for Carbonate Production: A Comparison between a Packed Column and a Membrane Contactor, *Appl. Sci.* 2018, vol. 8, pp. 996-1001.
13. Miran Yoo, Sang-Jun Han, Jung-Ho Wee. Carbon dioxide capture capacity of sodium hydroxide aqueous solution. *Journal Envrionmental Management*. 2013, vol.114, pp. 512-519.
14. Claus Fleisher, Stefan Becker and Gerhart Eigenberger. Detailed modeling of the chemisorption of CO_2 into NaOH a bubble column. *Chemical Engineering Science*. 1996, vol. 51, pp.1715-1724.
15. Jae-Goo Shim, Dong Woog Lee, Ji Hyun Lee, No-Sang Kwak. Experimental study on capture of carbon dioxide and production of sodium bicarbonate from sodium hydroxide. *Environmental Engineering Research*. 2016, vol. 21(3), pp. 297-303. https://doi.org/10.4491/eer.2016.042
16. Andersen C.B. Understanding carbonate equilibria by measuring alkalinity in experimental and natural systems. *J. Geosci. Educ.* 2002, vol. 50, pp. 389-403.
17. Leventaki E., Baena-Moreno F.M., Sardina G., Ström H., Ghahramani E., Naserifar S., Ho P.H., Kozlowski A.M., Bernin D. In-Line Monitoring of Carbon Dioxide Capture with Sodium Hydroxide in a Customized 3D-Printed Reactor without Forced Mixing. *Sustainability*. 2022, vol. 14, p. 10795. https://doi.org/10.3390/su141710795
18. Guo Y., Niu Z., and Lin W. In Comparison of removal efficiencies of carbon dioxide between aqueous ammonia and NaOH solution in a fine spray column. *Energy Procedia.* 2011, vol. 4, pp. 512-518.

CO_2-nin NaOH MƏHLULU İLƏ UDULMASI PROSESİNƏ pH, XÜSUSİ KEÇİRİCİLİK VƏ TİTRLƏMƏ METODLARI İLƏ NƏZARƏT EDİLMƏSİ

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Xülasə: Məqalədə natrium hidroksidlə karbon qazının udulması tədqiq edilmişdir. Natrium hidroksid normal atmosfer şəraitində CO_2 ilə reaksiya girə bilir. Əsas xüsusiyyət CO_2-nin məhlulda karbonat və ya bikarbonat ionlarının əmələ gəlməsi reaksiyasıdır. Bu tədqiqat CO_2-nin bir reaktorda (qabarcıq sütununda) qələvi həlledici tərəfindən udulmasına yönəlmişdir. Karbonat və ya bikarbonat ionları, CO_2 udulması zamanı, pH, keçiricilik və titrləmə ilə müəyyen edilmişdir.
Açar sözlər: karbon qazı, natrium hidroksid, keçiricilik, titrləmə

КОНТРОЛЬ ПОГЛОЩЕНИЯ CO_2 РАСТВОРОМ NAOH С ПОМОЩЬЮ ИЗМЕРЕНИЙ PH, ЭЛЕКТРОПРОВОДНОСТИ И ТИТРОВАНИЯ

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Аннотация: В статье рассмотрен вопрос утилизации CO_2 путем абсорбции едким натром. Гидроксид натрия NaOH способен реагировать с CO_2 в атмосферных условиях с образованием ионов карбоната или бикарбоната в растворе. Это исследование фокусируется на поглощении CO_2 щелочным растворителем в барботажной колонке. Ионы карбоната или бикарбоната измеряли во время карбонизации с использованием pH, электропроводности и титрования.
Ключевые слова: углекислый газ, гидроксид натрия, электропроводность, титрование