



Carbon fixation using calcium oxide by an aqueous approach at moderate conditions



Dongwoo Kang, Sangwon Park, Hoyong Jo, Jinwon Park*

Department of Chemical & Biomolecular Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea

HIGHLIGHTS

- This research deals with carbon fixation using 5 and 30 wt% MEA, DEA, MDEA solutions.
- Precipitated calcium carbonate was formed in all solutions.
- Precipitated calcium carbonate was proven to be in three different crystal structures.
- This research contributes for CCS by forming PCC and reducing regeneration energy.

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ABSTRACT

This research deals with carbon fixation with a precipitation reaction utilizing 5 wt% and 30 wt% alkanol-amine absorbents in an aqueous calcium oxide solution. Unlike carbon fixation operated at high temperature and pressure that consumes a lot of energy, we conducted experiments at moderate temperature (303.15 K) and pressure (1 atm). Since loading capacity or absorption capacity of the amine solution depends on the order of amines, 5 wt% and 10 wt% of monoethanolamine, diethanolamine and N-methyldiethanolamine were used as primary, secondary, and tertiary amines. By adding 20 wt% calcium oxide solution into the carbon dioxide saturated solution, precipitated calcium carbonate (PCC) was formed. To verify the physical properties of PCC, XRD analysis was performed and SEM images were obtained. Formed PCC was proven to exhibit three different crystal structures. Also, by converting absorbed CO₂ into solid PCC, solution regeneration energy, which accounts for 50–80% of the total energy consumption in the CCS process, can be reduced.

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1. Introduction

Many researchers around the world are concerned about global warming due to greenhouse gases. There are many types of substances which are classified as greenhouse gases including water vapor, carbon dioxide, methane, ozone, and nitrous oxide [1]. These substances absorb radiation energy from the earth and help maintain a mild atmospheric temperature if the amount of these substances is in the optimum range. This is called the natural greenhouse effect. However, as industry is being developed, emitted greenhouse gases are drastically increasing, leading to an increasing concentration of greenhouse gases in the atmosphere due to their accumulation [2]. If the heat equilibrium on the earth is disturbed by a high concentration of greenhouse gases, then the average temperature may rise. Among various types of greenhouse gases, carbon dioxide is a representative gas which occupies 80% of

greenhouse gases produced by the combustion of fossil fuels [3], which may result in an enhanced greenhouse effect compared to the natural greenhouse effect [4].

In 1985, the World Meteorological Organization (WMO) and the United Nations Environment Programme (UNEP) officially announced that carbon dioxide is the main cause of global warming. Environmental problems caused by global warming include changes in ecosystems and coastlines, increasing sea levels, and melting glaciers. In order to reduce these environmental problems and other risks derived from them, research on carbon capture and storage (CCS) technologies is being conducted globally by many researchers.

There are several ways to capture carbon dioxide including chemical absorption, physical adsorption, and separation using membranes [5–7]. The main sources of CO₂ emissions are post combustion gas, which is generally at high temperature [8]; however, physical adsorption and membranes often have temperature limitations and may therefore be unsuitable for these applications. Further, these technologies require a significant amount of post

* Corresponding author. Tel.: +82 2 2123 2763; fax: +82 2 312 6401.

E-mail address: jwpark@yonsei.ac.kr (J. Park).

combustion gas at high pressure, and there are also limitations on mass transfer [9]. So, a chemical absorption method using liquid absorbents is of interest.

In chemical absorption, selecting adequate liquid absorbents is very important. There are many properties to be considered: absorption capacity, absorption rate, acidity, regeneration energy, corrosiveness, toxicity, and environmental impact [10–12]. But, fulfilling all of the conditions is virtually impossible, and it is expected that chemical absorption technology using alkanolamine solutions as absorbents is the most promising method for commercialization by the year 2030 [13]. Alkanolamine can be classified into 3 categories according to the number of alkyl groups attached to the amine group. For monoethanolamine (MEA), there is only one alkyl group attached to the amine, making it a primary amine. Diethanolamine (DEA) is classified as a secondary amine, and N-methyldiethanolamine (MDEA) is a tertiary amine. The property of each amine differs according to the order of the amine. For primary and secondary alkanolamines such as MEA and DEA, very fast reaction kinetics are observed when reacting with carbon dioxide to form carbamates [14]. But, CO₂ loading capacity is low compared to tertiary amines, and the heat of absorption is high due to carbamate formation [15]. This requires a high regeneration energy for primary and secondary amines [14–16]. For tertiary alkanolamines such as MDEA, a high CO₂ loading capacity compared to primary and secondary amines is observed. Also, MDEA forms bicarbonate by hydrolysis of carbon dioxide, and the heat of absorption with bicarbonate formation is lower than that with carbonate [17]. So, the generation energy of a tertiary alkanolamine is lower than that of primary and secondary alkanolamines [15,17]. However, the reaction kinetics of tertiary alkanolamines is usually slower than that of primary and secondary alkanolamines. Hence, tertiary amine systems mixed with rate promoters such as piperazine can enhance absorption rate and carbon dioxide capture efficiency [18]. Also, it is reported that amines mixed with piperazine can have improved resistance to heat and oxidizers such as oxygen and sulfur [18,19].

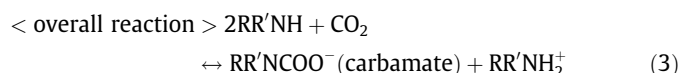
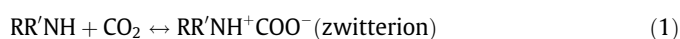
In this research, 30 wt% and 5 wt% aqueous solutions of MEA, DEA, and MDEA were used as liquid absorbents and carbon dioxide absorption and desorption experiments were done using a gas analyzer and mass flow controller (MFC). Amine solutions of 30 wt% were used because most commercialized CCS processes use absorbents containing 30 wt% of amine-type substances.

When 30 wt% solutions were used as absorbents, it was expected that only part of the absorbed carbon dioxide would be converted into PCC. However, we also sought to demonstrate what occurs when all of the absorbed carbon dioxide is converted into PCC. In order to achieve this, the amount of carbon dioxide to be absorbed into the solution should be reduced, which can be achieved by lowering the concentration of absorbents. Hence, 5 wt% absorbent solutions were also examined. Absorption experiments were done at a temperature of 303.15 K and desorption experiments were performed at a temperature of 343.15 K. Absorption and desorption experiments and conversion of absorbed carbon dioxide to calcium carbonate using calcium oxide prior to desorption were performed. In the process of converting absorbed carbon dioxide to calcium carbonate, the concentration of absorbed carbon dioxide in the absorbent solution decreases, and this led to a reduction in regeneration energy required in the desorption process. Since the regeneration energy of alkanolamines is large (e.g., 4 GJ/ton CO₂ for MEA) [20], this can lead to large energy savings. In much previous research, captured carbon dioxide was desorbed after it was stored in a separate high pressure tank. But, this requires additional construction and management costs. Also, accidental leakage of stored carbon dioxide may cause environmental issues even when the leakage is minimal.

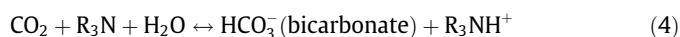
Even if carbon fixation that converts absorbed carbon dioxide into metal carbonate is adopted to prevent such an event, it requires high temperature and pressure, as shown in many previous studies [21,22]. In those works, solid-state metal salts (e.g. calcium oxide) reacted with gaseous carbon dioxide in a high temperature and pressure system. However, high temperature and pressure systems are expensive to operate in these extreme conditions. Further, high electricity consumption does not help control carbon dioxide emissions since most power plants produce lots of carbon dioxide during electricity generation.

In this research, carbon fixation was done in an aqueous approach where carbonation occurs in solution in an ionic state at normal and moderate temperature and pressure. We selected alkanolamine absorbents since carbon dioxide absorbs to them in the form of ionic carbon dioxide like carbamate, bicarbonate and zwitterion complexes [11,16,17,26]. The following reactions are involved in the system where amines and CO₂ react with each other.

For primary and secondary amines:



For tertiary amine:



So, carbonation with metallic ions (calcium ions used here) in solution at normal temperature and pressure can easily occur. This can help reduce energy consumption in the CCS process and ensure economical feasibility by reducing energy costs and the reuse of calcium carbonate [16,23–25]. Precipitated calcium carbonate resulting from carbon fixation can be used for various purposes such as in steel-making, medicine, manufacturing cement, paper and engineering plastics. X-ray diffraction analysis was also performed in this research to determine the composition of the solid. SEM (scanning electron microscopy) images were obtained to investigate the crystalline structure of calcium carbonate. The results obtained from this experiment can be used to develop carbon reduction systems for practical use in modern industry.

2. Experimental

2.1. Material

MEA (purity >0.99 mass fraction, CAS 141-43-5) and DEA (purity = 0.99 mass fraction, CAS 111-42-2) were purchased from Alfa Aesar and were used without further purification. MDEA (purity >0.99 mass fraction, CAS 105-59-9) was obtained from Acros Organics and was used without further purification. Calcium oxide (practical grade, CAS 1305-78-8) was purchased from Duksan Reagents and was also used without further purification. Fig. 1 shows the molecular structures of MEA, DEA and MDEA. For the experiments, 30% MEA(aq), 5% MEA(aq), 30% DEA(aq), 5% DEA(aq), 30% MDEA(aq), 5% MDEA(aq) absorbents solutions were prepared. In order to convert absorbed carbon dioxide to calcium carbonate, a

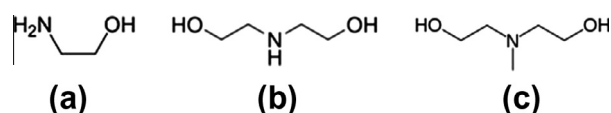


Fig. 1. Molecular structures of (a) MEA, (b) DEA and (c) MDEA.

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